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REVIEW

Nanotechnologies for increasing the crop use efficiency of fertilizer-micronutrients

C. M. Monreal[1,2] · **M. DeRosa**[3] · **S. C. Mallubhotla**[4] · **P. S. Bindraban**[5] · **C. Dimkpa**[5]

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Abstract Billions of people and many soils across the planet suffer from micronutrient (MN) deficiencies impairing human health. In general, fertilization of deficient soils, according to soil test, with MNs alone and in combination with nitrogen, phosphorous, and potassium (NPK) baseline treatment increases crop yield. The soil applied fertilizer-MN use efficiency (MUE) by crops is <5 % due to a lack of synchronization between the fertilizer-MN release and their crop demand during growth. Nanotechnology and biotechnology have the potential to play a prominent place in transforming agricultural systems and food production worldwide in the coming years. MNs added in microcapsules and nanocapsules, nanomaterials (NMs), and nanoparticles (NPs) are taken up and translocated within plants when grown to maturity, increasing crop yield and MN concentration in plants. Noteworthy, many of the effects of NPs and NMs on crop yield and quality, human health, and associated environmental risks remain to be explored. Increasing MUE requires synchronizing the release of nutrients from fertilizers with crop demand during the growing season. Development of intelligent MN fertilizer delivery platforms (IMNDP) may be possible on the basis of elucidating communication signals between plant roots and soil microorganisms. Important benefits from the development and farm adoption of intelligent MN delivery platforms include increased MUE, reduced fertilizer use, and minimal toxicity and environmental impacts. This article proposes for the first time a novel model for IMNDP to enhance MUE and food quality by enabling the synchronization of MN release from fertilizers according to crop demand.

Keywords Micronutrients · Deficiency · Crops · Nanomaterials · Nanoparticles · Nanotechnology · Biotechnology · Intelligent nanofertilizer · Nutrient delivery platform

Introduction

The consumption of micronutrient (MN)-deficient food adversely affects human health resulting in anemia, reduction of growth, reproductive health, and decreased cognitive and physical performance (Swaminathan et al. 2013). Because human nutrition is directly linked to that of plants, the production of nutritious foods requires a balanced content of essential macronutrients, mesonutrients, and MNs. Soils are the main source of MNs for plants, and their deficiency in soil is highly correlated with decreased food quality and human health deterioration (Alloway 2008; World Health Organization - WHO 2009). Soil MN deficiencies may be corrected with fertilization as shown by data obtained from many field experiments conducted around the world. Average grain yield increases are observed in MN-deficient soils of Asia and other regions after addition of fertilizer-MNs to soils and/or leaves (Table 1) (e.g., Imtiaz et al. 2010; Malakouti 2000). Proper

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✉ C. M. Monreal
Carlos.Monreal@agr.gc.ca

[1] Agriculture and Agri-Food Canada (AAFC), Eastern Cereal and Oilseed Research Center, Ottawa, Ontario, Canada

[2] Department of Biology, Carleton University, Ottawa, Ontario, Canada

[3] Department of Chemistry, Carleton University, Ottawa, Ontario, Canada

[4] 266 Celtic Ridge Cr., Ottawa, Ontario K2W 0C3, Canada

[5] Virtual Fertilizer Research Center, NW, Washington, DC 20006, USA

Table 1 Summary of selected average data showing the effect of micronutrient fertilizer application on relative grain yield increases in micronutrient-deficient soils

Micronutrient added	Crop	Relative yield increase (%)	Control treatment	Country-reference
Zn	Rice	12	No Zn	Iran-Imtiaz et al. (2010)
	Wheat	13	No Zn	Iran-Imtiaz et al. (2010)
	Maize	18	No Zn	Iran-Imtiaz et al. (2010)
	Potato	22	No Zn	Iran-Imtiaz et al. (2010)
	Sunflower	22	No Zn	Iran-Imtiaz et al. (2010)
	Sugarcane	8	No Zn	Iran-Imtiaz et al. (2010)
Fe	Potato	16	No Fe	Pakistan-Imtiaz et al. (2010)
	Chickpea	15	No Fe	Pakistan-Imtiaz et al. (2010)
	Peanut	30	No Fe	Pakistan-Imtiaz et al. (2010)
Fe, Zn, Cu, B	Wheat	4–11	Each MN alone or MN + NPKS	Iran-Malakouti (2008)

From Imtiaz et al. 2010; Malakouti 2008. The specific rate use of NPKS not reported

MN fertilization also helps increase the concentrations of MNs in grain and plant leaf tissues under different soils, management, and climate conditions (Cakmak et al. 2010, Cakmak 2008; Singh et al. 1987). Many annual cereal crops and orchard trees also benefit from the addition of fertilizer-MNs to MN-deficient soils in Australia, Europe, USA, and Canada (Alloway 2008). Published data show that fertilizer-MNs can also increase crop MN use efficiency (MUE). For example, grain yield increases of up to 30 % as well as increase macronutrient use efficiency were reported. The addition of each of Fe, Zn, Cu, and B increased grain yield of various crops from 8 to 30 % or from 4 to 11 % when the four MNs were added together to a soil planted with wheat (Malakouti 2008). Other studies have shown that the addition of Fe and/or Zn to deficient soils planted with peanut, potato, chickpea, rice, and beans increased the average yield from 15 to 30 % in Asia (Adhikary et al. 2010; Malakouti 2008). In spite of the latter, current fertilizer technologies are unable to synchronize the release of MNs from fertilizer according to crop demand during the growing season, which ultimately results in low (<5 %) MUE by crops (Ryan et al. 2013; Singh 2008). On the other hand, interactions of MNs with macronutrients can either increase or decrease crop yields, depending on the macronutrient element (e.g., Roshan et al. 2011; Fageria 2001). For example, high concentrations of soil P addition (i.e., >1000 kg/ha) can induce Cu deficiency in citrus and avocados and in common crops such as corn, beans, and tomatoes (Bingham and Garber 1960). It is also known that plant homeostasis regulates MN uptake from soils and the intracellular plant mobilization, re-mobilization, translocation, and storage of MNs, including Fe, Zn, Cu, and Mn (e.g., Milner et al. 2013; Bernal et al. 2012).

