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REVIEW

A review of the use of engineered nanomaterials to suppress plant disease and enhance crop yield

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Abstract Nanotechnology has the potential to play a critical role in global food production, food security, and food safety. The applications of nanotechnology in agriculture include fertilizers to increase plant growth and yield, pesticides for pest and disease management, and sensors for monitoring soil quality and plant health. Over the past decade, a number of patents and products incorporating nanomaterials into agricultural practices (e.g., nanopesticides, nanofertilizers, and nanosensors) have been developed. The collective goal of all of these approaches is to enhance the efficiency and sustainability of agricultural practices by requiring less input and generating less waste than conventional products and approaches. This review evaluates the current literature on the use of nanoscale nutrients (metals, metal oxides, carbon) to suppress crop disease and subsequently enhance growth and yield. Notably, this enhanced yield may not only be directly linked to the reduced presence of pathogenic organisms, but also to the potential nutritional value of the nanoparticles themselves, especially for the essential micronutrients necessary for host defense. We also posit that these positive effects are likely a result of the greater availability of the nutrients in the "nano" form. Last, we offer comments on the current regulatory perspective for such applications.

Keywords Nanotechnology · Agriculture · Pathogen

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Introduction–the role of plant nutrition in crop diseases suppression

Before discussing the use of nanoscale micronutrients to suppress crop disease, the relationship between nutritional status and plant disease must be explored. Approaches for managing crop disease are numerous and include genetic breeding, cultural schemes with sanitation, host indexing, enhanced eradication protocols, new pesticide products, and integrated pest management (IPM)(USDA-ARS). The development of host resistance is clearly the most successful strategy for plant disease control. However, most crops lack available resistance genes, and further development of genetically modified food crops remains an issue of public concern. An alternative viable strategy for suppressing crop disease is to manage plant nutritional status. Robust nutrition often mediates the responses of crop susceptibility and resistance to a disease. One major limitation to adequate nutrition is that crops vary significantly in their nutrient requirements, and that different nutrient amounts interact with the range of plant diseases in variable ways. In addition, amendment protocols necessary to maximize plant health often vary with the level of infection or absence of the pathogen.

Micronutrients are critical in the defense against crop disease, with tissue infection inducing a cascade of reactions commonly resulting in the production of inhibitory secondary metabolites. Notably, these metabolites are often generated by enzymes that require activation by micronutrient cofactors. For example, Mn, Cu, and Zn enhance disease resistance by activating the host defense enzymes phenylalanine ammonia lyase and polyphenol oxidases (Duffy 2007; Evans et al. 2007; Huber and Thompson 2007; Römheld 1991). Importantly, the difference between resistance and susceptibility to infection is often how quickly cell can generate its defensive metabolites. It is clear that sufficient micronutrient content in key tissues will enhance plant defense in the presence of pathogens but a number of factors may limit this supply. Low element availability in neutral to alkaline soils often severely restricts available micronutrient levels. For example, Fe, Mn, and Zn become increasingly unavailable as soil pH approaches alkaline, which limits uptake by roots and compromises root tissue for infection (Sims 1986). In addition, the application of nutrients to shoot tissues with subsequent shoot-to-root translocation delivery is highly ineffective since most micronutrients are not basipetally transferred, unlike N, P, and K (Bukovac and Wittwer 1957).

Another potential strategy for enhanced disease defense may involve non-essential elements such as Al and Si. For example, Si-accumulating species are known to show resistance to a number of foliar and root pathogens (Datnoff et al. 2007). Although many species accumulate this element in robust amounts (1–10 % dry mass), Si tissue content actually depends on availability in the soil, which is frequently limited. Alternatively, a number of field studies have shown that amendments to acidify soil can be used to facilitate root disease and soilborne pathogen management. However, the use of Al has been limited because over-application can cause significant crop damage and yield reduction, whereas insufficient amendment confers no benefit to disease reduction (Shew et al. 2007). Importantly, the role that non-essential inorganic compounds may play in the activation of host defense mechanisms remains largely unexplored. For example, orthophosphate and $CaCl_2$ amendment increased the levels of phenolic compounds that subsequently reduced damage from *Fusarium* wilt (Biswas et al. 2012). It is possible that metal oxides could induce similar responses but this remains unknown, but similar limitations involving low availability in soil and minimal shoot-absorption/root-translocation will likely confound the efficacy of disease suppression. Importantly, as discussed below, one of the most notable characteristics of nanoscale metals and metal oxides is the greatly enhanced availability to, and translocation within, plants. Consequently, the use of nanoparticle-based micronutrient formulations may offer a highly effective novel platform for crop disease suppression and yield enhancement through more targeted and strategic nutrition-based promotion of host resistance.

Nanomaterials synthesis

Prior to discussing the potential use of nanomaterials for disease suppression efforts in agriculture, we must first address the issue of nanomaterial synthesis. The primary reason for this is to highlight the multiple steps during production by which by-products and impurities can contaminate the final formulation and cause negative impacts on the receiving agricultural system (Petersen et al. 2014). A number of both chemical and physical methods have been developed for nanoparticle (NPs) synthesis, and there are a number of newer approaches seeking more "ecofriendly" platforms such as biosynthesis using plant extracts (Mittal et al. 2013). The traditional methods of synthesis often rely on chemical reduction in a liquid phase as this enables greater control over structure and yield (Charitidis et al. 2014). Common reducing agents include citric acid, hydroxylamine, cellulose, hydrogen peroxide, sodium carbonate, and sodium hydroxide. Stabilizing agents are frequently added to promote dispersion and uniform particle size distribution; common stabilizers are polyvinyl alcohol and sodium polyacrylate. Detailed chemical reduction methods have been reported for Ag (Guzmán et al. 2009), Au (Akbarzadeh et al. 2009), and Pt (Charitidis et al. 2014), among others. Metal oxide NP synthesis such as ZnO, CeO_2, TiO_2, CuO, and Al_2O_3 typically relies on vapor phase-based techniques (Comini 2013). Hydrothermal techniques are seeing increasing use due to greater control of product properties and purity.

A number of physical techniques can also be used for NM synthesis, with common approaches being laser ablation, chemical vapor deposition (CVD), sonochemical reduction, supercritical fluids, and gamma radiation (Charitidis et al. 2014). For carbon, fullerenes are often synthesized by arc discharge or gas combustion methods (Swihart 2003), whereas carbon nanotubes are produced by CVD through the decomposition of gaseous hydrocarbon. Notably, a major shortcoming of CVD is related to product purity, which is inversely related to yield (Lai and Zhang 2011). Given the sensitivity of many crops to the heavy metals and solvents common to these synthesis protocols and the potential for food contamination from these constituents, it is clearly important to consider and recognize the potential for significant toxicological impacts from NP impurities and perhaps more importantly, to adequately characterize the material prior to use in agriculture.

NP effects on disease suppression and plant growth

Nanoparticle-induced phytotoxicity

Table 1 lists a range of nanofertilizers and nanopesticides that are or will soon be commercially available, although it is also clear that a number of other products are under development (Suppan 2013). It is worth noting that the rapid deployment of nanotechnology, along with the general lack of particle size-specific regulatory framework, has raised concerns over the potential impacts NPs could have on human health and the environment. The toxicity of metal NPs has been reviewed a number of times (Hawthorne et al. 2014; Ma et al. 2010; Miralles et al. 2012; Rico et al. 2011), and several studies have reported on particle toxicity to different crops. Figure 1, reprinted with permission from Rico et al. 2011, summarizes the mechanisms of interactions between NPs and terrestrial plants. Nanoparticle Cu exposure to *Elodea densa* Planch was found to increase lipid peroxidation by 180 %, whereas catalase and superoxide dismutase activity increased by 1.5-2.0-fold (Nekrasova et al. 2011). *Z. mays* L. leaf cell wall pore diameters were decreased from 6.6 to 3.0 nm upon exposure to TiO_2 (1000 mg/L) (Asli and Neumann 2009). Ghosh et al. described a 5 % reduction in *Allium cepa* root growth (−4.81 %) upon exposure to TiO_2 at 6 mM of (Ghosh et al. 2010). Nanoparticle Ag was shown to completely inhibit ryegrass (*Lolium*) and flax (*Linum usitatissimum*) germination at 750 and 1500 mg L^{-1}, but a reduction of only 13 % was observed for barley (*Hordeum vulgare* L.) at 1500 mg L^{-1} (El-Temsah and Joner 2012). Similarly, zucchini (*Cucurbita pepo*) growth was decreased by 60 and 75 % in the presence of Ag NPs and multi-wall carbon nanotubes (MWCNT), respectively (Stampoulis et al. (2009). The potential for NP bioaccumulation within crops and transfer among trophic levels is another concern related to NM use in agricultural systems (Hawthorne et al. 2014). For example, NP CeO_2 was recently shown to accumulate in the roots of exposed soybean, followed by particle translocation to edible tissue (Hernandez-Viezcas et al. 2013). Although these and a large number of other studies have reported NP phytotoxicity and accumulation, a similar number have reported negligible or in some cases, positive effects. The general consensus is that too little information exists to accurately assess NP hazard and risk in the environment, and as such, the use of nanotechnology to suppress crop disease and enhance yield should proceed with caution.

