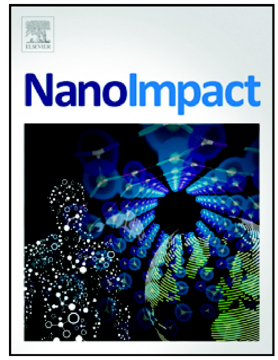
Journal Pre-proof




# Nanotechnology in agriculture: A solution to global food insecurity in a changing climate?

Shital Vaidya, Chaoyi Deng, Yi Wang, Nubia Zuverza-Mena, Christian Dimkpa, Jason C. White

PII: S2452-0748(24)00012-0

DOI: https://doi.org/10.1016/j.impact.2024.100502

Reference: IMPACT 100502

To appear in: *NANOIMPACT*

Received date: 3 December 2023

Revised date: 28 February 2024

Accepted date: 17 March 2024

Please cite this article as: S. Vaidya, C. Deng, Y. Wang, et al., Nanotechnology in agriculture: A solution to global food insecurity in a changing climate?, *NANOIMPACT* (2023), https://doi.org/10.1016/j.impact.2024.100502

**NanoImpact**- The Legacy of Nanosafety Research and Future Perspectives

**Nanotechnology in agriculture: A solution to global food insecurity in a changing climate?**

Shital Vaidya[1], Chaoyi Deng[1], Yi Wang[1], Nubia Zuverza-Mena[1], Christian Dimkpa[1], Jason C. White[1*]

[1]Connecticut Agricultural Experiment Station (CAES), New Haven CT 06511 United States

[*]Corresponding Author: Jason.White@ct.gov



Abstract- Although the Green Revolution dramatically increased food production, it led to non-sustainable conventional agricultural practices, with productivity in general declining over the last few decades. Maintaining food security with a world population exceeding 9 billion in 2050, a changing climate, and declining arable land will be exceptionally challenging. In fact, nothing short of a revolution in how we grow, distribute, store, and consume food is needed. In the last ten years, the field of nanotoxicology in plant systems has largely transitioned to one of sustainable nano-enabled applications, with recent discoveries on the use of this advanced technology in agriculture showing tremendous promise. The range of applications is quite extensive, including direct application of nanoscale nutrients for improved plant health, nutrient biofortification, increased photosynthetic output, and greater rates of nitrogen fixation. Other applications include nano-facilitated delivery of both fertilizers and pesticides; nano-enabled delivery of genetic material for gene silencing against viral pathogens and insect pests; and nanoscale sensors to support precision agriculture. Recent efforts have demonstrated that nanoscale strategies increase tolerance to both abiotic and biotic stressors, offering realistic potential to generate climate resilient crops. Considering the efficiency of nanoscale materials, there is a need to make their production more economical, alongside efficient use of incumbent resources such as water and energy. The hallmark of many of these approaches involves much greater impact with far less input of material. However, demonstrations of efficacy at field scale are still insufficient in the literature, and a thorough understanding of mechanisms of action is both necessary and often not evident. Although nanotechnology holds great promise for combating global food insecurity, there are far more ways to do this poorly than safely and effectively. This review summarizes recent work in this space, calling out existing knowledge gaps and suggesting strategies to alleviate those concerns to advance the field of sustainable nano-enabled agriculture.

Keywords- Nano-enabled agriculture, nanotoxicology, food security, climate change

## 1. Nanotoxicology and Plants

The integration of nanotechnology into fields such as medicine[1][2], cosmetics[3], diverse consumer products[4], and agriculture has resulted in a major source of nanomaterial (NMs) exposure for soil, air and water bodies[5]. This level of exposure significantly increased interest on the fate and effects of NMs in the environment, including specific impacts on plant species. Not surprisingly, many of these investigations focused on nanotoxicity, although much of the early work was focused on aquatic systems[6]. In addition, looking at that early literature, it is clear that the focus was on acute toxicity, which might have overlooked the positive impacts of nanotechnology in agriculture [7][8]. Still, plants being the primary step in the trophic transfer, represent a potential conduit for nanoparticles (NPs) to enter the food chain through contamination of plant/fruit biomass, raising food safety concerns[9]. Nanoparticle accumulation in the plant tissue depends on several factors such as NP size, shape, dose, and the method of application or exposure route (i.e. root vs foliar exposure)[10] [11][12]. It is important to note that phytotoxicity and residual NPs in edible plant parts are often only observed at relatively high exposures (ranging from 500 to 1000 ppm and above)[7][8]. However, reports of NP toxicity are preponderant in the literature. For example, Ziquian Li et al. showed that phytotoxicity in rice is inversely proportional to the size of ZnO NPs [13]. In fact, the importance of size to phytotoxicity has been established by several groups, although, again, at doses that are quite high. Smaller NPs (5-50 nm) showed greater transfer into root and shoots, and accumulation of NPs increased malondialdehyde content and antioxidant enzymes, suggesting one mechanism of phytotoxicity and the associated plant response [13]. More recently, Wang et al (2023) reported that NPs less than 50 nm can penetrate the plant through stomatal openings[14] on the shoot surfaces, suggesting potentially significant exposure of NPs to plants. Moreover Siegel et al (2018) showed that gold NPs of 10 nm size induced negative effects on *Arabidopsis thaliana* root growth, compared to untreated plants[15]. Musante et al (2012) showed in *Cucurbita pepo* that nano sized Cu and Ag NPs (size < 50 nm and <100 nm, respectively) induced more toxic effects than their bulk counterparts[16]. Conversely, application of carbon nanotubes at low concentration, 20 mg/L, accelerated the growth of rice leaves[17]. Ralia et al (2013) showed that nano scale ZnO (size <10 nm and 10 ppm application rate) increased photosynthesis parameters and overall growth of clusterbean plants[18]. Similarly, Badway et al. (2021) showed that foliar application of CuO NPs (10-50 nm at <200 ppm) enhanced growth parameters in wheat plants[19]. Thus, it is evident that the effect of nanomaterials and their interaction with plants varies with type, size, shape and concentration[20]. Perhaps the most important finding from well over a decade of nanotoxicology research with plants is the lack of clear identification of a nanoparticle-specific or unique mechanism of toxicity. That being said, it is worth noting that a large number of studies have insufficient experimental design to appropriately address mechanistic understanding. For example, inadequate systematic studies and the frequent lack of non-nanoscale controls (material as ion and bulk size) further confound an understanding of mechanisms of toxicity[6]. Despite this, interest in plant nanotoxicology began to wane as it became clear that nanoscale specific impacts were unlikely under realistic exposure scenarios. Figure 1 displays the number of publications focused on nanotoxicity to plants from 2000-2023, demonstrating maximum interest in this field from 2008-2015. In fact, the decline in publications post-2015 has been accompanied by an even larger increase in published work focused on the sustainable application of nanotechnology in agriculture (Figure 2).

While there is a possibility for the contamination of soil, water, and air with the application of nanotechnology in agriculture, with optimization and preventive measures, environmental contamination can be minimized. It is worth noting that for both the implication and application perspectives, a thorough and mechanistic understanding of plant-NP interactions is crucial. In the next section we note the importance of sustainable application of nanotechnology in agriculture, and bring focus on how it can improve conventional agricultural practices.

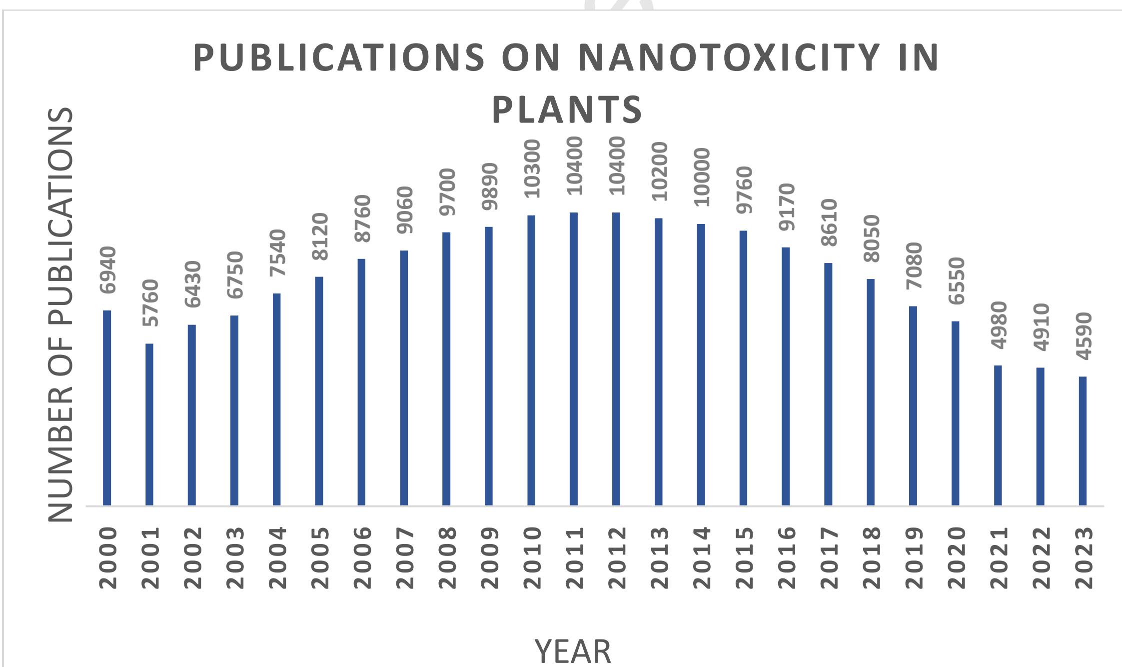



Figure 1: Research publications related to plant-nanotoxicology during the years between 2000 and 2023. This graph was generated by searching the phrase ‘’nanotoxicity in plants’’ in Google Scholar.