In agriculture, nascent efforts involve the application of nanotechnology aimed at improving crop yield and nutrient uptake efficiency, food nutrition, and pest control, among other (Servin et al. 2015; Liu and Lal 2015). Nanotechnology has the potential to play a prominent place in transforming agricultural systems, crop nutrient delivery, and food production worldwide in the coming years (Akhter et al. 2013; DeRosa et al. 2010). New reports show that controlled-release fertilizer products and nutrients encapsulated in microspheres and assemblies of nanomaterials (NMs), especially nanoparticles (NPs) of Zn, Fe, Mn, and Cu oxides, have the potential for delivering plant nutrients via soil or leaves with increased crop yield and MUE (Bandyopadhyay et al. 2014; Yuvaraj and Subramanian 2014; Imtiaz et al. 2010). There is no field-scale information on MUE and crop production associated with the soil or foliar application of MNs in NMs and NPs, although these materials appear to stimulate growth during the early plant growth stages (Khodakovskaya et al. 2011; Yang et al. 2007). Published information indicates that NPs, such as Mn oxides, concentrate at the root surface and are subsequently taken up and translocated within plants (Miralles et al. 2012a, b; Lin et al. 2009). Many of the effects of NMs and NPs on crop yield and quality, human health, plant-beneficial soil microorganisms, and environmental risks remain largely unknown (Gardea-Torresdey et al. 2014).

This review provides new insights on how nanotechnology and nanobiotechnology may help increase MUE by crops and food nutrition, with a focus on Fe, Zn, Cu, and Mn. The review identifies knowledge and technology gaps existing in the safe use of NMs as nutrient sources in crops and their potential environmental impacts. The article also offers a vision for developing a model intelligent nanofertilizer (INF) delivery system for MNs to increase MUE and food quality by enabling the synchronization of MN release from fertilizers according to crop demand. The proposed MN-INF delivery system is based on the detection of specific plant root exudate signals by nanobiosensors (i.e., aptamers) housed in polymer films that coat fertilizer particles.

Regulation of MN uptake and mobility in plants and the environment

The uptake, intracellular translocation, and storage of MNs are regulated by plant homeostasis (Grotz and Guerinot 2006). The homeostasis regulating the uptake, mobilization, re-mobilization, translocation, and storage for several MNs including Fe, Zn, Cu, and Mn have been characterized (Kim and Guerinot 2007; Kobayashi and Nishizawa 2012; Milner et al. 2013; Bernal et al. 2012; Pittman 2005). For example, the disruption of the *OsYSL15* gene leads to Fe inefficiency in rice (Lee et al. 2009). In general, MNs are taken up from the soil solution by roots via chelation and oxidoreduction reactions. Following uptake, which is assisted by diffusion, proton solubilization and chelator-dependent mobilization, tissue precipitation, and remobilization, MNs reach vascular tissues for their translocation with soluble proteins in leaves, stems, flowers, and seeds (Waters and Sankaran 2011). In addition, MNs in xylem and phloem have to be loaded and unloaded, with further exchange between these tissues (Clemens et al. 2013). Intracellular co-translocation of macronutrients with MNs appears to be a possible mechanism to move them from the soil solution to the seeds (Waters and Sankaran 2011). MNs are also stored in a few cellular structures of the grain in cereals, such as the embryo and aleurone (Ockenden et al. 2004).

The translocation of Fe and other MNs in plants involves various steps, including transport across root tissues, xylem loading, transport, and unloading and xylem-to-phloem transfer. Complementary steps include phloem loading, transport, and unloading; symplastic movement toward the site of demand; and retranslocation from source or senescing tissue (Kim and Guerinot 2007). The question whether the same plant molecular controls exist in the uptake and transportation of NMs and NPs of Fe, Zn, Cu, and Mn oxides, or other, is yet unknown and will need to be answered in future research studies. Notably, however, are current findings showing that some of these NPs can be taken up as intact particles, with potential for release in planta (Dimkpa et al. 2012a, 2013; Ghafariyan et al. 2013; Wang et al. 2012). In a different study, carbon nanotubes (CNTs) and CNT quantum dots were found in the leave tissues after foliar exposure of tomato and rice plants (Alimohammadi et al. 2011).

A suggested mechanism for plant uptake and transport of intact NPs and NMs is endocytosis via endosomes, based on the presence of such endosomes in plants treated with NPs, as well as the activity of endocytosis inhibitors (Liu et al. 2009; Wang et al. 2012).