Nano-enabled disease suppression and enhanced crop growth

Annual agricultural crop losses that directly result from plant diseases are measured in billions of dollars in the United States alone (USDA). Pathogen control efforts through fungicide applications exceed $600 million per year (Gonzalez-Fernandez et al. 2010). Plant diseases are caused by viruses, bacteria, fungi, and nematodes; the resulting infection/infestation causes economic loss by decreasing yield, product quality, and/or shelf life. Patel et al. (2014) reported that mycotoxins impact up to 25 % of food crops worldwide. Given the additional stresses on agricultural productivity anticipated by an expanding global population and a changing climate, the economic losses may prove to be of secondary concern.

Novel platforms for crop disease management are critically needed and will be a central component to

Table 1 Nano-enabled products/patents in agriculture

Name of product/patent	Product type	Relevant NP composition	Patent number	Inventors
Active nano-grade organic fine humic fertilizer and its production	Active organic fertilizer	Nano-fermented active organic fertilizer	CN1472176-A	Wu et al.
Application of hydroxide nano rare earth to produce fertilizer products	Fertilizer	Hydroxide of nano rare earth	CN1686955-A	Wang et al. .
Application of oxide nano rare earth in fertilizer	Fertilizer	Nano rare earth	CN1686957-A	Wang et al.
Biological organic compound liquid nanofertilizer and preparing process	Nano-composite liquid fertilizer/pest resistant	Unclear	CN1452636-A	Ni J.
Coated slow-releasing fertilizer and its production	Fertilizer	Inorganic filler; polar bonding material	CN1854111-A	Ying et al.
Environment-friendly carbon-nano synergistic complex fertilizers	Fertilizer	Carbon nanomaterials	US 0174032-A1	Lui et al.
Liquid complex fertilizer which contains nanosilver and allicin and preparation methods to provide antibacterial effects thus to increase crop production	Fertilizer/ antibacterial	Nanosilver	KR 000265-A	Kim et al.
Nano-composite superabsorbent containing fertilizer nutrients used in agriculture	Fertilizer	Nano-composite carbohydrate graft copolymer	US 0139347-A1	Barati et al.
Nano-diatomite and Zeolite ceramic crystal powder	Fertilizer	Nano diatomite and zeolite	US 0115469 -A1	Yu et al.
Nano-leucite for slow-releasing nitrogen fertilizer and Green environment	Fertilizer	Potassium aluminum silicate (Leucite) NPs occluded by calcium ammonium nitrates	US 0190226 -A1	Farrukh et al.
Nano long-acting selenium fertilizer	Fertilizer	Nano-selenium	US 0326153-A1	Yin et al.
Nano-micron foam plastic mixed polymer fertilizer adhesive coating agent preparation method	Fertilizer	Nano-micron-foamed plastic organic compound mixed polymer	CN1631952-A	Zhang et al.
New method for preparation of controlled release special fertilizer comprises mixing and granulating Ximaxi clay minerals, coating with various fertilizers, trace elements, and additives	Fertilizer	Nano-clay	CN1349958-A	Li et al.
Non-metallic nano/micro particles coated with metal, process and applications	Fertilizer	Core of the non-metallic nano/micro particles is selected from inorganic material such as silica, barium sulfate. The metal coating is selected from Ag or transition/noble metals: copper, nickel, silver, palladium, osmium, ruthenium, rhodium	US 0047546-A1	Malshe et al.
Plant growth liquid containing titanium dioxide nanoparticles comprises an aqueous titanium dioxide colloid solution incorporating a surfactant	Fertilizer	Nano-titanium dioxide	BR03721-A	Lee et al.

Table 1 continued

Name of product/patent	Product type	Relevant NP composition	Patent number	Inventors
Process compromises combining soil repairing technique and nanobiological fertilizer to promote growth of microbes, improve soil, and remove residual herbicides	Biological fertilizer	Nano-class biological fertilizer	CN1413963-A	Min et al.
Production of novel precision customized control release fertilizers	Controlled release fertilizers	Transition metal silicates	US 8375629 B2	Prasad et al.
Production technology of nano-clay-polyester mixed polymer fertilizer coating cementing agent	Controlled releasing fertilizer; soil improver	Nano-clay polyester mixed polymer	CN1414033-A	Zhang et al.
Production technology of coating cement for nano sulfonaate lignin mixture fertilizer	Coating cement for controlled release fertilizer	Nano-sulfonated lignin mixture water solution	CN1417173-A	Zhang et al.
Preparation of nanometer-scale olefin/starch mixed polymer fertilizer covering agent	Slow release fertilizer	Nano-level non-homogeneous phase mixed polymer of hydroxyethyl methacrylate	CN1546543-A	Zhang et al.
Silicon Nanocarrier for delivery of drug, pesticides, and herbicides, and for waste water treatment	Pesticide	Nano-silicon carrier	US 0225412-A1	Sardari et al.
Stable nanoparticulate composition for release of active agents	Fertilizer	Nano-sized particle of an active agent	WO 56866-A1	Bosch et al.
HeiQ AGS-20	Pesticide	Silver-silica composite material	US 0294919-A1 *Product available in the market	Company: HeiQ materials
Nano-Argentum 10	Fertilizer/antifungal/bug repellent	Silver	*Product available in the market	Company: NanoSys GmbH

Patents retrieved from FPO IP Research & Communities, and Derwent Innovations Index in ISI Web of Knowledge. Table reprinted from Servin et al. *Nanoscale Micronutrients Suppress Disease*. VFRC Report 2015/x. Virtual Fertilizer Research Center, Washington, D.C

any long-term strategy for sustaining or increasing agricultural production. The potential use of NP amendments to address these needs has been a topic of discussion for a number of years. Navarro et al. (2008) speculated that high-surface area nanoscale materials could more effectively retain nutrients and serve as a longer term and more stable nutrient reservoir to plants. However, this review focuses on the more direct effects of nanoscale amendments on plant pathogens. Specifically, can NPs be used to directly suppress pathogen infection and activity, leading to an increase in crop growth and yield? Notably, many of the NPs that have been or could be effective are also required plant micronutrients, raising the potential for additional enhanced growth through nutritional benefits. Traditional pesticide and fertilizer formulations currently in use often have active ingredients with low water solubility and as such, availability to targeted crops can be quite low. Out of necessity, larger volumes/quantities of these formulations must be used by the grower to effectively control pathogens to attain acceptable yield. In addition, fertilizer and metal-based pesticide formulations currently in use are subject to leaching, precipitation by soil constituents, and volatilization. The end result has been a highly inefficient and expensive approach to pathogen control and plant fertilization. The key question then becomes whether