## 2. Nanomaterials can benefit plants

Many of the earlier studies on nanomaterial interaction with plants focused on exploring plant responses under conditions that could be considered less relevant, or unlikely to be encountered in agriculture and food production [21][6]. This approach is the first necessary step when trying to understand the inherent hazard and acute toxicity of a new material or chemical. Also, as noted above, it became immediately apparent that dose was a critical factor underlying plant response to NP exposure[22]. Incidentally, this impact of dose is also a hallmark of the Green Revolution, which ushered in higher crop productivity due to, among other factors, applying highly reactive agrochemicals (fertilizers, pesticides) at high rates. Although such strategies did increase crop yields, the approaches are inherently unsustainable due to excessive inefficiencies of delivery and utilization, as well as intensive energy and water use. The resulting heightened environmental pollution and land degradation due to inefficient use of agrochemicals; dwindling natural resources, including of mineral deposits and water; and the geographic imbalance in the benefits derived from the Green Revolution, have produced a global agroecosystem that has become increasingly unsustainable. Therefore, novel ways of exploiting and applying agrochemicals to sustain production while maintaining a healthy environment have become necessary[23]. The need for such paradigm shift is further justified by increasing concerns over the role of agriculture in climate change, as well as the effects of climate change on agriculture[24], including increased incidences of diseases, drought, and nutrient deficiency. Although conventional agrochemical inputs drove and continues to sustain current levels of food production, it, unfortunately, left in its wake an increase in climate change-driving factors such as increased greenhouse gas emissions from the transformation of nitrogen fertilizer into nitrous oxide, and human health impacting atmospheric pollution by ammonia from the same process.

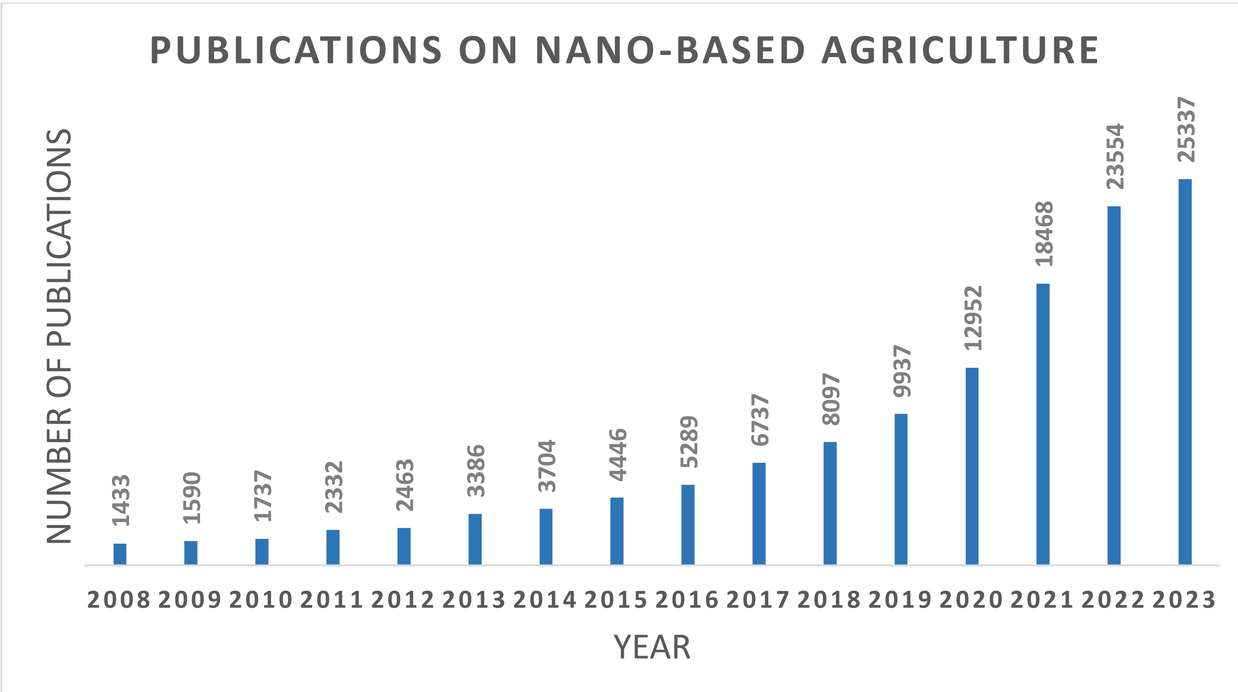



Figure 2: Research publications on the benefits of NPs or NMs in agriculture between 2008 and 2023. This graph was generated by using the keywords "nano-fertilizers, nano-pesticides, nano-enabled agriculture, nano/plant/growth" from Google Scholar.

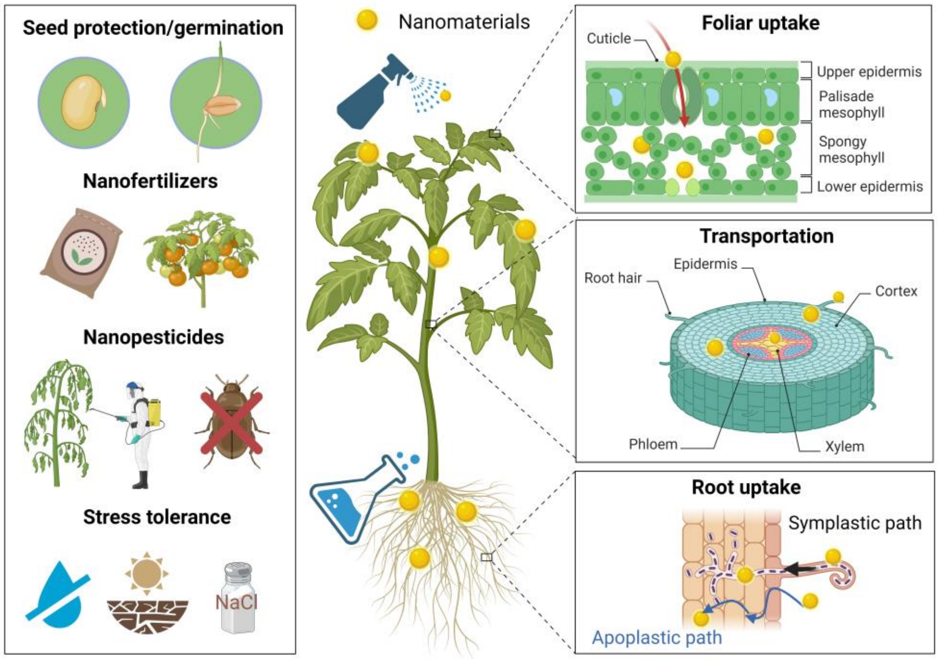



Figure 3. Applications of nanoscale materials to promote climate resilient crops.

## 2.1. Nanoparticles as antimicrobial and plant disease suppressing agents

Pathogenic microbes are among the most important factors inhibiting crop production. Having demonstrated in the earlier studies that NPs are toxic to microbes in a dose-dependent fashion, a number of groups leveraged this dose effect to apply specific nanoscale materials as antimicrobials for protection directly or indirectly against plant pathogens - bacteria, fungi, and viruses (reviewed in Dutta et al (2022), Elmer et al (2018), Krishnaraj et al (2012))[25][26][27]. For example, an in vitro study by He et al. (2012) demonstrated that ZnO NPs inhibited the growth of fungal plant pathogens. Specifically, exposure to the ZnO NPs (70nm; 3-12 mM) during a 12-day period significantly reduced the growth of *Penicillum expansum* and *Botrytis cineria*[28]. Pathogen growth inhibition by 12 mM NP exposure reached 63% and 68%, respectively, on day 12, compared to the control (zero) treatment. These fungi cause molds in grapes (*Vitis vinifera*), apples (*Malus domestica*), and pears (*Pyrus* spp.), resulting in significant economic losses[28]. Likewise, Jayaseelan et al. (2012) showed that growth of the common grain and fruit mold-causing fungi, *Aspergillus flavus* and *A. niger*, was inhibited by ZnO NPs (58 nm; 25 ppm) in vitro. Compared to water used as control, the inhibition zone in the presence of the NPs in assay plates was 19 mm for *A. flavus* [29]. Notably, many early studies on NP use in such assays did not include appropriate non-nanoscale or conventional controls, making it difficult to ascertain the true significance of the claimed nanotoxicity. Dimkpa et al (2013) reported that the growth of *Fusarium graminearum* was significantly inhibited (by 31-49%) by inclusion of the ZnO NPs (size <100 nm; 100-500 ppm) as part of in vitro systems, agar or sand. At 500 ppm, the inhibitory effect was related to the release of Zn ions from the NPs and, importantly, was shown to be more effective than bulk-scale ZnO NPs, 47% vs 24% [30]. This is an important finding as Fusarium isolates are ubiquitous in soil and cause wilting and root rot in different crop species. Notably, ZnO NPs demonstrated the potential to suppress Fusarium hyphal proliferation in wheat in a sand matrix and visibly reduced root rot[31]. The growth of Pythium isolates, *P. ultimum* and *P. aphanidermatum*, was significantly inhibited in a concentration-dependent manner when exposed to CuO and ZnO NPs (50 – 500 ppm). Within this concentration range, CuO NPs reduced growth between 50 and 62% in *P. ultimum,* and between 27 and 88% in *P. aphanidermatum.* Likewise, ZnO NPs reduced growth in *P. ultimum* between 23 and 48%, and between 17 and 46% in *P. aphanidermatum*. These fungi-like oomycetes are pervasive in soil, causing die-back, rot, and other symptoms in a wide range of crop plants. The inhibitory mechanism of these NPs on the isolates could be related to deprivation of iron metabolism due to inhibition of siderophore production [32].