The path of NMs and NPs in plants and the environment has been proposed in several publications (e.g., Dimkpa et al. 2013; Ma et al. 2010). The main mechanisms for the reactions of NP in soil-plant systems seem to involve dissolution of NPs into ions, aggregation of individual NPs into larger size units, the dissolution of aggregates in soils, interaction of NPs with root exudates or labile soil organic matter, adsorption to root surfaces, and root absorption of intact free or chelated NPs, by primary or lateral roots, followed by transport from root through stem, leaves, and their storage in grain. The dissolution of ZnO NPs in soil is higher in acidic soil compared to alkaline soil (Watson et al. 2015). NPs of magnetite (Fe_3O_4) are taken up, are translocated, and can be accumulated in various plant tissues of pumpkin (*Cucurbita maxima*) (Zhu et al. 2008). Reduced Mn (Mn^{2+}) is taken up via an active transport system in epidermal root cells and transported as divalent cation Mn^{2+} into the plants (Marschner 2012; Bouain et al. 2007), as is Mn NPs (Pradhan et al. 2013). Wang et al. (2013) reported that when cowpea (*Vigna unguiculata* L. Walp) was grown in a soil with and without Zn NPs, there was no significant difference in plant growth and accumulation or the speciation of Zn between soluble Zn and ZnO-NP treatments. The latter suggested that the added ZnO NPs underwent rapid aggregation and dissolution following entry into the soil and then moved from soil to the root and shoot as Zn ions and other Zn-organic ligand compounds.

Much information and data are yet to be provided to allow modeling of the fate of NMs through the environment (Pan and Xing 2012). Further research is required before each of the molecular components and mechanisms responsible for the root uptake and intracellular translocation of NPs or NMs in plants is elucidated. In addition, the interaction mechanisms influencing the dynamics and fate of MNs in NPs need to be studied in in vivo soil-plant systems, as their fate is different than when studied in plants alone. To date, a great number of published studies are conducted in artificial plant growth media.

Interactions of MNs with macronutrients and disease in plants

This section updates earlier published reviews on MN and focuses attention on crop yields and molecular control of the interactions between micronutrients and macronutrients, as they have important implications for novel fertilizer technology. The interaction of MNs with macronutrients may result in positive (synergistic), negative (antagonistic), or no effect on crop growth and yield (Fageria 2001). These nutrient interactions in plants are very complex, and much remains to be learned about their specific mode of action. Important efforts have been made to improve macronutrient (N, P, K) and MN (i.e., Fe, Zn, Mn, Cu) nutrition in crops, based on determining how plants respond to deficiencies of these nutrients at the agronomic, physiological, and molecular levels.

In general, both solid granular and liquid macronutrient fertilizers are commonly used as carriers of MNs. The combined application of MNs with macronutrient fertilizers presents the following advantages: (a) allows more uniform distribution with conventional application equipment, (b) reduces costs of application, (c) permits bulk blending of fertilizer grades that provide the recommended MN rates, (d) coating powdered MN on to granular fertilizers decreases the possibility of segregation that results in uneven nutrient distribution when powdered MN is coated on to granular fertilizer, and (e) allows mixing MN with fluid fertilizers when there is compatibility in mixing and suspension.

In crops, the interactions of MNs with fertilizer N occur frequently and mostly synergistically. Increasing the rates of fertilizer N and MNs (Zn, Cu, Mn, Fe, Mo, and B) added in combination to a silty loam soil of Iran resulted in significant (30 %) grain yield increase of rice (Roshan et al. 2011). In a separate study conducted in rice, increased levels of fertilizer N addition enhanced the uptake and storage of Fe, but not of Zn in rice grain (International Rice Research Institute (IRRI) 1999). In general, MN-N interactions stimulate plant growth. However, such stimulation may cause MN deficiency under limited supply of soil MNs (Fageria 2001). Zebarth et al. (1992) reported average increases in grain concentrations of 10 mg Fe/kg and 4 mg Zn/kg, when wheat was fertilized with 160 kg N/ha compared to 40 kg N/ha broadcast as ammonium nitrate.

Phosphorus fertilizer interacts synergistically or antagonistically with MNs to influence plant growth and nutrition, especially in calcareous soils. Specific examples of P-MN interactions include P-Zn, P-Fe, P-Cu, P-Mn, P-Mo, and P-B couples (Murphy et al. 1981). Very high rates of added P may induce Zn, Fe, Cu, and Mn deficiencies in plants. For example, addition of $Ca(H_2PO_4)_2 \times H_2O$ at 180 mg P kg^{-1} to a siliceous and ferruginous sand matrix decreased the concentration of Zn in clover (Loneragan et al. 1979). The P-Fe interaction can also decrease their plant uptake by forming precipitates of Fe-phosphates near the root surface (Murphy et al. 1981) or in the grain. The direct P-Zn interaction on wheat and its residual effect on maize were investigated in a silty clay loam soil of India (Verma and Minhas 1987). When Zn was added at rates of 20 and 40 kg ha^{-1} to wheat in the absence of fertilizer P, grain yield did not increase. When P was added at 60 or 120 kg ha^{-1} and Zn added at 20 kg ha^{-1}, wheat grain yield increased significantly, demonstrating the positive effect of P-Zn interaction in wheat. In maize, only 20 kg ha^{-1} of Zn with no P addition was needed to significantly increase grain yield. When P was applied, even 40 kg ha^{-1} of Zn increased the grain and straw yield of maize (Verma and Minhas 1987). In a different study, the application of Mn and Zn (among other MNs) in combination with nitrogen, phosphorous, and potassium (NPK) applied at 120:60:40 kg ha^{-1} increased the number of kernels and grain yield of maize grown in a soil of Nepal (Adhikary et al. 2010).

Increasing the rates of K fertilizer addition increases Zn^{+2} utilization by corn (Shukla and Mukhi 1980). Topdressing of alfalfa with K adequately fertilized with P reduced Cu levels in the forage (Smith 1975). Potassium has been shown to have direct synergistic interactions with Fe and Mn. For example, potato fertilized with K reduced Fe deficiency symptoms (Bolle-Jones 1955). It is also known that K, Ca, and Mg regulate Mn absorption in plants. These cations either promote Mn absorption when Mn is in low amounts or effectively decrease Mn uptake when it is present in high amounts that might be toxic (Ramani and Kannan 1974). So far, most of the agronomic and physiological interactions between K and MNs were reported in earlier publications. Much work is required to study the K-MN interactions not only at the molecular level but also in relation to the homeostasis of MNs in plants.