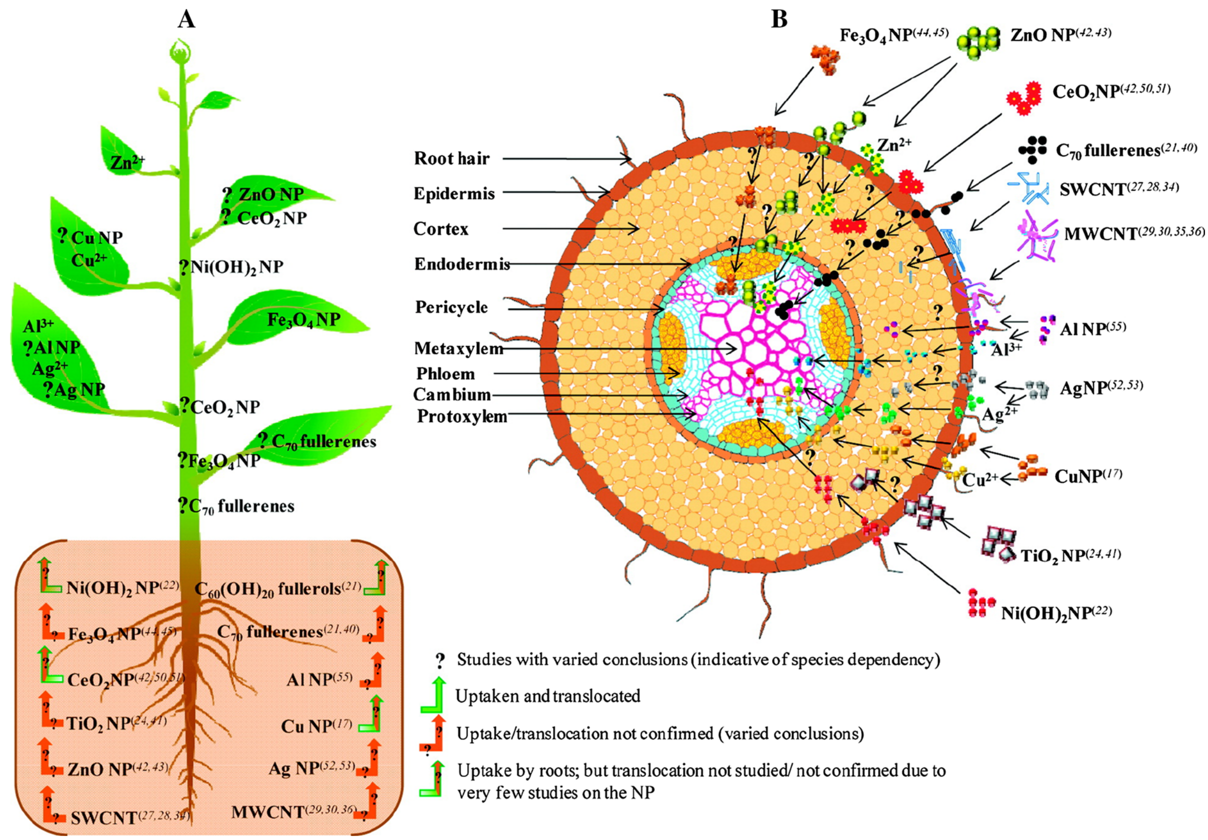

Fig. 1 Uptake, translocation, and biotransformation pathway of various nanoparticles in a plant system: **a** plant showing the selective uptake and translocation of nanoparticles; **b** transverse cross section of the root absorption zone showing the differential nanoparticle interaction on exposure. The superscripts depict the reference cited in the original article. Reprinted with permission from Rico CM, Majumdar S, Duarte-Gardea M, Peralta-Videa JR, Gardea-Torresdey JL (2011) Interaction of Nanoparticles with Edible Plants and Their Possible Implications in the Food Chain *J Agric Food Chem* 59:3485–3498. Copyright 2011 American Chemical Society

the solubility and effectiveness of these agrichemical formulations could be enhanced through the use of NP additives or carriers, as well as by the NPs themselves as an active ingredient (Naderi and Danesh-Shahraki 2013). Additionally, nanofertilizers could offer more controlled release so as to synchronize nutrient flux over time with the uptake by the developing crop. This approach would both increase nutrient availability and minimize wasteful interactions with soil or air that result in nutrient losses from the agricultural system. As reported in Table 1, the production of nano-enabled pesticides and fertilizers with greater solubility, more stable dispersal, decreased persistence, and greater target specificity is proceeding at a rapid pace (Rai et al. 2012).

As shown in Table 2 (and Fig. 2), a survey of the current literature reveals that NP effects vary with both plant species and NP type. It is clear that a large number of reports have shown positive impacts from metal/metal oxide NP exposure on crop growth and/or pathogen inhibition. Particles such as Ag, ZnO, Mg, Si, and TiO_2 likely suppress crop diseases directly, through antimicrobial activity (Ram Prasad and Prasad 2014). Silver NPs display a strong inhibitory activity to microorganisms and as such, there has been significant research into applications for phytopathogens management. Although the mechanism of NP Ag toxicity is not fully characterized, the antimicrobial activity seems to be driven by released Ag+ ions, with some additional effect mediated through the elemental NPs themselves. For example, it is known that Ag+ ions bind to cysteine-containing proteins on plasma membranes, causing both physiological and biochemical damage that compromise

Table 2 Positive effects of nanoparticles in food crops: nanoparticle versus bulk

NP	Particle size	Bulk/control treatment	Concentration	Mode of exposure	Plants	Growth media	Effects	References
MWCNTs	Outer diameters 10–35 nm, an, length of 6 μm	Activated carbon, graphene (2-5 nm)	50 ug mL^{-1}	Roots	Tomato	Murashige and Skoog medium	Enhanced fresh and dry biomass, Changes in gene expression (water channel protein)	(Khodakovskaya et al. 2011)
	Outer diameters 10–35 nm, an, length of 6 μm	Activated carbon	0.1–500 ug mL^{-1}	Culture	Tobacco cells	Murashige and Skoog medium	Enhanced cell growth and regulate cell division by activating water channel protein.	(Khodakovskaya et al. 2012)
							Activated gene regulators of cell division and extension.	
	Outer diameters 10–35 nm, an, length of 6 μm	Activated carbon	50 and 200 ug mL^{-1}	Roots	Tomato	Germinated in Murashige and Skoog medium and transferred to soil mix	Increased plant height, number of flowers and fruits.	(Khodakovskaya et al. 2013)
SWNTs	Diameters 0.86 nm to 2.22 nm	Activated carbon, graphene	50 ug mL^{-1}	Roots	Tomato	Murashige and Skoog media	Enhanced fresh and dry biomass	(Khodakovskaya et al. 2011)
ZnO	18.5 nm	Bulk TiO_2	10 mg L^{-1}	Foliar	Pearl millet	Soil	Increase in shoot length (15.1 %), root length (4.2 %) and area (24.2 %).	(Tarafdar et al. 2014)
							Increases in chlorophyll (24.4 %), soluble leaf protein (38.7 %).	
							Increase in acid phosphatase (76.9 %), alkaline phosphatase (61.7 %), and phytase (>3x),	
							Enhancement in microbial population and activity in the rhizosphere	
	1.2- 6.8 nm	Bulk ZnO	10 mg L^{-1}	Foliar	Cluster bean	Soil	Increase in shoot length (31.5 %), root area (73.5 %), dry biomass (27.1 %), and grain yield.	(Raliya and Tarafdar 2013)
							Increase in chlorophyll ($\sim$ 2.8 x) and soluble leaf protein (27.1 %).	
							Increase in enzyme activity of acid phosphate (73.5 %), alkaline phosphate (48.7 %), phytase (72.4 %).	
							Increased rhizospheric microbial population (11–14 %)	
	???	Bulk ZnO and $ZnSO_4$	1.5–10 mg L^{-1}	Foliar	Chickpea		Increased biomass accumulation compared to bulk and $ZnSO_4$	(Burman et al. 2013)