Importantly, eliminating viruses in vegetatively propagated crops has been quite challenging owing to the diversity of viral infections, their lack of susceptibility to conventional pesticides and antimicrobials, and their complex interactions with the host. However, nanotechnology has also demonstrated significant potential to counteract viral infection of agricultural crops[33]. Viruses use the machinery of plant cells to propagate. To defend themselves, plants have evolved a gene silencing defense mechanism known as RNA interference (RNAi), in which the plant recognizes a portion of the pathogen genetic material and codes for its destruction instead of its replication. While it is possible to topically apply molecules (e.g. double stranded, dsRNA) to initiate the RNAi pathway, that genetic material is highly susceptible to degradation and can be challenging to cost effectively get inside plants. The development of nanocarriers to protect and supply RNAi molecules is an emerging strategy for viral disease control[33]. Current efforts are focused on finding specific viral genome regions that induce a strong host response[34], as well as optimizing loading efficiency and controlled delivery to achieve a stable, safe, and functional nanocarrier complexes for effective viral control[35][36].

Taken together, these findings of controlled plant pathogen growth demonstrate that NPs can directly and uniquely inhibit plant pathogen populations, thereby opening the possibility of using nanoscale formulations as an integral component of plant protection strategies in field settings. However, NP efficacy can be temporary, inducing stasis and allowing recovery, rather than killing or yielding permanent inactivation, as has been shown in test media [30]. This indicates that the NPs may be transforming to less toxic forms over time, allowing fungal and possibly other pathogens to become acclimated to exposure, and to develop tolerance, even at otherwise acutely toxic doses. This suggests that in certain instances, NP application to crops may have to be done multiple times during the growing season, as is often the case with conventional pesticide applications.

Segueing from in vitro laboratory-scale studies, further research was motivated by the need to scale up the effects of NPs on plants under realistic soil (or soil-like)-plant systems where countervailing environmental factors can alter impacts from NP exposure to plants during pathogen infection. To this end, several studies have focused on greenhouse and field-grown crops. One of the earliest studies in which NP effects were assessed in a plant-pathosystem under greenhouse conditions was described by Giannousi et al. (2013), who showed that foliar application of Cu-based NPs of different compositions (Cu, CuO, $Cu_2O$, 11-55 nm) at low rates of 0.15 to 0.34 g/l could more effectively control infection of tomato by *Phytophthora infestans* than several commercial Cu-based pesticides, including Kocide 2000, Kocide Opti, Cuprofix disperss, and Ridomil Gold Plus used at higher rates (0.35 – 2.24 g/l)[37]. Similarly, in the study of Elmer and White (2016), shoots of tomato and eggplant seedlings were immersed only once in suspensions of NPs of CuO (30 nm), MnO (40 nm), or ZnO (10-30 nm) (100 or 1000 ppm) and transferred to artificial media infested with *F. oxysporum* and *Verticillium dahlia* in the greenhouse[38]. Both pathogens cause wilt in different plant species and are endemic in the Northeastern US. All three NPs reduced Fusarium disease severity in tomato by 28-31%, and in the case of eggplant, CuO NPs reduced the severity of the wilt damage caused by Verticillium by 69%. This effect improved plant biomass by 64%, compared to the conventional Cu fertilizers[38]. In a more recent study, sulfur (S) NPs (200 ppm) in pristine (65 nm) and stearic acid-coated (38 nm) forms were added to soil infested with *F. oxysporum* and grown with tomato. Compared to the control and conventional S types, the strong disease incidence occasioned in the plants by the fungi was noticeably reduced by both S NPs forms by as much as 56%. This outcome was linked to a novel particulate S assimilation pathway and a time-sensitive nanoscale-specific disease resistance transcriptomic and metabolomic response profile [39]. Importantly, the efficacy of this strategy was validated under field conditions, where compared to bulk S, nanoscale sulfur significantly suppressed disease, more than doubling fruit yield under healthy and disease conditions, and leading to a biofortification of key nutrients in the tomato fruit [40].

Additional innovative approaches have explored the concept of bio-nanotechnology to demonstrate beneficial applications of NPs for plant protection. Notable in this regard are the so-called green-chemistry methods involving the use of plant or microbial extracts to synthesize the NPs, as well as the incorporation of NPs and plant growth promoting microbes into composites. Indeed, the use of plant or microbial extracts in synthesizing NPs (reviewed in Giri et al. (2023) and Sharma et al. (2023) saw significant increased interest several years ago in studies originating from India and other South Asia countries[41][42]. Informed by the overall findings from the literature, Karmous et al. (2023) synthesized CuO and ZnO NPs using extracts from hemp (*Cannabis sativa*) leaves[43]. When the biosynthesized NPs (hydrodynamic diameter 250 nm; at 200 ppm) were applied once at seedlings stage under greenhouse condition in soybean to protect against *F. virguliforme*, increased plant photosynthesis, nutrient accumulation, and the expression of soybean pathogenesis related genes encoding antifungal and defense proteins led to greater plant growth, compared to the unexposed diseased plants[43]. *F. virguliforme* is the fungal pathogen that causes soybean sudden death syndrome, resulting in significant economic losses in the United States and elsewhere (Bandara et al. 2020)[44]. In another example, chitosan-coated mesoporous nanoparticles (MSN; 38 nm) were examined for efficacy in improving tomato and watermelon performance under Fusarium infestation in potted plants. The MSN was bio-formulated with or without the plant-growth promoting bacteria (PGPB), *Azotobacter vinelandii* and *Bacillus megaterium*[45]. Among other observations, the bio-nano formulation with bacteria (250 ppm of the NPs) increased the chlorophyll content in infected tomato and watermelon by 60% and 62%, respectively; antioxidative metabolites by 56 and 135%, respectively; and ultimately, suppressed disease progression in both species after 28 days [45]. Such novel bio-nano-inspired approaches provide strong mechanistic support for a systemic suppression of fungal disease by NPs, and together with the synergistic positive effects of NPs and PGPBs, provide significant evidence in support of the use of NPs in agriculture in a sustainable and environmentally friendly manner[46].

As noted above, there have been limited studies on NP or NM effects on plant viruses. Among those, Elbeshehy et al. (2022) examined the effects of silver (Ag) NPs (size <100 nm, at 0.2, 0.3, and 0.4 ppm) on the Pepper Mild Mottle Virus (PMMoV) infection rate, infection severity, and the viral concentrations of infected pepper seedlings[47]. They found that higher concentrations of the NPs (0.3, and 0.4 ppm) inhibited the ability of the virus to spread systemically within the plant cells. Notably, these concentrations of Ag NPs did not affect the growth of healthy plants[47]. As alluded to previously, novel nanotechnology-based treatment of plants affected by viruses have consisted of the use of metallic NPs, as well as silica or carbon-based NMs in a range of viral pathogen-plant systems, including mosaic viruses. Using tobacco (*Nicotiana benthamiana*) as a model species, several studies have demonstrated effective delivery of genetic materials, specifically dsRNA, by the NP or NM to the plant, potentiating a ''nanovaccine'' regimen for counteracting the spread of viral pathogens[33][35][48][49]. A recent study along this line reported that amine-functionalized MSN (10-66 nm) facilitated the efficient delivery of dsRNA from the AC2 gene of the Tomato leaf curl New Delhi virus into tobacco, which led to a reduction in the viral load, and a 3-to-11-fold reduction in the expression of viral genes in the plant[50]. On the strength of these lab-scale observations, this ''nanovaccine'' strategy should now be evaluated under field conditions.

Elmer and White (2016) conducted one of the earliest field studies in this space, dipping the foliage of tomato and eggplant seedlings into suspensions of CuO, MnO and ZnO NPs (10-30 nm; 1000 ppm) and transferring to field soil heavily infested with *F. oxysporum* and *V. dahlia*[38]. Upon harvest, plants exposed to CuO NPs had at least 33% higher fruit yield than the control, for both tomato and eggplant[38]. Following these findings, this group has continued to explore the use of NPs as foliar sprays to alleviate fungal disease incidence in field-grown crops, with much more refining of the exposure rates. In watermelon under *F. oxysporum* infestation, a 1 to 2 ml application per plant of a 500 to 1,000 ppm of CuO NPs produced between 39 and 53% more yield than the control plants in geographically incontiguous field plots. These values were significantly greater than values obtained using conventional equivalents of these elements [51]. Such findings demonstrate the multi-locational applicability of the NPs. In another eggplant study, exposure to CuO NPs (500 ppm) in a *V. dahlia*-infested soil suppressed wilt symptoms by up to 28%, and increased fruit yield by up to 33%. Notably, the binary presence of other metallic NPs, namely $Mn_2O_3$ and ZnO, reduced the disease suppression outcome by 33% and 17%, respectively, compared to when individually present. Co-exposure to all three NPs resulted in reduced eggplant yield of up to 39%, relative to the CuO only treatment[52]. As will be further explored below, such studies, sometimes referred to as addition-omission studies, are designed to demonstrate the effect of co-exposure to other NPs and are a good surrogate for demonstrating how naturally-occurring environmental conditions could influence efficacy in the field. Additional field studies have demonstrated that CuO NP shape and surface chemistry influence Fusarium disease suppression outcomes in plants in a species-dependent manner. Specifically, CuO nanosheets inhibited disease progression in tomato, while CuO nano spikes did not. Conversely, positively-charged CuO nano spikes reduced disease progression in watermelon, while the negatively charged ones did not [53].

Notably, NP evaluation studies with non-traditional plant nutrients have also shown beneficial effects against fungal diseases in plant systems. For example, a field evaluation of the antifungal efficacy of NPs by Lamsal et al. (2011) reported a reduction in the symptomatic lesions caused by powdery mildew in cucumber and pumpkin resulting from infection by the fungi *Golovinomyces cichoracearum* and *Sphaerotheca fusca* following aerial spays of Ag NPs (10-100 ppm) before and after disease outbreak[54]. A further mechanistics evaluation demonstrated the inhibitory effects of the Ag NPs on mycelial growth and conidial germination as an underlying cause of toxicity. Similarly, cerium oxide NP foliar exposure in the greenhouse at 50 and 250 ppm to tomato (*Solanum lycopersicum*) growing in soil infested with *Fusarium oxysporum* increased disease tolerance, fruit weight and lycopene content, with minimal negative effects on the overall nutritional value of tomato fruit [55][56]. Taken together, the above examples clearly show that protecting plants from pathogenic attack can be realized using NPs and nano-enabled strategies. As the reader would notice, most of the studies have focused on fungi. This is presumably because fungal pathogens are causal agents of many of the prevalent and devastating diseases faced by crop species (reviewed in Nazarov et al. 2020)[57]. Clearly, more field demonstrations involving bacteria, nematodes and viruses are necessary to tease out specific NP-plant-pathogen systems with broader economic value for growers, as well as to expand the product portfolio for the agrochemical industry.