Fertilizer-MUE—soil addition

From a plant viewpoint, fertilizer-MUE by crops can be defined as the yield of biomass per unit input of nutrient content (Hawkesford 2014; Reich et al. 2014). Alternatively and from a soil fertility viewpoint, MUE can be defined as the relative proportion of fertilizer-MN added to the soil that is absorbed and concentrated by crops. Depending on the author preference, both concepts are usually reported independently. For a whole soil-plant system, however, the total efficiency of macronutrients or MNs used by crops depends on the genetic and environmental abilities of the plant to produce biomass and extract the MN from fertilizer applied to soils or leaves. Thus, the preferred units of efficiency should consider the yield of biomass per unit of nutrient content in plant tissue per unit of nutrient added to soils (i.e., kg MN in total biomass × kg^{-1} MN in fertilizer added to soils). In this review, we define the term MUE as the amount of the added fertilizer-MN that ends up in the crop, as traditionally defined in studies of soil fertility. Plant biomass yield and nutrient content may be influenced by other factors, such as plant genetics and weather. In this article, the concept of MUE is associated with the transport, usage, and storage within the plant and indirectly with MN fate in the environment.

Iron, Mn, Zn, and Cu rapidly react in soil components via oxidation and/or precipitation. Accordingly, the MUE of inorganic MN fertilizers is <5 % (Ryan et al. 2013; Singh 2008; Samra and Benbi DK, Brar MS, Bansal, S 2006). Malakouti (2008) reported that relative to NPK, soil fertilization in a large number of field trials resulted in increases of fertilizer N use efficiency in potato and wheat, when MNs were added in combination with NPK. Higher rates of addition are required when MNs are broadcasted relative to band application (Kaiser 2011). An important practical issue associated with MUE deals with the application to soil of small amounts of MNs (from a few g to <5 kg ha^{-1}) resulting in large, uneven spatial distribution of the trace elements. Thus far and relative to soluble metal salts, chelated MN fertilizers appear to help improve MUE (Liu et al. 2012b). The low MUE increases crop production costs for farmers and adversely influences their content in crops, in addition to its negative effect on environmental health.

Fertilizer-MUE—foliar application

Application of foliar sprays implies that nutrients applied will be absorbed and exported from the point of application (leaf) to the point of utilization. Thus, in foliage applications, nutrients need to first travel through the leaf cuticle. For Fe, Zn, and Mn applied either in chelated or in sulfate salt form, an extensive nutrient fixation by cuticle may occur at the point of application (Ferrandon and Chamel 1988). Foliar absorption of MNs was lower from chelates than from the inorganic salt, but the translocation within the plant was greater when chelated forms were applied (Rengel et al. 1999). Information for increasing MUE via foliar fertilization of macronutrients and MNs is starting to emerge. Zinc sulfate added together with urea in foliar applications doubled the yield and size of apple fruit and the concentration of Zn in plant tissue (Amiri et al. 2008). In a rice and wheat rotation, fertilizer P increased the utilization efficiency of Zn applied to leaves, which was more effective in wheat than in rice (Srivastava et al. 2014). Some chemical inputs used in crop production can also influence the MUE. For example, ferric reductase is required for iron absorption in dicotyledonous and non-grass monocotyledonous plants. However, when glyphosate is used in crop production, the herbicide reduced the activity of plant ferric reductase by 50 % within 6 h of application (Ozturk et al. 2008). Glyphosate also tied up the MNs and reduced the bioavailability of Fe, Mn, and other minerals and metals such as Al with obvious implications to plants and human health through the food chain (Seneff et al. 2015). In general, MUE with foliar application appears to be also associated with the presence and thickness of cuticle waxes that limit nutrient penetration because of their hydrophobicity. Another practical challenge of foliar applications deals with the passage of the nutrient through the stomata that represent very small fraction of the total leaf area. In addition, the stomata in most plants are located on the adaxial (upper) surface as against the abaxial (lower) surface of leaves, depending on species or varieties. For example, wheat leaves have a greater proportion of stomata frequency on the adaxial side, with an average distribution abaxial/adaxial distribution ratio of ~0.73 (Teare et al. 1971). Rain on leaf surface or rapid leaf drying affects the absorption of MNs in foliar applications (Kaiser 2011).

The uptake efficiency varies widely when MNs are applied to plant leaves. From the published studies, however, it is unclear the exact reasons responsible for such large variability. Further research conducted on the mechanisms influencing MUE in foliar applications is necessary to help understand how high levels of MUE may be achieved via MN delivery to leaves.

Novel technologies for MNs

Controlled release of MNs

Microencapsulation and low-solubility products

Most research and development work on encapsulated MNs has been in the areas of food and medicine (Moslemy et al. 2014; Han et al. 2008). The microencapsulation of MNs produces tiny capsules (i.e., μm diameter) that have several nutritional advantages: (1) enhancement of the contact surface for absorption, resulting in bioavailability increases; (2) low cost of production, and (3) biodegradability and biocompatibility with the environment (Moslemy et al. 2014). Different coating polymer materials have been used, depending on the target molecule, cell tissue or organism, type of active ingredient, and environmental conditions. Examples of these polymers include ethylene vinyl acetate, alginate, chitosan, lignosulfate, pectin, and starch (Wang et al. 2013; Abedi-Koupai et al. 2012). For example, a cocktail of MNs of ferrous fumarate and of ascorbic acid and beta-carotene was delivered in functionalized alginate and chitosan microcapsules into gastrointestinal simulated solutions, resulting in enhanced stability and absorption of MNs (Han et al. 2008).