Table 2 continued

NP	Particle size	Bulk/control treatment	Concentration	Mode of exposure	Plants	Growth media	Effects	References
	????	Chelated bulk $ZnSO_4$	1000 mg kg^{-1} in soil	Foliar and root	Peanut plant	Soil	Promoted both seed germination and seedling vigor Early flowering manifestation and higher leaf chlorophyll content. Increased stem and root growth, and yield.	Prasad et al. (2012)
Fe_2O_3	6 nm	Bulk and bulk citrated coated Fe_2O_3	Germination 50-200 mg L^{-1}. Soil and foliar 500 and 1000 mg L^{-1}.	Foliar and root	Soybean	Soil	Increased root elongation and photosynthetic parameters by foliar application.	Alidoust and Isoda (2013)
Mn	20 nm	Bulk $MnSO_4$	0.05–1 mg L^{-1}	Roots	Mung bean	Hoagland culture solution	Increase in shoot and root length, dry and fresh biomass, and rootlet number. Enhancement in chlorophyll, carotene photophosphorylation, and oxygen evolution.	Pradhan et al. (2013)
	20.88 nm	Bulk $MnSO_4$	0.05–1 mg L^{-1}	Roots	Mung bean	Hoagland culture solution	Increased nitrogen metabolism	Pradhan et al. (2014)
TiO_2		Bulk TiO_2	0.25–6 %	Roots	Spinach	Hoagland culture solution	Accelerated seed germinantion, growth rate and chlorophyll. Enhanced rubisco activity and photosynthetic rate	Zheng et al. (2005)
		Bulk TiO_2	0.25 %	Roots	Spinach	Soil	Enhanced growth rate and chlorophyll. Enhanced rubisco activity and photosynthetic rate	Linglan et al. (2008)
		Bulk TiO_2	0.01–0.03 %	Foliar	Wheat	Field soil	Increase in ear weight, ear number, seed number, final yield, and biomass. Increased gluten and starch.	Jaberzadeh et al. (2013)
		Bulk TiO_2	0.25 %	Roots	Spinach	Hoagland culture solution	Enhanced growth rate and chlorophyll. Enhanced total nitrogen, NH^{4+}, and oxygen.	Yang et al. (2007)

Table reprinted from Servin et al. Nanoscale Micronutrients Suppress Disease. VFRC Report 2015/x. Virtual Fertilizer Research Center, Washington, D.C

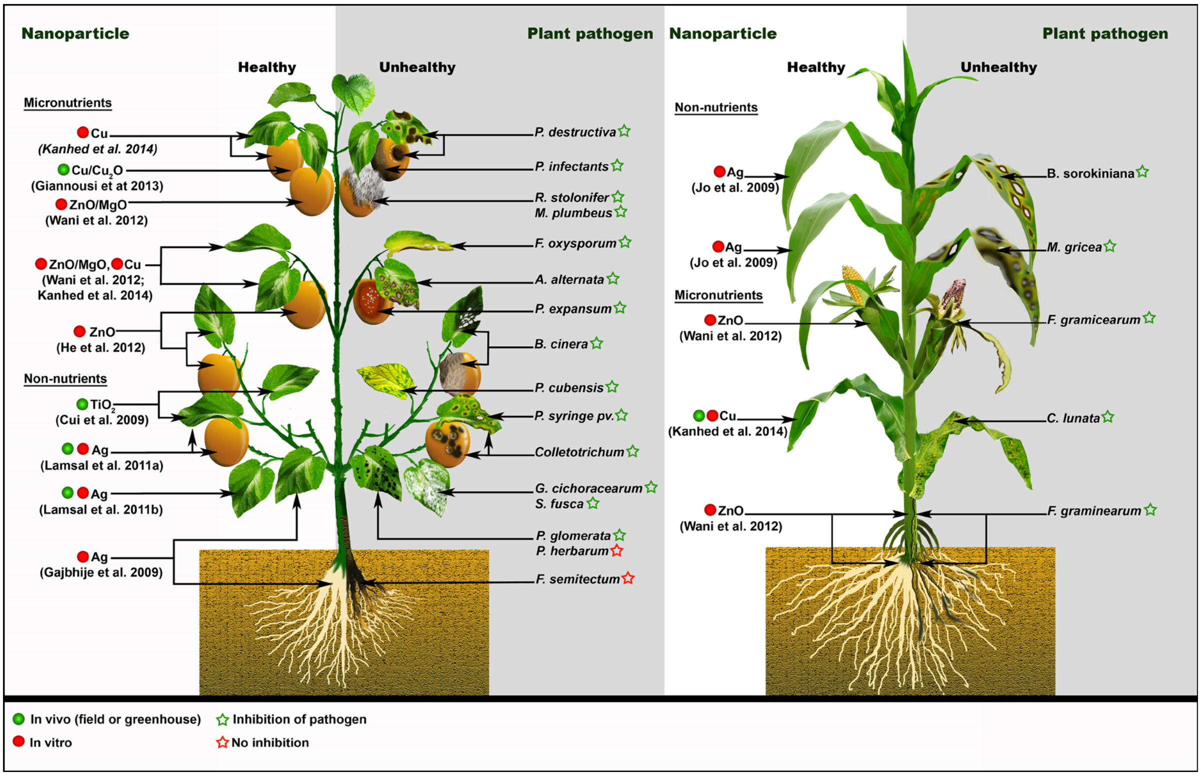

Fig. 2 Effect of nanoparticle nutrients and non-nutrients on crop disease

membrane integrity. Subsequent penetration of Ag into the cytoplasm causes the inactivation of critical enzyme systems and cell death (Ocsoy et al. 2013). Jo et al. (2009) evaluated the impact of Ag NPs on pathogenic fungi that cause disease in perennial ryegrass (*Lolium perenne*) and observed a 50 % reduction in colony formation at 200 mg/L Ag NPs. Lamsal et al. (2011a) showed that Ag NPs inhibited the activity of *Colletotrichum* spp. (anthracnose pathogen) in field trials. Both papers indicate that the Ag NPs damaged and penetrated the cell membrane, subsequently reducing infection (Jo et al. 2009; Lamsal et al. 2011a). Lamsal et al. (2011a) also reported that the prophylactic application of Ag NPs (4-8 nm) enhanced the disease suppression, suggesting that alternative mechanisms such as the induction of resistance mechanisms may be important. Similarly, Gajbhiye et al. (2009) used a disk diffusion assay to study the combined activity of NP Ag with the fungicide fluconazole against several pathogenic fungi. The authors reported that combined fungicide NP Ag had the greatest antifungal activity, achieving maximum activity against *Candida albicans*, followed by *Phoma glomerata* and *Trichoderma* sp.

Nanoparticle ZnO is another agent recently shown to provide effective pathogen growth control. With lower toxicity and secondary benefits on soil fertility, NP ZnO has clear advantages over Ag for fungal pathogen control efforts (Dimkpa et al. 2013). Nanoparticle ZnO reduced *Fusarium graminearum* growth in a mung bean broth agar by 26 % when compared to bulk oxide and controls (Dimkpa et al. 2013). He et al. showed that ZnO NPs (3-12 mmol) significantly inhibited *Botrytis cinerea* (63–80 %) and *Penicillium expansum* (61–91 %) growth in a plating assay (He et al. 2011). The authors reported systemic disruption of cellular function within both pathogens, thereby resulting in hyphal malformation and fungal death. Jayaseelan et al. (2012) demonstrated that biosynthesized ZnO NPs (25 µg/mL) yielded high suppression of pathogenic bacteria (*Pseudomonas aeruginosa*) and fungi (*A. flavus*). Wani and Shah (2012) reported a high inhibition rate in the germination of fungal spores of *Alternaria alternate, F.*

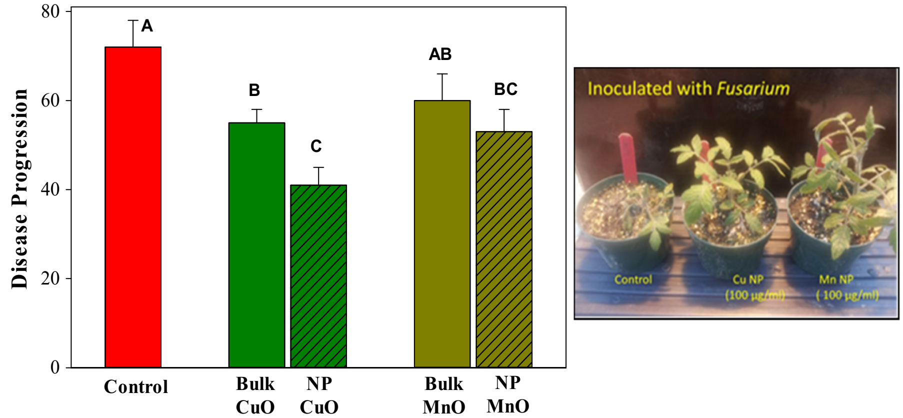

Fig. 3 Effect of NP or bulk equivalents MnO and CuO application on Fusarium disease progression on tomato grown in soil infested with *Fusarium oxysporum f.* sp *lycopersici* (*left*). Effect of NP Mn application on tomato biomass grown in soil infested with *Fusarium* (*right*). Figure reprinted from Servin et al. Nanoscale Micronutrients Suppress Disease. VFRC Report 2015/x. Virtual Fertilizer Research Center, Washington, D.C

oxysporum, Rhizopus stolonifer, and *Mucor plumbeus* upon exposure to NP ZnO and MgO at concentrations as low as 100 mg/L. Several reports have shown that quantum dots (QDs) may increase plant growth, potentially through selective activity against specific pathogens. For example,Rispail et al. (2014) showed the intracellular internalization of QDs (500 nM) by pathogenic *F. oxysporum* and observed a 20 % decrease in fungal germination and a 15 % reduction in hyphal growth.