### 2.2. Nanoparticles to alleviate the negative impacts of drought

Drought is a global problem and is severely confounding agriculture in a significant part of the United States. According to the National Integrated Drought Information System[58], as of May 2023, about 16% of the U.S was under drought, where the West and New England regions of the country were most affected. Globally, total farm losses have been reported following prolonged and recurrent drought events[59][60]. Therefore, drought can have severe economic consequences on crop production and farmer's livelihoods, while threatening food security at local, regional, and national scales. Importantly, select NPs can increase plant tolerance to drought[61][62], as demonstrated in several crops, including soybean, wheat, and sorghum, among others. Unfortunately, evaluating NPs for drought alleviation under field conditions is hampered by the difficulty of conducting controlled studies under a range of uncontrollable environmental conditions. As such, much of the literature on the mitigation of drought effects by NPs contains findings demonstrated under greenhouse conditions. Specific examples of such studies where NPs have sustained plant growth under drought stress follow below, but of particular interest is the quite low concentrations of added nanomaterials that can induce drought resistance. In soybean, a composite formulation of ZnO, $B_2O_3$, and CuO NPs (respectively, 2.8 ppm Zn, 0.6 ppm B, and 1.3 ppm Cu) alleviated drought (50 % field moisture capacity determined by measuring weight of the pots twice daily) effects and increased soybean shoot growth by 33% and grain yield by 36% [63]. In sorghum, ZnO-NPs (1 – 5 m ppm Zn) reduced the delay in flag leaf and grain head emergence imposed by drought from 6-17 days to 4-5 days, and improved grain yield by 22-183%[64]. In wheat, ZnO NPs (approximately 2 ppm) accelerated plant development by reducing the time to panicle emergence by 5 days and by increasing grain yield by up to 51%. Notably, both effects were not recorded with bulk scale ZnO used at twice the dose of Zn [65]. Thus, a critical finding of the later study was that a 50% Zn rate was used in the NP treatment relative to the conventional Zn, demonstrating a key benefit of nanofertilizers, which is the reduction of agrochemical input in the biosphere without a penalty against yield. Though many of the studies evaluating NP effects in drought systems have focused on Zn, other NPs have also been evaluated, with similar benefits demonstrated for the plants. For example, Cu NPs (3 - 7 ppm) applied to wheat at 40 - 80 % field moisture capacity significantly improved the chlorophyll stability index, stomatal conductance, and plant yield[66]. $SiO_2$ NPs have also been reported to ameliorate drought effects in various crops, including banana, coriander, and cotton, largely by modulating the antioxidant and relative moisture capacities of the plants[67][68][69].

Broadly speaking, the ability of NPs to accelerate plant development and promote yield under drought stress is critical for promoting cropping systems resilience and sustaining food security in the face of climate change. In terms of mechanistic understanding, the modulation of hormonal and enzymatic processes regulating stomatal operations, root development and antioxidant homeostasis are implicated in the increased tolerance of drought-stressed plants[70]. However, metal-based NPs tend to interact with soil constituents such as phosphates, limiting their efficacy under field situations. Therefore, foliar application to young seedlings or seed priming with the NPs prior to sowing under drought stress may offer a preventive strategy, reducing the effect of limited water access over the growing period and allowing crops to produce significant marketable yield[70][71].

### 2.3. Nanoscale nutrient management

As noted, N and P are the most important fertilizer agrochemical drivers for increased crop productivity. However, these nutrients suffer from very low utilization efficiency, resulting in losses that impinge upon farmers production cost due to the need to use more fertilizers, as well as negative environmental impacts. In fact, N and/or P losses are linked to the pollution of air and water, increases in greenhouse gas production, and reduced crop yields. As described in several recent reviews, considerable efforts, including the exploitation of nanotechnology, have been aimed at developing enhanced efficiency N and P fertilizers to minimize nutrient losses and associated negative environmental consequences[72][73][74]. In one early nano-focused approach towards managing nutrients for increased use efficiency, Liu and Lal (2014) developed a nanoscale hydroxyapatite (nHAP, 15.8±7.4nm) via the reaction of calcium hydroxide and phosphoric acid[75]. The synthetic nHAP improved plant performance, compared to commercial triple super phosphate. This outcome was hypothesized to result from the controlled dissolution of P from the nHAP, as compared to the high solubility of conventional P fertilizers and the highly insoluble rock phosphate. A subsequent work by Kottegoda et al. (2017) integrated urea into the synthetic nHAP system, confirming that N and P release rates can indeed be slowed in nanoscale formulations, compared to conventional urea. The authors reported that using less than 20% P and 50% N in the product resulted in nutrient uptake at levels comparable to those from conventional fertilizers used at the full rate[76]. Thus, using P in nanoscale form could enable the use of much less P to produce same uptake efficiency. This is particularly important given the limited nature of P resource globally and the significant negative impacts associated with its inefficient use.

It is well known that N loss is significant under conventional N application rates. However, Dimkpa et al. (2017) could demonstrate that amendment of soil with ZnO NPs (6 ppm) under low (100 ppm) and high (200 ppm) N application levels significantly increased N accumulation by sorghum under both conditions, with a significant N mobilization to the grain[77]. In wheat, a 6 ppm soil amendment of ZnO NPs (size 18 nm, of varying shapes ranging from rectangular, tubular, angular, and circular) significantly increased grain yield by 15% and N concentration by 10% [78], further demonstrating nanoscale-enhanced mobilization of the N to edible plant tissues. In soybean, an addition-omission strategy elucidated the role of elements from different metal oxide NPs; namely, Zn (2 mg Zn/kg; 18 nm), Cu (1 mg Cu/kg; 40 nm), and B (1 mg B/kg; 100 nm), in the soil-plant dynamics of N and P [79]. While the mixed NP treatment stimulated shoot N accumulation, it inhibited P uptake, and tended to increase P retention in soil. By contrast, omission of ZnO NPs reduced N uptake but stimulated P uptake, while omission of CuO NPs enhanced N retention in soil. Thus, the specific strategy used when adding multiple nanoscale nutrients will depend greatly on soil conditions and physiological needs of the specific plant species.

Further advances towards formulating enhanced nano-enabled fertilizers have been made in several recent studies. In one case, a urea-nHAP (100–120 nm length and 25–35 nm width, elongated and rod shaped) composite fertilizer was optimized by doping with Zn and Mg[80]. Containing lower N, 42%, as compared to the standard 46% N in conventional urea, the doped nanocomposite at a 50 % lower application rate of urea increased N and P acquisition by wheat, facilitating the mobilization of the nutrients to the grain. Dimkpa et al. (2023) used chitosan as a nanoscale polymer without and with ZnO NP doping to evaluate tripolyphosphate (TPP) (TPP-Chitosan 440 nm, and TPP-ZnO-Chitosan 301 nm) with the goal of repurposing TPP as a P-fertilizer source[81]. Notably, the TPP-chitosan and TPP-chitosan-ZnO composites significantly reduced P leaching from soil when compared to monoammonium phosphate and TPP alone. Doping with ZnO NPs was found to be 65% more effective in reducing P leaching, compared with undoped TPP-chitosan, corroborating studies showing the significant potential of metal doping in modulating nutrient dynamics in nanocomposites. Similarly, a chitosan-coated MSN formulated with PGPB (*A. vinelandii* and *B. megaterium*) was reported[45] significantly increased N and P accumulation in tomato and watermelon, compared to the control and MSN-only treatments. Sigmon et al. (2021, 2023) employed another nanoscale polymer-based approach to improve P use efficiency by using polyhydroxyalkanoate (PHA) to develop a suite of composite P fertilizers[82], [83]. When evaluated in tomato as a P delivery platform, formulating calcium phosphate NPs (size <150 nm) with PHA (PHA−CaP-PNC) (100 ppm in soil) significantly reduced P leaching loss from the soil, while supporting plant growth and P accumulation at levels similar to the conventional P fertilizer source, dicalcium phosphate. In a separate strategy, Gomez-Maldonado et al (2023) used a gas esterification procedure to create a tunable hydrophobic shell on the surface of nanocellulose based hydrogel particles, yielding highly controllable PK release profiles[84]. Importantly, the use of biopolymers to develop nanoscale fertilizers is particularly attractive due to its environmentally friendly nature, with little, if any, toxic residue deposits, and highly tunable chemistry that allows for loading and delivering a wide range of nutrients. In addition, incorporating nutrient recycling or repurposing goals into the strategy can help to engender greater environmental resilience and sustainability[85].

Of considerable relevance to the subject of nutrient management is the observation that NPs can contribute to addressing the serious problem of drought-induced nutrient deficiency. Low nutrient use efficiency experienced under normal environmental conditions can be exacerbated under intense drought stress. Under such conditions, soil water availability is greatly affected, leading to diminished nutrient mobility, reduced rhizosphere function, and decreased uptake of nutrients by plants[86][87][88]. Notably, in contrast to N addition alone, adding NPs in soil together with NPs can increase N uptake and yield under drought. Indeed, in various crops, including soybean, sorghum, and wheat, where drought stress significantly inhibited the acquisition of N leading to strong yield reductions, studies have demonstrated that individual NPs or their composite formulations can increase the mobilization and accumulation of N in the plant[77][64][65]. For example, Li et al demonstrated that low a concentration (10 ppm) of a molybdenum-based nanofertilizer significantly increased nitrogen fixation through delayed nodule senescence and increased in planta nutritional content. Viewed broadly, these outcomes suggest that nano-enabled platforms can be used to develop fertilizers that can be deployed in managing the fate of critically important nutrients in agriculture[89]. The NPs can not only be used under N limiting conditions to facilitate uptake, but also to potentially reduce N loss by managing overall availability. These studies also indicate that N uptake can be facilitated by NP formulations or amendments at low N application rates, helping to limit the introduction of new

N inputs into the biosphere. In the case of P, the formation of metal-P aggregates can inhibit uptake, although this will also prevent loss of the nutrient via leaching or run-off and will contribute to the legacy P pool in soil. Holding a legacy P pool in soil that can be tuned to permit release when needed could dramatically minimize inputs of new P into agro-ecosystems, thereby improving environmental health outcomes. Equally notable is that these nano-enabled strategies can be used to facilitate the enrichment of cereal grains with N, which is an important precursor for the protein diets critical in human health, especially for populations dependent on staple crops.