In contrast to human medicine, only sparse information exists on the encapsulation of MN fertilizers and their effects on crops and associated MUE (Abedi-Koupai et al. 2012). Likewise, the agronomic, environmental, and polymer efficacy of encapsulated macronutrient sources, such as urea, has received little attention (Blackshaw et al. 2011; González et al. 2015). Notably, the encapsulation of commercial fertilizers uses polymer films to protect nutrients from rapid abiotic and biotic stabilization reactions in soils and control their release rates into the soil solution. Release of MNs from fertilizers coated with organic polymers occurs according to soil moisture content and/or temperature, pH, ionic content, and microbial activity, among other factors. Release of MNs is based on either direct diffusion or by decreasing the rate of product hydrolysis, such as urea, and the release is controlled by the properties and structure of polymers together with the microcapsule architecture (Abedi-Koupai et al. 2012). For example, a controlled-release polyphosphate MN fertilizer containing Zn, Fe, Mn, and Cu with low solubility in water was tested in different crop field trials. This fertilizer type increased rice yield from 10 to 55 % over the control treatment (no MNs added), and up to 17 % over the conventional MN sulfate salts, resulting in significantly increased accumulation of Zn, Fe, and Mn in the grain (Bandyopadhyay et al. 2014). Significant increases in the yield and vitamin C content of potato have been observed for the same type of fertilizer (Bandyopadhyay et al. 2008). The exact mechanisms controlling rice yield increase were not reported.

Nanoencapsulated MNs

Mesoporous silica and aluminosilicates have important properties such as highly ordered channels with accessible large porosity, large surface areas, active sites for adsorption, and ion exchange and catalysis (Xu et al. 2009; Wu et al. 2008). Mesoporous aluminosilicates have been used as carriers of CuO NPs (Huo et al. 2014). In earlier studies, Hossain et al. (2008) compared pore-expanded mesoporous silica (PE-MCM-41) with MCM-41 and silica gel (SGA), for their capacity to immobilize urease and hydrolyze urea into ammonium. Urease loaded on PE-MCM-41 slowed down the hydrolysis rate of urea when compared to that of bulk urease and urease loaded on MCM-41 and SGA. It was suggested that the latter technique could be used as an alternative to urease inhibitors to control the ammonia release from urea fertilizer in soil-plant systems. The industrial preparation of mesoporous materials as fertilizer carriers may be possible, as various types of natural silicates are abundant in nature and have structural similarities to those of synthetic mesoporous materials (Yang et al. 2010a, b).

The use of hollow core-shell NMs and other nanostructures has been studied in agriculture and biomedicine (Burda et al. 2005). A nanosized Mn carbonate hollow core-shell loaded with $ZnSO_4$ regulated Zn release not only in an in vitro solution, but also in a Black Inceptisol sample placed in a percolation reactor (Yuvaraj and Subramanian 2014). The latter authors suggested that the hollow core-shell could serve as a plant growth medium for supplying plant roots with additional nutrient ions. They demonstrated that the hollow core-shell released Zn more slowly than the $ZnSO_4$ salt, through dissolution and ion exchange reactions. When rice plants were fertilized with the Zn-fortified core Mn carbonate shell, significant increases in grain yield and nutrition under submerged and aerobic soil moisture regimes were obtained. The nanoencapsulation of Zn using the Mn-hollow core-shell appeared to improve Zn use efficiency by rice, while reducing the loss of nutrients. From the published information, it was not clear whether the presence of Mn in the core-shell contributed in influencing the rice growth.

Relative to microencapsulation and on a weight-by-weight basis, nanoencapsulation appears to only load a fraction (i.e., 1 to 10 %) of catalytic proteins or crop nutrients into the mesoporous structures of silica or aluminosilicates (Yuvaraj and Subramanian 2014; Hossain et al. 2008). On the other hand, microcapsules loaded with Fe have a high loading efficiency >90 %, meaning that the majority of the added Fe remained encapsulated (Khosroyar et al. 2012; Choi et al. 2009). No studies appeared to be published on the economics for the microencapsulation and nanoencapsulation of crop nutrients.

NMs and NPs in soil-plant systems

Growth promoters and MN sources

Synthetic NMs and/or engineered NPs (ENPs) closely interact with biotic and abiotic components in terrestrial ecosystems. The outcomes from many of the discrete studies of MN-plant interactions suggest the potential use of commercial NMs and NPs of Zn, Fe, Mn, and Cu oxides as nutrient sources in crops produced in MN-deficient soils. Reports indicate that NPs of ZnO (<100 nm) used with a variety of crops such as cucumber (Zhao et al. 2013); peanuts (Prasad et al. 2012), sweet basil (El-Kereti et al. 2013); cabbage, cauliflower, and tomato (Singh et al. 2013); and common chickpea (Pandey et al. 2010) increased biomass, yield, and nutrient accumulation. For example, *Moringa peregrine* plants sprayed with a Hoagland solution containing NPs of ZnO and Fe_3O enhanced various growth parameters either under non-saline and saline growth water when compared to a control with no NPs added. The presence of the NPs also resulted in significant reduction in Na^+ and Cl^- and an increase in macronutrient and MN contents in plant tissues (Soliman et al. 2015). Similarly, Raliya and Tarafdar (2013) demonstrated dramatic increase in biomass of cluster bean when leaves were sprayed with ZnO NPs compared to bulk ZnO (Fig. 1). Prasad et al. (2012) and Moghaddasi et al. (2013) demonstrated increase in yield of peanut and cucumber, respectively, upon treatment with ZnO or Zn NPs, relative to Zn salts. Increased accumulation of Zn from ZnO NPs in different crop species has also been observed (Dimkpa et al. 2012a, 2013, 2015b; Dimkpa 2014; Watson et al. 2014). With other MN-NPs, such as Fe and Mn NPs have shown positive indications in terms of enhancing plant growth, metabolism, or nutrient accumulation from the NPs (Zhu et al. 2009; Ghafariyan et al. 2013; Pradhan et al. 2013, 2014; Alidoust and Isoda 2014; Kim et al. 2014). Recently, a review by Liu and Lal (2015) indicated that ENPs have a great potential as fertilizers (including macronutrient and MNs) for increasing crop production and reduce adverse environmental impacts by excess nutrients from conventional fertilizer sources.