Nanoparticle metal oxides such as TiO_2 have also shown promise as agricultural amendments, due to both their photo-catalytic and antimicrobial properties. In a field study, Cui et al. (2009) showed that NP TiO_2 reduced *P. syringae* pv. *lachrymans* and *P. cubensis* infection of cucumber by 69 and 91 %, respectively, and also increased photosynthetic activity (30 %). Paret et al. (2013a, b) showed that after NP TiO_2 photo-activation, bacterial spot (*Xanthomonas* sp.) control on roses and tomato was equivalent to or better than conventional treatment options. Nanoparticle MgO was shown to have significant antimicrobial activity due to strong interactions with the negative surfaces of bacterial membranes and spores (Huang et al. (2005). Similarly, NP Cu application (73.5 % control) was shown to be more effective than currently available non-nano Cu formulations (57.8 %) in a field study where tomato (*Lycopersicon esculentum*) was exposed to *Phytophthora infestans* (Giannousi et al. 2013). Conversely, chemically synthesized NP Cu demonstrated promising antifungal activity against *Phoma destructiva*, *Alternaria alternata*, *Curvularia lunanata*, and *Fusarium oxysporum* (Kanhed et al. 2014) Moreover, NP Cu showed higher pathogenic fungal inhibition in comparison to the commercially available fungicide bavistin.

Notably, in many of the studies discussed above, and in the literature in general, increased plant growth is reported with nanoscale amendments but the mechanism of action is often unclear. The increase in crop growth/yield may simply be the result of reduced disease presence, at least in the case of the studies conducted under non-sterile conditions. This may occur from either the anti-pathogenic activity of the NP itself, or indirectly through the induction of key defensive pathways and metabolites within the plant. However, many of the nanoscale amendments mentioned above involve elements that are required micronutrients and as such, the increased growth and yield may in fact be due to a combination of pathogen suppression and enhanced plant nutritional status.

Positive effects of nanoparticles on crops: nano versus bulk

As mentioned above, there are a number of instances in the literature citing positive effects of nanoparticle exposure on crop germination, growth, and yield. However, of greater importance is the comparison between the effects of NPs and their equivalent bulk material counterparts. The success of NP use for disease suppression, nutritional improvement, and yield increase may well rest on the particle size difference between "bulk" and "nano." Consequently, the literature reviewed here is largely restricted to papers that included a direct comparison of plant exposure to NPs and corresponding bulk controls (Table 2).

Much of the current literature here is dominated by metal and metal oxide NPs (Table 2). Zheng et al. (2005) observed that a 2.5 % rutile TiO_2 NPs solution enhanced germination and vigor of spinach *(Spinacia oleracea)* as compared to bulk exposed seeds. Specifically, growth and chlorophyll formation were increased by 63–76 and 28 %, respectively; similar increases were noted for rubisco and overall photosynthetic activity. A similar study using anatase TiO_2 NPs yielded 58.2 and 69.8 % increases in spinach fresh and dry mass, respectively, as well as 19.0, 29.9, and 250 % increases in chlorophyll content, photosynthetic rate, and rubisco activity (Linglan et al. 2008). Interestingly, spinach exposed to bulk TiO_2 was statistically equivalent to controls for all measured parameters. In a field study with wheat (*Triticum aestivum*), Jaberzadeh et al. (2013) showed that foliar application of NP Ti at 20 g/L increased stem elongation, biomass, flowering, ear mass and seed number, yield, gluten and starch content as compared to the bulk material amendment. Last, Yang et al. (2007) also observed increased spinach growth upon exposure to NP TiO_2 (anatase); the authors speculated that under nitrogen deficient conditions in sunlight, nano-TiO_2 directly reduced atmospheric nitrogen to ammonia, which subsequently promoted plant growth.

Tarafdar et al. (2014) biosynthesized NP Zn by exposing ZnO salt solution to a cell-free filtrate of *Rhizoctonia bataticola* and then compared the effect of 10 mg/L foliar bulk and NP Zn amendment on soil-grown pearl millet (*Pennisetum americanum*). The Zn NPs significantly increased shoot length (10.8 %), chlorophyll content (18.4 %), root area (18.4 %), dry biomass (12.0 %), grain yield (29.5 %), and soluble leaf proteins (19.9 %), compared to the bulk particles. Interestingly, the NP Zn also increased the activity of a number of key enzymes, including phytase (72.7 %), alkaline phosphatase (22.58 %), acid phosphatase (14.18 %), and dehydrogenase (9.22 %). Raliya and Tarafdar (2013) biosynthesized ZnO NPs from the extracellular secretions of *Aspergillus fumigatus* and reported similar findings upon foliar treatment of cluster bean (*Cyamopsis tetragonoloba* L.). Nanoparticle ZnO treatment increased cluster bean shoot length (22.7 %), root length (43.4 %), total protein (17.2 %), chlorophyll (54.5 %), and rhizosphere microbial population (13.6 %), compared to bulk ZnO-amended plants. Prasad et al. (2012) exposed peanut (*Arachis hypogaea*) to 1000 mg/L ZnO NPs and observed increases in germination, chlorophyll, stem and root growth, compared to plants exposed to $ZnSO_4$. In a subsequent field study, foliar application of ZnO NP on peanut increased the pod yield by 29.5 %, compared to bulk $ZnSO_4$. Notably, at high amendment levels (2000 mg/L), phytotoxicity, as measured by reduced crop growth and yield, was observed. Similarly, Burman et al. (2013) showed that a foliar application of a 1.5 mg/L NP ZnO solution on chickpea (*Cicer arietinum* L var. HC-1) increased biomass relative to $ZnSO_4$ amendment but 10 mg/L amendment negatively impacted root biomass(Burman et al. 2013). It is evident from the above ZnO literature that both particle concentration and plant species will be major factors controlling the success of NP amendment strategies.

Alidoust and Isoda (2013) exposed soybean to NP Fe_2O_3, citrate-coated Fe_2O_3 NPs, bulk Fe_2O_3, and citrate-coated bulk Fe_2O_3 by foliar or soil routes. For the foliar application, the authors observed that NP Fe_2O_3 significantly enhanced root elongation and photosynthetic potential as compared to the other treatments. Interestingly, the enhancement was far less pronounced with a soil exposure, likely due to extensive precipitation of Fe ions. Conversely, *Spathyphyllum* (an ornamental species) had no significant physiological changes upon foliar and soil exposure to Fe_2O_3 NP, bulk Fe_2O_3, iron chelate EDDHA, and Fe ethylenediaminetetraacetic acid (Fe-EDTA) (Raziyeh Mohamadipoor and Ali Mahboub Khomami2 2013). Perhaps importantly, plants receiving the foliar application of NP Fe_2O_3 did have higher nutrient content, including N, P, K, Fe, Zn, Mn, and Mg); this may suggest more subtle positive impacts from NP exposure. Pradhan et al. (2013) exposed mung bean (*Vigna radiate*) to NP Mn or $MnSO_4$ hydroponically and noted that at doses up to 1 mg/L, the NPs had no deleterious effect on the plant but that $MnSO_4$ caused phytotoxicity even at lower concentrations. This may have been a result of the large initial burst of Mn release from the salt form, whereas dissolution from the NP is much slower and more controlled. At the more moderate doses, NP exposure increased bean shoot, root, fresh weight, dry weight, and rootlet number by 10–100 % over that with the $MnSO_4$ amendment. In parallel and follow-up studies, NP Mn also increased chlorophyll content, carotene photophosphorylation, oxygen evolution, and nitrogen metabolism relative to controls (Pradhan et al. 2013, 2014). Liu and Lal (2014) exposed soybean (*Glycine max*) plants to nano-hydroxyapatite (nHA) as a new class of P fertilizer under greenhouse conditions. The authors reported significant increases in growth rate (32.6 %) and seed yield (20.4 %) when nHA was applied, in comparison with soluble counterpart phosphoros fertilizers ($Ca(H_2PO_4)_2$) with known linkage to surface water eutrophication. The authors speculated that this may have been due to a longer retention time of nHA in the porous medium as a function of its higher stability and viscosity as compared to traditional soluble phosphorous fertilizers. Last, Almeelbi and Bezbaruah (2014) investigated the effect of phosphate-sorbed zero-valent Fe NPs on spinach in hydroponic solution. The authors reported that plant growth and biomass was increased by fourfold with NP amendment relative to controls, and the Fe content in spinach roots, stem, and leaves was increased 11–21 times.