## 3. Future Perspectives

Seven years ago, Servin and White (2016) described future research needs on nano-enabled agriculture[6]. Although the amount of work being done in this space has increased dramatically, much of what was described there still applies, including the need to focus on a comprehensive understanding of efficacy, exposure and risk at low doses that are relevant for desirable agronomic outcomes[6]. In doing so, sensitive endpoints that include subtle effects must be measured, especially transgenerational and trophic transfer of the NPs that are not immediately discernible. Also, impacts on the nutritional quality of crop harvests, the effect of co-contaminants in soil, and effects of rhizosphere processes such as root exudation and microbial activities on NP fate and dynamics remain important topics of investigation. Importantly, several subsequent studies have considered several of the points raised by Servin and White (2016)[6]. Evaluating NPs under low exposure concentrations has become much more routine[63][77][22][79][65]. This effort has minimized some of the concerns regarding apparent toxicity of NPs in plants, particular NPs of nutrient elements required by plants. The effects of co-contaminants are also now being investigated, as exemplified in two studies discussed in this work and several ongoing research focused on organic contaminants and NPs[52][79]. However, more field studies are required to account for the diversity of contaminants in different soils. And importantly, progress towards improved understanding of transgenerational and trophic transfer of NPs has been inadequate. Perhaps, the most advanced of the proposed research areas has been in the role of NPs at improving food nutritional quality. While this can be gleaned from earlier described studies where NPs facilitated N translocation to the edible tissues of crops, it is worth noting that the addition of micronutrient NPs as fertilizers in either foliar or soil amendments has resulted in significant improvement in produce quality for trace elements that are critically deficient in many human diets. For example, Zn and iron (Fe) are among the most important micronutrients in human health. Evidence for nano-enabled fortification of edible portions of food crops with Zn and Fe through exposure to NP forms of these nutrients can be found in several studies from our group and those of others involving staple crops of global importance[77][90][91][92]. In that regard, grain Zn and Fe fortification via NP fertilization can represent a significant nutritional outcome for human populations that depend on grain staples for meeting their Zn and Fe dietary needs. Nevertheless, significant knowledge gaps surrounding some of the novel possibilities with NPs need to be addressed, such as:

(i) The use of NPs of elements like B and Ca for extending produce shelf life and understanding the role of these NPs in maintaining plant cell membrane structural integrity. Efforts here could focus on the use of novel nanoscale or even conventional biopolymer coatings that are edible and that release these important nutrients to the crop tissues over time, or even novel packaging materials that do the same. In addition, nanoscale sensors can be developed that give an actual readout of the impact of spoilage microorganisms or their associated byproducts, effectively extending shelf life and minimizing food waste.

(ii) Assessing the biological mechanisms directing NP-induced increase in N uptake by plants, focusing on mechanisms related to ammonia volatilization, nitrous oxide emission and nitrate leaching. Here, nanoscale materials could be used to induce changes in the rhizosphere microbiome that promote biological nitrogen fixation in ways that maximize nitrogen use efficiency and minimizes losses from the system.

(iii) Developing scalable precision strategies for P and N delivery and utilization. Biopolymer delivery strategies can be developed that are responsive to the plant condition and dramatically enhance the precision of delivery, both temporally and spatially, maximizing use efficiency. Depending on the cropping system, either soil-based or foliar strategies of delivery could be possible.

(iv) Conceiving strategies for evaluating nutrient-based NPs for mitigating temperature, drought, and salinity stress under field conditions. The use of important nutrients such as Cu, Zn, S, and Si, among many others, can be used to modulate ROS homeostasis, either after a stress has occurred or even prophylactically, to promote climate resilient crops. Both seed and foliar strategies could be developed here.

(v) Developing nanoscale micronutrient approaches to enhance photosynthesis, including the efficiency of light capture, conversion to chemical energy (ATP, NADPH) and carbon fixation. Such approaches can be applied with both spatial and temporal precision, maximize carbon production and growth, as well as upregulating nitrogen cycling to ensure appropriate C-N balance.

(vi) Advancing the utilization of agriculture-derived wastes for developing novel nano-enabled composite macronutrient fertilizers such as cellulose, lignin, and chitosan doped with essential secondary and micronutrients to simultaneously provide multiple agronomic benefits, such as crop protection against biotic and abiotic environmental stressors, fortifying edible plant tissues with essential nutrients, and discouraging the input of new reactive nutrients into the biosphere via recycling and repurposing.

(vii) The development of nano-enabled strategies for increased agricultural production must be accompanied by a realistic understanding of economics, scalability, regulatory hurdles, and societal acceptance. A life cycle analysis approach can be used to comprehensively capture all benefits and costs relative to conventional approaches, thereby providing a realistic perspective on what can be achieved with these strategies.

Notably, very few studies have undertaken to comprehensively evaluate the cost-benefit implications of nanotechnology adoption in agriculture in the form of nano agrochemicals (e.g.,Kah et al. 2018; Su et al. 2022)[93], [94] These studies indicate widescale benefits of nano agrochemicals over their conventional counterparts, including positives for environmental outcomes, particular those related to climate change. Clearly, however, more studies by way of meta-analysis of existing data across different cropping systems and nano agrochemical types can provide greater assurance for both the agrochemical industry and product end users (farmers) on the profitability of producing and utilizing nano agrochemicals. As previously discussed, for the agrochemical industry, laying out a suitable framework for scaling of NP production is crucial to prevent drastic changes in existing production lines or platforms, which otherwise adds cost to the end user (23). Such economic analysis must be congruent with policy regulations and advocacy that highlights the regulatory frameworks for NP deployment in agriculture to adequately address any concerns regarding use or potential misuse, thereby promoting societal confidence in the technology. Hence, regulatory agencies such as the US EPA and equivalent agencies in other countries would have to redouble efforts in the areas of risk assessment and promoting more environmentally friendly methods to develop nanomaterials for agricultural and environmental applications. In this regard, deepening the knowledge in green chemistry involving biogenic synthesis of nanoagrochemicals with precursors from agricultural or biological feedstocks such as plants and microbial extracts, chitosan, cellulose, and others, can contribute to both understanding and mitigating risks[95] [96]. More than likely, as the climate continues to change and food insecurity inevitably increases, perhaps dramatically, the risk calculus and the cost-benefit calculus of all novel strategies, including nanotechnology, will shift. It is incumbent on researchers to be ready with viable solutions today, not tomorrow.

In conclusion, our comprehensive review of the relationship between nanomaterials and agriculture has revealed a multifaceted landscape that encompasses both potential challenges and promising solutions. As we navigate the complexities of addressing food security, environmental sustainability, and the impacts of a rapidly changing climate, it becomes evident that there is no "silver bullet" solution. Instead, we find a diverse range of tools at our disposal to sustainably increase food production while simultaneously decreasing environmental impact.

The suitability and effectiveness of these tools will inevitably vary based on local conditions and geographical locations, whether it be rural Iowa in the United States, sub-Saharan Africa, rural Brazil, or urban Singapore. The acknowledgment of this diversity underscores the importance of tailoring our agricultural approaches to meet the unique challenges and opportunities presented by each region. It is encouraging to note that a global scale, organizations such as the European Union are recognizing the significance of this field and are investing in research and development in this area. This international commitment highlights the shared responsibility we all bear in finding solutions to the pressing issues facing our global food system. Societal perceptions and ethical considerations related to nano enabled agriculture is another issue which is worth more attention, particularly on public acceptance and potential ethical concerns.

In the face of mounting challenges, we must conclude on a positive note: failure in addressing these critical issues is simply not an option. The urgency of achieving sustainable and efficient agricultural practices cannot be overstated. As researchers, policymakers, and stakeholders in the agriculture sector, we are tasked with harnessing the potential of nanotechnology and other innovative approaches to ensure food security and safety, mitigate environmental impact, and support livelihoods worldwide. The road ahead may be complex and demanding, but it is also one of boundless opportunities. It is through continued collaboration, innovation, and a shared commitment to positive change that we can pave the way for a brighter and more sustainable future for agriculture.

**Acknowledgements**- The authors graciously acknowledge the USDA NIFA AFRI and Hatch Programs for supporting much of this work, including USDA NIFA AFRI 2020-67022-32416, 2021-67021-34001, 2022-67021-36345, and 2023-67021-39747. Contributions from JCW, CD, and CD were also supported in part by the National Science Foundation under Grant No. CHE-2001611, the NSF Center for Sustainable Nanotechnology (CSN).

References:

[1] A. Haleem, M. Javaid, R. P. Singh, S. Rab, and R. Suman, “Applications of nanotechnology in medical field: a brief review,” *Global Health Journal*, vol. 7, no. 2, pp. 70–77, 2023, doi: https://doi.org/10.1016/j.glohj.2023.02.008.

[2] M. C. Roco, “Nanotechnology: Convergence with modern biology and medicine,” *Curr Opin Biotechnol*, vol. 14, no. 3, pp. 337–346, 2003, doi: 10.1016/S0958-1669(03)00068-5.

[3] G. Fytianos, A. Rahdar, and G. Z. Kyzas, “Nanomaterials in Cosmetics: Recent Updates.,” *Nanomaterials (Basel)*, vol. 10, no. 5, May 2020, doi: 10.3390/nano10050979.