Relative to a control treatment lacking the addition of multiwalled carbon nanotubes (MWCNTs), the presence of MWCNTs in the soil-less growth media of tomato seedlings increased seedling growth after 3 days of incubation (Khodakovskaya et al. 2009). Other studies conducted with CNTs in wheat and alfalfa roots showed that most of the CNTs were adsorbed on root surfaces and rarely taken up into the plants during the early growth stages (Miralles et al. 2012b). On the basis of these findings, Mastronardi et al. (2015)

Fig. 1 Effects on cluster bean growth of ZnO nanoparticles (nZnO), compared to bulk ZnO (oZnO), upon foliar spraying of each product on the plant. Image is reproduced from Raliya and Tarafdar (2013), with permission

considered CNTs as plant growth promoters, as they stimulate growth, although their exact physiological functions are unknown. On the other hand, Lin et al. (2009) found that addition of CNTs resulted in their accumulation in various tissues by maturity. These contrasting findings on the effects of CNTs on plants suggest both systemic and non-systemic effects of CNTs on plants. In terms of the molecular mechanisms involved, the addition of CNTs could affect growth indirectly by inducing changes in gene expression in tomato leaves and roots, particularly, the up-regulation of stress-related genes, including those induced by pathogens and the water-channel LeAqp2 gene (Khodakovskaya et al. 2011). With metal-based NMs, a metal oxide suspension of anatase-TiO_2 NPs (4–6-nm diameter, 0.25 % TiO_2) was used to immerse spinach plants (*Spinacia oleracea*) for 48 h at 10 °C under light. Under these conditions, NPs of TiO_2 influenced N metabolism in spinach by significantly increasing the activities of nitrate reductase, glutamate dehydrogenase, glutamine synthase, and glutamic-pyruvic transaminase during growth (Yang et al. 2007). The NPs of TiO_2 also increased the fresh and dry weight of spinach during 45 days of growth in the soil-less growth media.

Bioavailability of MN NPs in soils

The plant availability of MNs depends on several biotic and abiotic soil properties, such as soil pH and soil organic matter (SOM); this is also true for MNs in NPs. In general, the contents of MNs, such as Fe and Zn, in shoot and root are inversely proportional to rhizosphere pH. Similarly, the content of Mn is shown to increase with decreasing pH (Sarkar and Wynjones 1982). Intact CuO NPs were adsorbed on root surfaces and taken up into aboveground wheat tissues from the sand growth matrix (Dimkpa et al. 2012a, 2013). Wheat growth increased the dissolution of both CuO and ZnO NPs and microparticles in the sand growth matrix. The dissolution ranged from <0.3 mg kg^{-1} to about 1.0 mg kg^{-1} for the CuO products and from ≤ 0.6 mg kg^{-1} to between 1.0 and 2.2 mg kg^{-1} for the Zn products (Dimkpa et al. 2013). These authors noted that the nominal negative surface charge of NPs was also reduced by the presence of wheat. In addition, they also reported that the average size of CuO and ZnO NPs increased from their nominal size <50 and <100 nm to 317 and 483 nm, respectively, after 14 days of incubation in the sand-wheat system. The formation of larger-size NP aggregates may be associated with the Brownian motion or the Ostwald ripening effect (Ostwald 1897).

Toxicity of NMs in plants and soil organisms

Publications on the phytotoxicity of NMs and NPs have increased rapidly since 2005. The high reactivity of NMs and NPs has continued to cause concerns about their potential toxicity in biological systems. Concerns are based on published evidence that materials and particles at the nanoscale have chemical, electrical, magnetic, mechanical, and optical properties that are quite different from bulk materials. The ENPs can adhere to plant roots and exert physical or chemical toxicity on plants and soil organisms, depending on their properties and concentration. Publications have emerged recently concerning the interactions of ENPs with soil organisms and plants (Dimkpa et al. 2015a, b; Lin and Xing 2007, 2008). Most studies indicate that the positive or adverse effects of NPs on plants are exerted on biomass production, decreasing the lengths of roots, shrinking of root tips, and high vacuolation or collapse of root epidermal and cortical cells, and positive effects on chlorophyll and carotenoid contents (Nair and Chung 2014). These effects depend on particle dose, size, and specific NPs. However, fewer studies have focused on the plant gene and anatomic impacts caused by NPs and NMs to explain their toxic effects. These effects are dependent on plant species, cell tissues, particle dose, size, and specific NPs. For example, exposure of maize and cabbage seedlings (*Brassica oleracea* var. *capitata* L.) to citrate-nAg, nZnO, $AgNO_3$, and $ZnSO_4$ solutions for 7 days revealed structural changes in the primary root cells of maize. Microscopic evidence showed "tunneling-like effect" with nZnO treatment (1000 mg L^{-1}), while exposure to $AgNO_3$ (7.5 μg Ag L^{-1}) led to cell erosion in the root apical meristem (Pokhrel 2013; Pokhrel and Dubey 2013). In maize, a significant change in metaxylem count was evident with citrate-nAg, $AgNO_3$, and $ZnSO_4$ treatment, but not with nZnO treatment (Pokhrel and Dubey 2013). These anatomical anomalies were observed at nanogram Ag per milligram level of biouptake, which corresponded to higher exposure concentrations (i.e., ≥ 73.4 μg mL^{-1}) that were chosen based on root elongation measurements. Interestingly, in both maize and cabbage, measures of germination and root elongation revealed lower NP toxicity compared to free ions.