Effect of soil on NP-enabled fertilization

Nanoparticle activity is obviously highly influenced by the chemical and physical characteristics of the surrounding environment. Understanding NP fate in soil is highly challenging given the complex array of potential interactions and the general lack of adequate particle detection platforms for environmental matrices. Consequently, the literature here is not robust, although some recent work has focused on the importance of transformation reactions for NPs in the environment. The initial NP properties will most certainly be transformed through interactions with both biotic and abiotic soil components, and those changes will subsequently influence NP stability, aggregation, transport, and availability to biota. For example,Tolaymat et al. (2010) observed that NP Ag had greater mobility in what the authors described as "negatively charged soils" and that significantly impacted long-term transport potential of the NP. The authors did note that the addition of stabilizing agents such as polyvinyl pyrrolidone, sodium citrate, amines, sugars, and amides altered the interaction with soil and dramatically influenced resulting mobility. Thalmann et al. (2014) reported that sulfidation of NP Ag occurred under both oxic and anoxic conditions and that the transformed particles had different activity and mobility. Cornelis et al. (2012) correlated NP Ag mobility in soil with the clay content, although no specific mechanisms of interaction were shown. Interestingly, Hu et al. (2014) reported that graphene phytotoxicity to hydroponically grown wheat was almost completely alleviated by humic acid, a common soil constituent. Wang et al. (2013) reported on the rapid dissolution of ZnO NPs in the rhizosphere of cowpea, prior to uptake of the ionic Zn into plant tissues. Much more work needs to be done but the existing literature clearly indicates that properties such as particle type, size, surface charge, and stability, as well as soil physical–chemical properties, will control the fate and transport nanoscale amendments in soil systems and the resulting bioavailability to crop plants.

As discussed above, low element availability in neutral and slightly alkaline soils significantly limits micronutrient-based disease suppression strategies. For example, Sims (1986) reported that the nutrients Cu, Fe, Mn, and Zn become progressively less available as soil pH approaches 7.0 and that low uptake by crop roots and compromised nutritional status can result. Notably, few studies have investigated the effect of soil pH or other characteristics on NP fate and effects in soil. Given that changes in soil pH could progressively restrict nutrients availability, successful soil-based nanoscale amendment for pathogen control will need to consider soil physicochemical properties such as pH. Watson et al. (2015) grew wheat (*Triticum aestivum*) in acidic and alkaline soils that had been amended with ZnO NPs; the authors reported a 200-fold higher soluble Zn content in the acidic soil, as well as tenfold higher concentration in wheat shoots, compared to the alkaline soil. However, plants grown in the ZnO NP (500 mg kg^{-1})-amended alkaline soil had increased lateral root production; wheat in the acidic soil had decreased root growth. Priester et al. (2012) observed high Zn accumulation (344.07 mg/kg) in the soybean leaves after 50-day exposure to NP ZnO; the authors did comment that soil components such as organic matter would significantly impact particle stability and aggregation. Yang et al. (2009) reported pH-dependent humic acid adsorption onto NP TiO_2, Al_2O_3, and ZnO but that electrostatic interactions and ligand exchange with SiO_2 NPs prevented adsorption onto the oxide surface. Tian et al. (2010) noted that NP Ag had increased mobility in the presence of humic acid. Another factor that must be considered is the presence of organic carbon in the form of biochar, which is being increasingly added as a soil amendment. Biochar can be generated by a range of techniques using different feedstock materials; these variations may greatly influence the sorptive characteristics of the resulting char. Some researchers have reported that biochar is capable of sorbing and retaining other substances in soil (Chen et al. 2008; Elmer and Pignatello 2011). However, in preliminary work from our group, biochar amendment had negligible impact on the availability of NP CeO_2 to plant or worm species. Concern does still exist that the biochar could significantly decrease the availability of other metal oxide NPs, as well as plant-required nutrients in general. These findings are not conclusive but do highlight the potentially significant effect that soil properties will have on the availability and accumulation of NPs; an understanding of these processes is clearly going to be necessary prior to the successful use of nanoscale materials as a soil amendment both for pathogen control and for crop nutrition.

Potential of Foliar NP application for disease suppression

Given the above-discussed limitations on macro- and micronutrient availability in soil, interest in foliar-based fertilizer applications has been significant for some time. Physiological investigations have shown that particles may enter plant leaves through stomata and the cuticle structures (Eichert et al. 2008; Schonherr 2006). We speculate that this entry or absorption behavior may well be more rapid and efficient for smaller diameter NPs. For example, although no bulk comparison was made, Corredor et al. (2009) observed that magnetic NPs penetrated pumpkin leaf cells via stomata. In addition, it is known that NP metals/metal oxides are more effectively translocated than corresponding bulk elements and that this greater transportability exists in both xylem- and more importantly, phloem-based vasculature (Wang et al. 2012).Wang et al. (2013) evaluated the leaf-to-root translocation of NPs after an aerosol-based foliar application to watermelon and showed significantly higher percentages of NP-derived Ti, Mg, and Zn in root tissue (5.45, 21.2, and 13.9 %, respectively) as compared to a corresponding NP solution applied to the leaves (1.87, 8.13, and 5.74 %, respectively). The authors suggested that smaller aerosolized NPs (TiO_2, MgO, and ZnO diameters were 27, 35, and 45 nm, respectively) entered the stomata more efficiently than the larger solution-based particles (corresponding diameters of 150, 623, and 1,020 nm, respectively). Raliya and Tarafdar (2013) biosynthesized ZnO NPs with extracellular secretions of *Aspergillus fumigatus* TFR-8 and applied the particles as a foliar spray on cluster bean plants. The authors reported significant increases in a number of physiological parameters, including biomass, shoot/root length, root area, chlorophyll content, and P-mobilizing enzymes. Importantly, the residual protein from the fungal extract acted as a capping agent and significantly increased particle stability.

The application of NP TiO_2 in agriculture, including protection from pathogenic disease, is based on the material's photo-catalytic surface properties (Ahmad and Rasool 2014). Chao and Choi (2005) showed that NP TiO_2 application on crops could increase yield by 30 % and also significantly reduce pathogenic disease. The use of NP TiO_2 in food products at levels up to 1 % of the product mass is FDA approved as it is considered harmless and non-toxic (Ahmad and Rasool 2014). Although not an essential nutrient, evidence shows that TiO_2 may extend a number of potential benefits to crops. Studies with foliar applied NP TiO_2 on wheat showed increases in starch and gluten content; the authors hypothesized that the increase was due to NP TiO_2-promoted rubisco activity and resulting enhanced photosynthesis. Importantly, the authors reported enhancement was more pronounced when the TiO_2 amendment was in the NP form (Jaberzadeh et al. 2013). Similarly, soybean was shown to have increased water absorption after treatment with foliar NP TiO_2 and SiO_2 (Lu et al. (2002). Hong et al. (2014) exposed cucumber to foliar applications of NP CeO_2 both in suspension and as a nano-ceria powder. A higher leaf-to-root Ce translocation was evident upon application of the NP suspension compared to the solid powder, suggesting significant accumulation through the leaves and subsequent phloem-based transport throughout the plant. Notably, larger particles can obstruct and hinder stomatal function in the leaf, which would decrease transpiration rates (Asli and Neumann 2009) and photosynthetic potential of the crop and effectively limiting the effectiveness of foliar applications. As such, consideration of factors such as particle size, concentration, aggregation, plant species, and application method will greatly influence the foliar uptake of NPs (Wang et al. 2013).