[4] S. H. Nile, V. Baskar, D. Selvaraj, A. Nile, J. Xiao, and G. Kai, “Nanotechnologies in Food Science: Applications, Recent Trends, and Future Perspectives,” *Nanomicro Lett*, vol. 12, no. 1, p. 45, 2020, doi: 10.1007/s40820-020-0383-9.

[5] A. A. Keller, S. McFerran, A. Lazareva, and S. Suh, “Global life cycle releases of engineered nanomaterials,” *Journal of Nanoparticle Research*, vol. 15, no. 6, p. 1692, 2013, doi: 10.1007/s11051-013-1692-4.

[6] A. D. Servin and J. C. White, “Nanotechnology in agriculture: Next steps for understanding engineered nanoparticle exposure and risk,” *NanoImpact*, vol. 1, pp. 9–12, 2016, doi: 10.1016/j.impact.2015.12.002.

[7] D. Stampoulis, S. K. Sinha, and J. C. White, “Assay-dependent phytotoxicity of nanoparticles to plants,” *Environ Sci Technol*, vol. 43, no. 24, pp. 9473–9479, 2009, doi: 10.1021/es901695c.

[8] M. Rui *et al.*, “Phytotoxicity of Silver Nanoparticles to Peanut (Arachis hypogaea L.): Physiological Responses and Food

Safety," *ACS Sustain Chem Eng*, vol. 5, no. 8, pp. 6557–6567, 2017, doi: 10.1021/acssuschemeng.7b00736.

[9] C. M. Rico, S. Majumdar, M. Duarte-Gardea, J. R. Peralta-Videa, and J. L. Gardea-Torresdey, "Interaction of Nanoparticles with Edible Plants and Their Possible Implications in the Food Chain," *J Agric Food Chem*, vol. 59, no. 8, pp. 3485–3498, 2011, doi: 10.1021/jf104517j.

[10] A. Avellan *et al.*, "Nanoparticle Size and Coating Chemistry Control Foliar Uptake Pathways, Translocation, and Leaf-to-Rhizosphere Transport in Wheat," *ACS Nano*, vol. 13, no. 5, pp. 5291–5305, 2019, doi: 10.1021/acsnano.8b09781.

[11] J. Borgatta *et al.*, "Influence of CuO Nanoparticle Aspect Ratio and Surface Charge on Disease Suppression in Tomato (Solanum lycopersicum).," *J Agric Food Chem*, vol. 71, no. 25, pp. 9644–9655, Jun. 2023, doi: 10.1021/acs.jafc.2c09153.

[12] A. Avellan, J. Yun, B. P. Morais, E. T. Clement, S. M. Rodrigues, and G. V Lowry, "Critical Review: Role of Inorganic Nanoparticle Properties on Their Foliar Uptake and in Planta Translocation," *Environ Sci Technol*, vol. 55, no. 20, pp. 13417–13431, Oct. 2021, doi: 10.1021/acs.est.1c00178.

[13] Z. Li *et al.*, "Particle Size Determines the Phytotoxicity of ZnO Nanoparticles in Rice (Oryza sativa L.) Revealed by Spatial Imaging Techniques," *Environ Sci Technol*, vol. 57, no. 36, pp. 13356–13365, Sep. 2023, doi: 10.1021/acs.est.3c03821.

[14] X. Wang, H. Xie, P. Wang, and H. Yin, "Nanoparticles in Plants: Uptake, Transport and Physiological Activity in Leaf and Root," *Materials*, vol. 16, no. 8, pp. 1–21, 2023, doi: 10.3390/ma16083097.

[15] J. Siegel, K. Záruba, V. Švorčík, K. Kroumanová, L. Burketová, and J. Martinec, "Round-shape gold nanoparticles: effect of particle size and concentration on Arabidopsis thaliana root growth," *Nanoscale Res Lett*, vol. 13, 2018, doi: 10.1186/s11671-018-2510-9.

[16] C. Musante and J. C. White, "Toxicity of silver and copper to Cucurbita pepo: Differential effects of nano and bulk-size particles," *Environ Toxicol*, vol. 27, no. 9, pp. 510–517, Sep. 2012, doi: 10.1002/tox.20667.

[17] S. Tripathi, S. K. Sonkar, and S. Sarkar, "Growth stimulation of gram (Cicer arietinum) plant by water soluble carbon

nanotubes," *Nanoscale*, vol. 3, no. 3, pp. 1176–1181, Mar. 2011, doi: 10.1039/c0nr00722f.

[18] R. Raliya and J. C. Tarafdar, "ZnO Nanoparticle Biosynthesis and Its Effect on Phosphorous-Mobilizing Enzyme Secretion and Gum Contents in Clusterbean (Cyamopsis tetragonoloba L.)," *Agricultural Research*, vol. 2, no. 1, pp. 48–57, Mar. 2013, doi: 10.1007/s40003-012-0049-z.

[19] A. A. Badawy, N. A. H. Abdelfattah, S. S. Salem, M. F. Awad, and A. Fouda, "Efficacy assessment of biosynthesized copper oxide nanoparticles (Cuo-nps) on stored grain insects and their impacts on morphological and physiological traits of wheat (triticum aestivum l.) plant," *Biology (Basel)*, vol. 10, no. 3, Mar. 2021, doi: 10.3390/biology10030233.

[20] "Nano-enabled Sustainable and Precision Agriculture," 2023.

[21] P. A. Holden *et al.*, "Evaluation of Exposure Concentrations Used in Assessing Manufactured Nanomaterial Environmental Hazards: Are They Relevant?," *Environ Sci Technol*, vol. 48, no. 18, pp. 10541–10551, 2014, doi: 10.1021/es502440s.

[22] C. O. Dimkpa and P. S. Bindraban, "Nanofertilizers: New Products for the Industry?," *J Agric Food Chem*, vol. 66, no. 26, pp. 6462–6473, 2018, doi: 10.1021/acs.jafc.7b02150.

[23] F. Pulizzi, "Nano in the future of crops," *Nat Nanotechnol*, vol. 14, no. 6, p. 507, 2019, doi: 10.1038/s41565-019-0475-1.

[24] J. C. Angle *et al.*, "Methanogenesis in oxygenated soils is a substantial fraction of wetland methane emissions," *Nat Commun*, vol. 8, no. 1, p. 1567, 2017, doi: 10.1038/s41467-017-01753-4.

[25] W. Elmer and J. C. White, "The future of nanotechnology in plant pathology," *Annu Rev Phytopathol*, vol. 56, pp. 111–133, 2018, doi: 10.1146/annurev-phyto-080417-050108.

[26] C. Krishnaraj, R. Ramachandran, K. Mohan, and P. T. Kalaichelvan, "Optimization for rapid synthesis of silver nanoparticles and its effect on phytopathogenic fungi," *Spectrochim Acta A Mol Biomol Spectrosc*, vol. 93, pp. 95–99, 2012, doi: https://doi.org/10.1016/j.saa.2012.03.002.

[27] P. Dutta *et al.*, "Advances in Nanotechnology as a Potential Alternative for Plant Viral Disease Management," *Front Microbiol*, vol. 13, no. June, pp. 1–12, 2022, doi: 10.3389/fmicb.2022.935193.

[28] L. He, Y. Liu, A. Mustapha, and M. Lin, "Antifungal activity of zinc oxide nanoparticles against Botrytis cinerea and Penicillium expansum," *Microbiol Res*, vol. 166, no. 3, pp. 207–215, 2011, doi: https://doi.org/10.1016/j.micres.2010.03.003.

[29] C. Jayaseelan *et al.*, "Novel microbial route to synthesize ZnO nanoparticles using Aeromonas hydrophila and their activity against pathogenic bacteria and fungi.," *Spectrochim Acta A Mol Biomol Spectrosc*, vol. 90, pp. 78–84, May 2012, doi: 10.1016/j.saa.2012.01.006.

[30] C. O. Dimkpa, J. E. McLean, D. W. Britt, and A. J. Anderson, "Antifungal activity of ZnO nanoparticles and their interactive effect with a biocontrol bacterium on growth antagonism of the plant pathogen Fusarium graminearum," *BioMetals*, vol. 26, no. 6, pp. 913–924, 2013, doi: 10.1007/s10534-013-9667-6.

[31] C. O. Dimkpa, "Can nanotechnology deliver the promised benefits without negatively impacting soil microbial life?," *J Basic Microbiol*, vol. 54, no. 9, pp. 889–904, 2014, doi: 10.1002/jobm.201400298.

[32] Z. Zabrieski *et al.*, "Pesticidal activity of metal oxide nanoparticles on plant pathogenic isolates of Pythium," *Ecotoxicology*, vol. 24, no. 6, pp. 1305–1314, 2015, doi: 10.1007/s10646-015-1505-x.

[33] T. Farooq *et al.*, "Nanotechnology and Plant Viruses: An Emerging Disease Management Approach for Resistant Pathogens.," *ACS Nano*, vol. 15, no. 4, pp. 6030–6037, Apr. 2021, doi: 10.1021/acsnano.0c10910.

[34] T. Shidore, N. Zuverza-Mena, and W. da Silva, "Small RNA profiling analysis of two recombinant strains of potato virus Y in infected tobacco plants," *Virus Res*, vol. 288, p. 198125, 2020, doi: https://doi.org/10.1016/j.virusres.2020.198125.

[35] T. Shidore, N. Zuverza-Mena, J. C. White, and W. da Silva, "Nanoenabled Delivery of RNA Molecules for Prolonged Antiviral Protection in Crop Plants: A Review," *ACS Appl Nano Mater*, vol. 4, no. 12, pp. 12891–12904, Dec. 2021, doi: 10.1021/acsanm.1c03512.

[36] Rajani, P. Mishra, S. Kumari, P. Saini, and R. K. Meena, "Role of nanotechnology in management of plant viral diseases,"

*Mater Today Proc*, vol. 69, pp. 1–10, 2022, doi: https://doi.org/10.1016/j.matpr.2022.06.355.