ENPs can be potentially taken up by plant roots and transported to shoots through vascular systems depending upon the composition, dose, shape, and size of ENPs and plant species (Ma et al. 2010). Apparently, both NPs and their aggregates are taken up into the plant shoot (Wang et al. 2012), a hypothesis that is supported by the micron (≥1000 nm) and submicron (≈500 nm) size ranges of xylems and endosomes, respectively, of vascular plants (Wang et al. 2012; http://www.mapoflife.org/topics/topic_450_Xylem-vessels-in-vascular-plants). Upon shoot accumulation at high levels, toxic effects of ZnO NPs have been reported in wheat (*Triticum aestivum*), soybean (*Glycine max*), rye grass (*Lolium perenne*), and cucumber (*Cucumis sativus*). Other publications indicate that NPs of CuO are also toxic not only to wheat, ryegrass, and cucumber, but also to maize (*Zea mays*), radish (*Raphanus sativus*), and duckweed (*Landoltia punctate*) (Kim et al. 2012; Shi et al. 2011; Wang et al. 2012; Atha et al. 2012). NPs of Cu were bioavailable but agglomerated intracellularly resulting in greater toxic effects (inhibition of seedling growth) to mung bean (*Phaseolus radiates*) than to wheat (Lee et al. 2008). In wheat, CuO NPs were more toxic than ZnO NPs (Dimkpa et al. 2012a, b) correlating with the differential phytotoxicity of Cu and Zn ions (Warne et al. 2008). Silver and Cu NPs were significantly more phytotoxic than the corresponding bulk materials, and greater ion dissolution from the NPs only partly explained the toxicity (Stampoulis et al. 2009). The phytotoxicity of ZnO NPs was not directly from their limited dissolution in the bulk nutrient solution, suggesting the occurrence of nanospecific toxicity (Lin and Xing 2008).

The growth and balance of essential metals in beans exposed to ZnO or CuO NPs were influenced in a dose-dependent manner by the NPs and/or bacterial colonization of NP-exposed roots, indicating subtle effects of NPs in plant nutrition. Siderophores exuded by the bacteria in the bean rhizosphere were suggested to influence the activity of the NPs (Dimkpa 2014; Dimkpa et al. 2015b). Studies on the trophic transfer, effects, and allocation of NPs on microorganisms and fauna, such as earthworms and bullfrogs, in terrestrial systems are emerging (Dimkpa 2014; Unrine et al. 2012). For example, ENPs of metal oxides, such as CeO_2, Fe_3O_4, and SnO_2 were toxic on soil microbial biomass (Antisari et al. 2013). In a different study, NPs of Ag, Co, and Ni reduced microbial biomass C, whereas TiO_2 did not affect it (Antisari et al. 2015). In rhizosphere of maize and soybean, TiO_2 NPs did not influence the composition of soil bacterial communities; however, the addition of undoped N and N doped with TiO_2 NPs at low concentration influenced arbuscular mycorrhizal fungal communities (Burke et al. 2014). Also, the degree of unsaturation of fatty acids in worms fed with NP-contaminated food was reduced. However, a recent study indicates that root exudates have the potential to ameliorate the toxicity of MN-NPs toward a soil bacterium (Martineau et al. 2014). In the absence of fertilizer addition, wheat roots grown in soils are shown to exudate up to 70 % of its photosynthesized CO_2-C (Monreal and Schnitzer 2013), and as such, they can help reduce the mobility of MN-NPs, although the exact effects of root exudates on the fate of MNs delivered in NMs and NPs are unknown. Most of the studies focused on phytotoxicology of NPs and NMs have been performed using seed germination and incubation of plant seedlings over short periods in agar and pure nutrient solution cultures (Alidoust and Isoda 2014) and have used very high NP doses with little or no relevance to actual field situations. Moreover, only very few plant ecotoxicology studies (e.g., Watson et al. 2015) have been conducted in soil-plant systems. Yet, these studies are essential for determining the exact agro-environmental fate of NMs and NPs. However, it is noteworthy that in soil, the phytotoxicty of NPs applied even at a high dose could be negated, dependent on soil property (Watson et al. 2015).

Collectively, reviews of carbon-based NMs and NPs, their applications, and implications in the environment and food chain have been published (Gardea-Torresdey et al. 2014; Rico et al. 2011). These reviews indicate that in soil-plant systems, the penetration mechanisms, uptake, bioaccumulation, biotransformation, benefits, and risks for food crops and soils of NMs and NPs are still largely unknown and not well understood. However, it is noteworthy that in soil, the phytotoxicty of certain NPs applied even at high doses could be negated, dependent on soil properties (Watson et al. 2015). As documented by Servin et al. (2015), as well as others, novel nanofertilizer formulations have been patented. Still, little or no information on specific crop uses and responses to these patented formulations exists in the scientific literature (Mastronardi et al. 2015). In addition, the exact influence of MNs delivered in NPs on pesticide activity, plant pathogens for disease prevention and control, and on endophytic soil microorganisms for improving the cycling efficiency of macronutrients and MNs and their disposition and translocation in crops is unknown. Future research on the latter unresolved aspects is warranted.