Regarding the foliar application of nanoscale amendments for pathogen control, several studies have been published. (Giannousi et al. 2013) tested the antifungal activity of NP Cu_2O on *Phytothphora infestans* with tomato and reported that foliar application resulted in significantly greater protection (73.5 %) from the pathogen, compared to the bulk amendment (57.8 %). Given the lack of NP-induced phytotoxicity, the potential dual use of nanoscale amendments to both suppress disease and promote nutrient status becomes a topic worthy of further investigation (Giannousi et al. 2013). The inhibitory effects of NP Ag foliar application on powdery mildew was investigated in field-cultivated cucumber and pumpkin (Lamsal et al. 2011b). Not only did the authors report a dose-dependent increase in fungal control with foliar 100 mg L^{-1} but the NP treatment was also nearly 25 % more effective than was the corresponding bulk Ag amendment. The fungal inhibition was likely due to Ag accumulation in the fungal hyphae, which disrupted cellular function; a phenomena attributed to the greater ion release from the NP due to increased surface area (Yin et al. 2011). However, the use of NP Ag does raise concerns over potential negative effects on human health and the environment. Lettuce exposed to foliar application of NP Ag was shown to internalize the element into leaves, indicating potential transfer to humans via the food chain (Larue et al. 2014). Although NP Ag toxicity to humans is an area of active research, DNA and cell membrane damage from exposure have been noted (AshaRani et al. 2009; Gliga et al. 2014; Vrček et al. 2014). Environmental mesocosm experiments demonstrated that NP Ag caused significantly more toxicity to fish larvae than evident from $AgNO_3$ (Bone et al. 2014). It is important to note that the impact of particle weathering and transformation on toxicity, as well as overall particle fate and transport, is unknown (Levard et al. 2012).

Although the literature indicates significant potential for enhanced *in planta* translocation of metal/metal oxide NPs, there are little data on how foliar applied nanoscale micronutrients might uniquely affect root pathogens, either directly through toxicity after shoot–root transfer or indirectly through induced/facilitated host resistance. Preliminary data from our group demonstrate that foliar application of CuO solution onto tomato shoots results in significant inhibition of disease (*Fusarium*) progression (Fig. 3), as well as increased Cu content in the roots, compared to bulk CuO and untreated controls. This suggests that nanoscale size does indeed yield enhanced phloem-based shoot–root translocation and supports the hypothesis that NP metal oxides may not only directly inhibit pathogens but also indirectly affect disease by improving plant nutritional status. In fact, in recently completed field studies by our group with transplanted eggplant in *Verticillium dahliae*-infested soil, NP CuO treatment of the seedlings at planting resulted in significantly increased (17–31 % in comparison with bulk treatment) marketable yield in 2013 and 2014 (unpublished). Importantly, corresponding bulk CuO had no such effect.

Interestingly, although a comparison of the application pathways could not be found in the literature, there is clear reason to anticipate that foliar nanoscale amendments would have greater efficacy than soil-based treatment at both pathogen inhibition and at improved nutrition. Given the large array of NP element interactions with soil constituents, the relative lack of such complexity with foliar treatment, and the documented enhanced mobility of NPs within plants, greater effectiveness via foliar application may actually be predicted and future research should explore this potential.

Carbon nanomaterials and crop growth

The overall extent of nanomaterial application is still somewhat limited (Khot et al. 2012), and much of the focus to date has been on the use of NP-based metal/metal oxide formulations and polymers (Gogos et al. 2012). However, carbon-based NMs (CNM), including $C_{60/70}$ fullerenes, carbon NPs, fullerols, and single/multi-wall carbon nanotubes (SWCNT/MWCNT) have been the subject of recent interest with regard to enhancing crop growth (Khot et al.

2012). Although some published work reviewed below appears promising in terms of enhanced growth and/or pathogen suppression, the mechanisms of the interaction between plants and microbes with different CNMs is not well understood and reported instances of phytotoxicity do warrant caution.

Khodakovskaya et al. (2011) evaluated the effect of MWCNT, SWCNT, graphene, and bulk activated carbon (AC) on tomato plants grown in artificial medium (Table 2). The authors reported that both SWCNT and MWCNT enhanced plant biomass and used novel photothermal and photoacoustic mapping techniques to detect the materials in tomato roots, leaves, and fruit. The authors further showed that MWCNT significantly altered the total gene expression in exposed tomato, and they focused on changes to the water channel proteins known as aquaporins. A separate study involving tobacco in cell culture found that MWCNT (5–55 μg mL^{-1}) enhanced growth by 55–64 % in comparison to controls and noted that AC increased tobacco cell growth at low concentration (5 μg mL^{-1}) but was toxic at higher levels (Khodakovskaya et al. 2012). Interestingly, the AC-induced inhibition was due to the absorption of key plant growth regulators, vitamins, chelate, iron, and zinc from the medium. A molecular analysis showed that the MWCNT stimulated cell division and plant growth by activating the water channels (aquaporins) and regulatory genes for cell division and extension. The same research group published soil-based life cycle study with tomato exposed to MWCNT and AC (Khodakovskaya et al. 2013). Plant height, flower number, and water consumption were all higher in soil treated with MWCNT as compared to control and AC exposed plants, although fruit size did not vary by treatment. In work from another group, soybean, corn, and barley seeds and seedlings exposed to MWCNT-agar medium (50–200 μg/mL) or by foliar spraying (25–100 μg mL^{-1}), respectively, germinated more quickly and grew at a faster rate when compared to untreated controls (Lahiani et al. 2013). Similar to the work of Khodakovskaya et al. (2011), the enhanced growth was linked to increased water penetration in the seeds and to increased activity of key water channel proteins in the developing seedling. Although no bulk material controls were included, the similarly of the results across studies and research groups does suggest that MWCNT-stimulated growth may occur across a number of crop species.

In related work, Tripathi et al. (2011) exposed *Cicer arietinum* to citric acid-coated CNTs at 6 g/L for 10 days and observed both intercellular uptake and growth stimulation. The authors suggested that the nanotubes formed an "aligned network" inside the vascular tissue that subsequently increased the water efficiency of uptake. Lahiani et al. (2013) exposed soybean, corn, and barley in agar medium to MWCNT at 50–200 mg/L and measured effects on germination and growth of the plants for 11 days. The authors observed 50 % increase in germination in all species, with both soybean and corn demonstrating enhanced shoot development. Importantly, MWCNTs accumulation was demonstrated with Raman spectroscopy and transmission electron microscopy (TEM). Similarly, water-soluble carbon nano-dot exposure at 150 mg/L was shown to enhance wheat root growth (Tripathi and Sarkar 2014). Sonkar et al. (2012) showed dose-dependent growth enhancement with water-soluble carbon nano-onions (wsCNOs) exposure to *Cicer arietinum* at 10–30 mg/L in a life cycle study. Fullerol [C_{60} $(OH)_{20}$] or water-soluble fullerenes increased plant biomass and "phytomedicinal" content in exposed bitter melon (*Momordica charantia*) (Kole et al. 2013); fullerol accumulation and translocation were demonstrated by bright-field imaging and Fourier transform infrared spectroscopy (FTIR). Specifically, the exposed plants had a 54–128 % increase in biomass and fruit yield, as well as significantly increased levels of anticancer (cucurbitacin-B 74 %, lycopene 82 %) and antidiabetic compounds (charantin 20 %, insulin 91 %) (Kole et al. 2013).

Although not related to disease suppression or plant nutrition, several studies have demonstrated that CNM exposure can alter that fate of co-existing organic contaminants in model and soil systems. Ma and Wang (2010) observed fullerene-enhanced trichloroethylene (TCE) accumulation by hydroponically grown cottonwood. In a soil-based study (De La Torre-Roche et al. 2013), we found that MWCNT and fullerenes had different effects on the accumulation of field-weathered chlordane and DDx (DDT plus metabolites) residues. MWCNT decreased pesticide uptake in a dose-dependent fashion by four crops (zucchini, corn, soybean, tomato) whereas C_{60} showed mixed effects, ranging from suppressed uptake (similar to MWCNT), no effect, to a 35 % increase in chlordane accumulation in soybean and tomato. Hamdi et al. (2014)

showed that although non-functionalized MWCNT decreased chlordane content in lettuce roots and shoots by 78–88 %, the suppression was more modest with amino-functionalized tubes where root decreases were 57 % and shoots were only 23 %, relative to controls.