[37] K. Giannousi, I. Avramidis, and C. Dendrinou-Samara, "Synthesis{,} characterization and evaluation of copper based nanoparticles as agrochemicals against Phytophthora infestans," *RSC Adv.*, vol. 3, no. 44, pp. 21743–21752, 2013, doi: 10.1039/C3RA42118J.

[38] W. H. Elmer and J. C. White, "The use of metallic oxide nanoparticles to enhance growth of tomatoes and eggplants in disease infested soil or soilless medium," *Environ Sci Nano*, vol. 3, pp. 1072–1079, 2016.

[39] Y. Wang *et al.*, "Therapeutic Delivery of Nanoscale Sulfur to Suppress Disease in Tomatoes: In Vitro Imaging and Orthogonal Mechanistic Investigation," *ACS Nano*, vol. 16, no. 7, pp. 11204–11217, 2022, doi: 10.1021/acsnano.2c04073.

[40] Y. Wang *et al.*, "Surface Coated Sulfur Nanoparticles Suppress Fusarium Disease in Field Grown Tomato: Increased Yield and Nutrient Biofortification.," *J Agric Food Chem*, vol. 70, no. 45, pp. 14377–14385, Nov. 2022, doi: 10.1021/acs.jafc.2c05255.

[41] V. P. Giri *et al.*, "A Review of Sustainable Use of Biogenic Nanoscale Agro-Materials to Enhance Stress Tolerance and Nutritional Value of Plants.," *Plants (Basel)*, vol. 12, no. 4, Feb. 2023, doi: 10.3390/plants12040815.

[42] B. Sharma, S. Tiwari, K. C. Kumawat, and M. Cardinale, "Nano-biofertilizers as bio-emerging strategies for sustainable agriculture development: Potentiality and their limitations.," *Sci Total Environ*, vol. 860, p. 160476, Feb. 2023, doi: 10.1016/j.scitotenv.2022.160476.

[43] I. Karmous *et al.*, "Biologically synthesized zinc and copper oxide nanoparticles using Cannabis sativa L. enhance soybean (Glycine max) defense against fusarium virguliforme," *Pestic Biochem Physiol*, vol. 194, p. 105486, 2023, doi: https://doi.org/10.1016/j.pestbp.2023.105486.

[44] D. K. A. N. D. B. C. A. A. N. D. A. T. W. A. N. D. E. P. D. Bandara Ananda Y. AND Weerasooriya, "Dissecting the economic impact of soybean diseases in the United States over two decades," *PLoS One*, vol. 15, no. 4, pp. 1–28, Feb. 2020, doi: 10.1371/journal.pone.0231141.

[45] M. Pavlicevic *et al.*, “Nanoparticles and biochar with adsorbed plant growth-promoting rhizobacteria alleviate Fusarium wilt damage on tomato and watermelon,” *Plant Physiology and Biochemistry*, vol. 203, p. 108052, 2023, doi: https://doi.org/10.1016/j.plaphy.2023.108052.

[46] T. Ahmed *et al.*, “Bioengineered chitosan-iron nanocomposite controls bacterial leaf blight disease by modulating plant defense response and nutritional status of rice (Oryza sativa L.),” *Nano Today*, vol. 45, p. 101547, 2022, doi: https://doi.org/10.1016/j.nantod.2022.101547.

[47] E. K. F. Elbeshehy, W. M. Hassan, and A. A. Baeshen, “Controlling Pepper Mild Mottle Virus (PMMoV) Infection in Pepper Seedlings by Use of Chemically Synthetic Silver Nanoparticles.,” *Molecules*, vol. 28, no. 1, Dec. 2022, doi: 10.3390/molecules28010139.

[48] M. Adeel, T. Farooq, J. C. White, Y. Hao, Z. He, and Y. Rui, “Carbon-based nanomaterials suppress tobacco mosaic virus (TMV) infection and induce resistance in Nicotiana benthamiana.,” *J Hazard Mater*, vol. 404, no. Pt A, p. 124167, Feb. 2021, doi: 10.1016/j.jhazmat.2020.124167.

[49] Y. Hao *et al.*, “Engineered nanomaterials suppress Turnip mosaic virus infection in tobacco (Nicotiana benthamiana),” *Environ. Sci.: Nano*, vol. 5, no. 7, pp. 1685–1693, 2018, doi: 10.1039/C8EN00014J.

[50] A. Sangwan *et al.*, “Size variations of mesoporous silica nanoparticle control uptake efficiency and delivery of AC2-derived dsRNA for protection against tomato leaf curl New Delhi virus,” *Plant Cell Rep*, vol. 42, no. 10, pp. 1571–1587, 2023, doi: 10.1007/s00299-023-03048-z.

[51] W. Elmer and J. C. White, “The Future of Nanotechnology in Plant Pathology.,” *Annu Rev Phytopathol*, vol. 56, pp. 111–133, Aug. 2018, doi: 10.1146/annurev-phyto-080417-050108.

[52] W. H. Elmer *et al.*, “Influence of Single and Combined Mixtures of Metal Oxide Nanoparticles on Eggplant Growth, Yield, and Verticillium Wilt Severity.,” *Plant Dis*, vol. 105, no. 4, pp. 1153–1161, Apr. 2021, doi: 10.1094/PDIS-07-20-1636-RE.

[53] C. Deng *et al.*, “Nanoscale CuO charge and morphology control Fusarium suppression and nutrient biofortification in field-grown tomato and watermelon,” *Science of The Total*

*Environment*, vol. 905, p. 167799, 2023, doi: https://doi.org/10.1016/j.scitotenv.2023.167799.

[54] K. Lamsal, S.-W. Kim, J. H. Jung, Y. S. Kim, K. S. Kim, and Y. S. Lee, “Inhibition Effects of Silver Nanoparticles against Powdery Mildews on Cucumber and Pumpkin.,” *Mycobiology*, vol. 39, no. 1, pp. 26–32, Mar. 2011, doi: 10.4489/MYCO.2011.39.1.026.

[55] I. O. Adisa *et al.*, “Role of Cerium Compounds in Fusarium Wilt Suppression and Growth Enhancement in Tomato (Solanum lycopersicum),” *J Agric Food Chem*, vol. 66, no. 24, pp. 5959–5970, Jun. 2018, doi: 10.1021/acs.jafc.8b01345.

[56] I. O. Adisa *et al.*, “Nutritional Status of Tomato (Solanum lycopersicum) Fruit Grown in Fusarium-Infested Soil: Impact of Cerium Oxide Nanoparticles,” *J Agric Food Chem*, vol. 68, no. 7, pp. 1986–1997, Feb. 2020, doi: 10.1021/acs.jafc.9b06840.

[57] P. A. Nazarov, D. N. Baleev, M. I. Ivanova, L. M. Sokolova, and M. V Karakozova, “Infectious Plant Diseases: Etiology, Current Status, Problems and Prospects in Plant Protection.,” *Acta Naturae*, vol. 12, no. 3, pp. 46–59, 2020, doi: 10.32607/actanaturae.11026.

[58] “No TitleNational Integrated Drought Information System.” [Online]. Available: https://www.drought.gov/current-conditions

[59] J. Singh, M. Ashfaq, C. B. Skinner, W. B. Anderson, V. Mishra, and D. Singh, “Enhanced risk of concurrent regional droughts with increased ENSO variability and warming,” *Nat Clim Chang*, vol. 12, no. 2, pp. 163–170, 2022, doi: 10.1038/s41558-021-01276-3.

[60] P. K. Krishnamurthy R, J. B. Fisher, R. J. Choularton, and P. M. Kareiva, “Anticipating drought-related food security changes,” *Nat Sustain*, vol. 5, no. 11, pp. 956–964, 2022, doi: 10.1038/s41893-022-00962-0.

[61] M. T. El-Saadony *et al.*, “Role of Nanoparticles in Enhancing Crop Tolerance to Abiotic Stress: A Comprehensive Review,” *Front Plant Sci*, vol. 13, no. November, pp. 1–31, 2022, doi: 10.3389/fpls.2022.946717.

[62] A. Singh, S. Tiwari, J. Pandey, C. Lata, and I. K. Singh, “Role of nanoparticles in crop improvement and abiotic stress

management," *J Biotechnol*, vol. 337, pp. 57–70, 2021, doi: https://doi.org/10.1016/j.jbiotec.2021.06.022.

[63] C. O. Dimkpa, P. S. Bindraban, J. Fugice, S. Agyin-Birikorang, U. Singh, and D. Hellums, "Composite micronutrient nanoparticles and salts decrease drought stress in soybean," *Agron Sustain Dev*, vol. 37, no. 1, p. 5, 2017, doi: 10.1007/s13593-016-0412-8.

[64] C. O. Dimkpa, U. Singh, P. S. Bindraban, W. H. Elmer, J. L. Gardea-Torresdey, and J. C. White, "Zinc oxide nanoparticles alleviate drought-induced alterations in sorghum performance, nutrient acquisition, and grain fortification.," *Sci Total Environ*, vol. 688, pp. 926–934, Oct. 2019, doi: 10.1016/j.scitotenv.2019.06.392.

[65] C. O. Dimkpa *et al.*, "Interactive effects of drought, organic fertilizer, and zinc oxide nanoscale and bulk particles on wheat performance and grain nutrient accumulation," *Science of The Total Environment*, vol. 722, p. 137808, 2020, doi: https://doi.org/10.1016/j.scitotenv.2020.137808.

[66] F. Ahmed, B. Javed, A. Razzaq, and Z.-U.-R. Mashwani, "Applications of copper and silver nanoparticles on wheat plants to induce drought tolerance and increase yield.," *IET Nanobiotechnol*, vol. 15, no. 1, pp. 68–78, Feb. 2021, doi: 10.1049/nbt2.12002.

[67] M. A. Shallan, H. M. M. Hassan, A. A. M. Namich, and A. A. Ibrahim, "Biochemical and physiological effects of TiO2 and SiO2 nanoparticles on cotton plant under drought stress," *Res J Pharm Biol Chem Sci*, vol. 7, no. 4, pp. 1540–1551, 2016.

[68] L. M. Mahmoud, M. Dutt, C. I. Vincent, and J. W. Grosser, "Salinity-induced physiological responses of three putative salt tolerant citrus rootstocks," *Horticulturae*, vol. 6, no. 4, pp. 1–16, 2020, doi: 10.3390/horticulturae6040090.

[69] M. Afshari, A. Pazoki, and O. Sadeghipour, "Foliar-applied Silicon and its Nanoparticles Stimulate Physio-chemical Changes to Improve Growth, Yield and Active Constituents of Coriander (Coriandrum Sativum L.) Essential Oil Under Different Irrigation Regimes," *Silicon*, vol. 13, no. 11, pp. 4177–4188, 2021, doi: 10.1007/s12633-021-01101-8.

[70] S. Chen, H. Liu, Z. Yangzong, J. L. Gardea-Torresdey, J. C. White, and L. Zhao, "Seed Priming with Reactive Oxygen Species-Generating Nanoparticles Enhanced Maize Tolerance

to Multiple Abiotic Stresses," *Environ Sci Technol*, vol. 0, no. 0, p. null, doi: 10.1021/acs.est.3c07339.

[71] S. Chen *et al.*, "Engineering Climate-Resilient Rice Using a Nanobiostimulant-Based 'Stress Training' Strategy," *ACS Nano*, vol. 17, no. 11, pp. 10760–10773, 2023, doi: 10.1021/acsnano.3c02215.

[72] Q. ul Ain *et al.*, "Chapter thirteen - Use of nano-fertilizers to improve the nutrient use efficiencies in plants," in *Sustainable Plant Nutrition*, T. Aftab and K. R. Hakeem, Eds., Academic Press, 2023, pp. 299–321. doi: https://doi.org/10.1016/B978-0-443-18675-2.00013-4.

[73] N. Basavegowda and K.-H. Baek, "Current and future perspectives on the use of nanofertilizers for sustainable agriculture: the case of phosphorus nanofertilizer," *3 Biotech*, vol. 11, no. 7, p. 357, 2021, doi: 10.1007/s13205-021-02907-4.

[74] P. S. Bindraban, C. O. Dimkpa, and R. Pandey, "Exploring phosphorus fertilizers and fertilization strategies for improved human and environmental health," *Biol Fertil Soils*, vol. 56, no. 3, pp. 299–317, 2020, doi: 10.1007/s00374-019-01430-2.

[75] R. Liu and R. Lal, "Synthetic apatite nanoparticles as a phosphorus fertilizer for soybean (Glycine max)," *Sci Rep*, vol. 4, pp. 1–6, 2014, doi: 10.1038/srep05686.

[76] N. Kottegoda *et al.*, "Urea-Hydroxyapatite Nanohybrids for Slow Release of Nitrogen.," *ACS Nano*, vol. 11, no. 2, pp. 1214–1221, Feb. 2017, doi: 10.1021/acsnano.6b07781.

[77] C. O. Dimkpa, J. C. White, W. H. Elmer, and J. L. Gardea-Torresdey, "Nanoparticle and Ionic Zn Promote Nutrient Loading of Sorghum Grain under Low NPK Fertilization.," *J Agric Food Chem*, vol. 65 39, pp. 8552–8559, 2017.

[78] C. O. Dimkpa, U. Singh, P. S. Bindraban, W. H. Elmer, J. L. Gardea-Torresdey, and J. C. White, "Exposure to Weathered and Fresh Nanoparticle and Ionic Zn in Soil Promotes Grain Yield and Modulates Nutrient Acquisition in Wheat (Triticum aestivum L.)," *J Agric Food Chem*, vol. 66, no. 37, pp. 9645–9656, Sep. 2018, doi: 10.1021/acs.jafc.8b03840.

[79] C. O. Dimkpa *et al.*, "Addition-omission of zinc, copper, and boron nano and bulk oxide particles demonstrate element and size -specific response of soybean to micronutrients

exposure," *Science of The Total Environment*, vol. 665, pp. 606–616, 2019, doi: https://doi.org/10.1016/j.scitotenv.2019.02.142.

[80] B. Sharma, L. O. B. Afonso, M. P. Singh, U. Soni, and D. M. Cahill, "Zinc- and magnesium-doped hydroxyapatite-urea nanohybrids enhance wheat growth and nitrogen uptake," *Sci Rep*, vol. 12, no. 1, p. 19506, 2022, doi: 10.1038/s41598-022-20772-w.

[81] C. O. Dimkpa, C. Deng, Y. Wang, I. O. Adisa, J. Zhou, and J. C. White, "Chitosan and Zinc Oxide Nanoparticle-Enhanced Tripolyphosphate Modulate Phosphorus Leaching in Soil," *ACS Agricultural Science & Technology*, vol. 3, no. 6, pp. 487–498, Jun. 2023, doi: 10.1021/acsagscitech.3c00054.

[82] L. R. Sigmon *et al.*, "Biodegradable Polymer Nanocomposites Provide E ff ective Delivery and Reduce Phosphorus Loss during Plant Growth," 2021, doi: 10.1021/acsagscitech.1c00149.

[83] L. R. Sigmon *et al.*, "Role of Phosphorus Type and Biodegradable Polymer on Phosphorus Fate and Efficacy in a Plant-Soil System," *J Agric Food Chem*, vol. 71, no. 44, pp. 16493–16503, Nov. 2023, doi: 10.1021/acs.jafc.3c04735.

[84] D. Gomez-Maldonado *et al.*, "Modifying soluble NPK release with hydrophobized nanocellulose-based hydrogels for sustainable enhanced efficiency fertilizers," *Environ Sci Nano*, 2023, doi: 10.1039/d3en00306j.

[85] M. Li *et al.*, "Nano-enabled strategies to enhance biological nitrogen fixation," *Nat Nanotechnol*, vol. 18, no. 7, pp. 688–691, 2023, doi: 10.1038/s41565-023-01392-5.

[86] M. He and F. A. Dijkstra, "Drought effect on plant nitrogen and phosphorus: a meta-analysis.," *New Phytol*, vol. 204, no. 4, pp. 924–931, Dec. 2014, doi: 10.1111/nph.12952.

[87] S. Fischer, T. Hilger, H.-P. Piepho, I. Jordan, and G. Cadisch, "Do we need more drought for better nutrition? The effect of precipitation on nutrient concentration in East African food crops," *Science of The Total Environment*, vol. 658, pp. 405–415, 2019, doi: https://doi.org/10.1016/j.scitotenv.2018.12.181.

[88] E. Moreno-Jiménez, C. Plaza, H. Saiz, R. Manzano, M. Flagmeier, and F. T. Maestre, "Aridity and reduced soil

micronutrient availability in global drylands," *Nat Sustain*, vol. 2, no. 5, pp. 371–377, 2019.

[89] M. Li *et al.*, "Molybdenum Nanofertilizer Boosts Biological Nitrogen Fixation and Yield of Soybean through Delaying Nodule Senescence and Nutrition Enhancement," *ACS Nano*, vol. 17, no. 15, pp. 14761–14774, 2023, doi: 10.1021/acsnano.3c02783.

[90] A. Hussain *et al.*, "Responses of wheat (Triticum aestivum) plants grown in a Cd contaminated soil to the application of iron oxide nanoparticles.," *Ecotoxicol Environ Saf*, vol. 173, pp. 156–164, May 2019, doi: 10.1016/j.ecoenv.2019.01.118.

[91] N. Gupta *et al.*, "Impact of Foliar Application of ZnO and Fe(3)O(4) Nanoparticles on Seed Yield and Physio-Biochemical Parameters of Cucumber (Cucumis sativus L.) Seed under Open Field and Protected Environment vis a vis during Seed Germination.," *Plants (Basel)*, vol. 11, no. 23, Nov. 2022, doi: 10.3390/plants11233211.

[92] M. F. Seleiman, W. A. Al-Selwey, A. A. Ibrahim, M. Shady, and A. A. Alsadon, "Foliar Applications of ZnO and SiO2 Nanoparticles Mitigate Water Deficit and Enhance Potato Yield and Quality Traits," *Agronomy*, vol. 13, no. 2, pp. 1–16, 2023, doi: 10.3390/agronomy13020466.

[93] M. Kah, R. S. Kookana, A. Gogos, and T. D. Bucheli, "A critical evaluation of nanopesticides and nanofertilizers against their conventional analogues," *Nat Nanotechnol*, vol. 13, no. 8, pp. 677–684, 2018, doi: 10.1038/s41565-018-0131-1.

[94] Y. Su *et al.*, "Cost–benefit analysis of nanofertilizers and nanopesticides emphasizes the need to improve the efficiency of nanoformulations for widescale adoption," *Nat Food*, vol. 3, no. 12, pp. 1020–1030, 2022, doi: 10.1038/s43016-022-00647-z.

[95] D. Prajapati *et al.*, "Chitosan nanomaterials: A prelim of next-generation fertilizers; existing and future prospects," *Carbohydr Polym*, vol. 288, p. 119356, 2022, doi: https://doi.org/10.1016/j.carbpol.2022.119356.

[96] N. A. Shinde, P. G. Kawar, and S. G. Dalvi, "Chitosan-based nanoconjugates: A promising solution for enhancing crops drought-stress resilience and sustainable yield in the face of climate change," *Plant Nano Biology*, vol. 7, p. 100059, 2024, doi: https://doi.org/10.1016/j.plana.2024.100059.

**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- This review summarizes the legacy of nanotechnology in agriculture.
- The implications of nanomaterials due to dosage effect are noted.
- The benefits of nanomaterials for nano-enabled agriculture are highlighted.
- Nanotechnology can address productivity lapses under a changing climate.
- Nanotechnology can, therefore, contribute to global food and nutrition security.