It is also worth noting that there are scattered reports in the literature of phytotoxicity from carbon nanomaterial exposure (Stampoulis et al. 2009), although exposure levels are typically quite high when compared to estimated 'realistic' nanomaterial fluxes of 0.01 µg/kg/y (Mueller and Nowack 2008). In addition, there are numerous reports showing CNMs toxicity to soil microorganisms. Given the significant and important interplay between microbial biota and crop species in agricultural systems, these findings are worth noting. For example, Chung et al. (2011) added 0–5000 MWCNT to two soils for 11 days and noted significant decreases in microbial biomass and enzymatic activity (5000 µg g^{-1}). Jin et al. (2013) reported similar findings with CNT amendment to soil but observed that microbial toxicity was more pronounced for SWCNT. Rodrigues et al. (2013) noted that the soil fungal community was significantly decreased after exposure to functionalized SWCNT in soil and that community recovery did not occur over an extended period. Shrestha et al. (2013) noted that 3-month exposure to MWCNT at 10–10,000 mg/kg decreased many populations of bacterial species, but that certain groups, such as those capable of degrading polycyclic aromatic hydrocarbon (PAH), were actually increased. These results suggest a potential shift in the overall soil community toward more stress-tolerant bacterial species upon MWCNT exposure.

From the literature discussed above, CNMs clearly have significant potential to enhance plant growth, nutrient uptake, seed germination, and fruit yield/quality. MWCNTs are the most extensively studied material of this group and do indeed show promising positive effects on a range of crop species. Low to moderate doses of nanotubes seem to improve overall plant growth, with the mechanism involving at least in part the more effective uptake and transport of water by aquaporins. Given this, and the fact that nearly all required nutrients will be dissolved in this more effectively acquired water, there may be significant potential for CNT use in agricultural systems, including those with water stress or limitations. This also raises the possibility of combined nanomaterial amendments, low-level carbon nanomaterial addition in conjunction with nanoscale micronutrients that could result in improved water uptake, enhanced nutrient acquisition, and optimized pathogen inhibition. Notably, the magnitude of CNT-induced beneficial response is clearly dependent on crop species, as well as on the dose, the growth medium, and conditions. Importantly, CNM exposure often shows negative effects across several microbial populations in soil and as such, caution is thus warranted given the lack of mechanistic understanding with regard to toxicity. More research needs to be done but considering the available findings to date, CNMs may be considered as a promising nanoscale amendment for enhancing plant growth, potentially suppressing microbial pathogens and promoting crop quality/yield.

Nanotechnology and agriculture: regulatory perspective

There has been a large increase in the number of scientific publications addressing NMs applications in agriculture (Gogos et al. 2012), with approximately 40 % of those papers investigating CNMs, followed by NP TiO_2, Ag, SiO_2, and Al_2O_3 (Table 3) (Gogos et al. 2012). Although global NMs production and consumption has increased the risk of environmental exposure, the scientific community is in general agreement that there is inadequate information available for NM–plant and NM–microbe interactions to accurately characterize hazard or risk. Little information exists regarding environmentally relevant NMs concentration and thus, the traditional approach of predicting toxicity based on high-dose short-term exposure becomes even more problematic. There are a few publications that use theoretical modeling to estimate NP fluxes but uncertainty is high (Table 3). For example, a theoretical "realistic exposure scenario" for TiO_2, Ag, and CNTs was reported at 0.4, 0.02, and 0.01 µg/kg/y, respectively (Gogos et al. 2012; Mueller and Nowack 2008). However, the relationship between these predicted values and the actual concentrations in various environmental compartments is not known. In addition, as a direct consequence of this lack of robust NP/NM environmental fate and effect information, a particle size-specific regulatory framework has failed to develop. The European Food Safety Authority (EFSA) published a guideline emphasizing the potential toxicity of

Table 3 Modeled fluxes of different NMs and application rates of plant protection products (PPP) or fertilizers, selected from the scientific literature and patent applications

NM type	Modeled flux into soil	Ref	Application rate and calcd flux from PPP/fertilizer[b]	Ref	Flux ratio[c]
TiO_2	Realistic scenario: 0.4 μg/kg/year	Mueller and Nowack (2008)[d]	4.5–15 kg/ha ≈ 1607–5357 μg/kg/year	Ishaque et al. (2009)	334–1116
	High exposure scenario: 4.8 μg kg^{-1} y^{-1}		7.5 g/ha ≈ 2.7 μg/kg/year	Guan et al. (2008)	0.56
	0.28–1.28 μg/kg/year (US, EU, and CH)	Gottschalk et al. (2009)[e]	max 30 kg/ha ≈ 10,714 μg/kg/year	(Dookhith and Linares 1998)	2232
g	Realistic scenario: 0.02 μg/kg/year	Mueller and Nowack (2008)[d]	15 g/ha ≈ 5.4 μg/kg/year	Kim et al. (2008)	54
	High exposure scenario: 0.1 μg/kg/year				
	8.3–22.7 ng/kg/year (US, EU, and CH)	Gottschalk et al. (2009)[e]			
CNT	Realistic scenario: 0.01 μg/kg/year	Mueller and Nowack (2008)[d]			
	High exposure scenario: 0.02 μg/kg/year				
	0.56–1.92 ng/kg/year (US, EU, and CH)	Gottschalk et al. (2009)[e]			

[a] Limited to those NM for which data due to usage in the anthroposphere was available

[b] Assuming an application volume of 300 L ha − 1, 20 cm plow depth, a soil bulk density of 1.4 g/cm^3 (http://web.ead.anl.gov/resrad/datacoll/soildens.htm), and an application once per year. [c]Calculated as flux from PPP/fertilizer divided by the value of the highest modeled flux

[d] Based on an annual substance flow analysis from products to soil in Switzerland

[e] Based on a probabilistic material flow analysis from a life cycle perspective of engineered NM-containing products

NMs in 2009 (Ganzleben et al. 2011) In 2010, the US EPA approved the nanoparticle-based antimicrobial pesticide HeiQ AGS-20 (http://www.epa.gov/oppfead1/cb/csb_page/updates/2011/nanosilver.html), but regulations for NP/NM use in other agrichemicals remain elusive. Incidentally, a similar lack of specific regulatory guidance exists at the US FDA for NP/NM use in food packaging and processing. However, it is important to note that the lack of a regulatory framework has not, and likely will not, inhibit the application of NMs in agriculture.

Summary and future research

Plant pathogens reduce average crop yield by 10–20 %, resulting in billions of dollars of losses to US agriculture. Although disease management options exist for many crops, with the exception of host resistance, all options possess significant shortcomings. This, taken with the building pressure for increased food production and the potential challenges caused by a warming climate, highlights the need for novel disease management approaches. Plant microelements such as Cu, Fe, Ni, Mn, Si, and Zn are known to play critical roles in plant disease resistance through enzyme activation for defense barrier production. However, low micronutrient availability in soil and poor intra-plant translocation inherently limit the utility of amendment strategies.

There has been significant interest in using nanotechnology to promote agriculture, with most of the focus being on enhanced or more targeted delivery of pesticides and fertilizers, nanosensors to increase efficiency, and novel nano-based treatment approaches to minimize waste production. However, the use of nanomaterials for crop disease suppression has not been adequately explored. It is known that at the nanoscale, materials acquire unique chemical and physical characteristics not observed in equivalent bulk materials and the literature has repeatedly shown enhanced availability and transport in biota, including plants, as a function of nanometer particle size. As such, NP forms of plant micronutrients such as those mentioned above and other non-essential elements, such as TiO_2 and Al_2O_3, may have significant use in pathogen control efforts by directly inhibiting disease-causing organisms or by affecting the systemic-acquired resistance pathway. Given the enhanced accumulation and transport observed at the nanoscale, a secondary and perhaps related benefit of improved crop nutrition seems likely. Preliminary data from our group and from others suggest significant potential for nanoscale micronutrients, either by foliar or root application, to suppress disease and increase crop yield. Future research should be targeted at uncovering the precise nature of these enhancements, including efforts to optimize treatment success and maximize yield. Mechanistic investigations of these interactions will also enable an accurate assessment of fate and effects in the crop or cropping system so as to address concerns over risk and food safety.

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