Nanodevices

Nanoscience and nanotechnology encompass three fields: nanodevices, NMs, and nanomeasurement and nanocharacterization. A nanodevice can be simply defined as any manufactured device whose dimensions are on the scale of 1–100 nm and whose properties exploit the unique properties of nanoscale materials. A nanodevice may involve the control and manipulation of biomolecular constructs and macroassemblies that are critical to living cells (Tomalia et al. 2007). These constructs and assemblies include entities such as proteins, DNA/RNA, viruses, cellular lipid bilayers, and others. Thus far, much of the research on nanodevices is conducted for the diagnostic and therapy of cancer cells (Sailor and Park 2012; Akhter et al. 2013). However, similar nanodevice concepts used in nanomedicine can be applied for soil-plant systems to control the delivery of fertilizers in order to improve MUE and the nutritional quality of food.

Novel sensor devices have been incorporated into microbial cells for environmental and soil applications, such as the diagnosis of MN deficiency and toxicity in soils. For instance, a genetically modified microbial sensor was constructed and used to evaluate the immobilization and bioavailability of Zn in different soils (Liu et al. 2012a). The zinc-specific biosensor, *Pseudomonas putida* X4 (pczcR3GFP), was constructed by fusing a promoterless enhanced green fluorescent protein (egfp) gene with the czcR3 promoter in the chromosome of *P. putida* X4. The fluorescent reporter strain detected about 90 % of the Zn content in soil-water extracts of soil samples amended with Zn. The authors concluded that the biosensor constitutes an alternative system for the convenient evaluation of Zn toxicity in the environment (Liu et al. 2012a). The bioavailability and toxicity of Zn in laboratory soil-amended and field samples have also been assessed using a gene in *E. coli* HB101 (puCD607) as the biosensor and *E. coli* MG 1655 (pZNT-lux) as the bioreporter (Maderova and Paton 2013). The latter authors concluded that the bacterial sensors responded to the bioavailable fraction of Zn in soils. However, they could determine the biological response from the quantitative measurements of various chemical Zn species in soil.

Synthetic nanodevices also hold some promise for MN sensing and delivery platforms. Biosensors of magnetic NPs base their mode of action on magnetic properties and can have multiple uses such as sample preparation, wastewater treatment, water purification, disease diagnosis and therapy, cell labeling and imaging, tissue engineering, and pesticide sensing (Rocha-Santos 2014). Advances in research using graphene-based electrochemical sensors and biosensors such as graphene-based DNA sensing for bioscience and biotechnology, as well as environmental analysis, have also been summarized and reviewed by Shao et al. (2010). Engineered nanobiosensors and nanoprobes, such as DNA- or RNA-based aptamers, are highly specific and sensitive devices that allow the detection of very low quantities of analyte in individual living cells or fluids. Aptamers are synthetic nucleic acids that fold into unique three-dimensional structures capable of binding tightly to a target of interest, with affinities and specificities that rival or even surpass those of monoclonal antibodies (Bunka and Stockley 2006). These nanobiosensors have the capacity to sense individual chemical species in specific locations of tissues or organs or fluids (Lee et al. 2008; Vo-Dinh et al. 2006). In the soil solution of terrestrial ecosystems, the individual chemical species may be metabolites of chemical signaling networks resulting from interactions and communications established between plant roots and soil microorganisms (Monreal 2015; Monreal and Schnitzer 2015). Based on the latter, aptamer-based nanobiosensors appear as useful tools to study the origin and reactions of metabolites produced by living cells and how they relate to nutrient cycling in soil-crop rhizospheres.

Recently, novel aptamer-based materials have been investigated as potential controlled-released materials that may be applied in agriculture and medicine. For example, polyelectrolyte polymer films prepared by layer-by-layer assembly were prepared which could retain the ability of the aptamer to detect a selected molecule when it was incorporated into the functional film (Sultan et al. 2009). These films were found to have increased permeability when the target molecule was bound, suggesting that these materials could find applications in the controlled delivery of a payload (Sultan and DeRosa 2011). In another study, polyelectrolyte microcapsules with encapsulated recognition aptamers preloaded into their cores were found to collapse after the binding of the target molecule. The authors concluded that these microcapsules have potential for applications in targeted delivery systems for the controlled release of drugs, pesticides, or other payloads such as plant nutrients (Zhang et al. 2013).

The incorporation of nanodevices in plant nutrition may, therefore, allow for the development of efficient technological platforms to detect and treat nutrient deficiencies in soils and plants and in real time. Intelligent nanodevices or biosensors may help deliver macronutrient and MNs according to the temporal and spatial crop requirements during the growing season. In addition, nanodevices used in agriculture may help achieve a deeper understanding of the interactions between roots and soil organisms, MN cycling processes, disease control, and the maintenance of food crop quality.

The future—nanobiotechnology for crop MNs

In nature and terrestrial ecosystems, chemical communication exists among, within, and between animals, insects, plants, and microorganisms (Adler 2011; Witzany 2010). Secreted chemical signals, their diffusion, and signal detection components facilitate highly productive intraspecies and interspecies relationships (Bassler 2002). Plants and microorganisms in the environment and in vitro systems produce a bewildering array of low-molecular-weight organic molecules that have many biological activities (Goh et al. 2002). Most metabolites modulate gene transcription at low concentrations, and the primary effect of small organic compounds appears to be the maintenance of microbial communities in the environment (Yim et al. 2007). Some of the novel methods to visualize interactions of NPs and their chemical reactions in plants have been presented by Wild and Jones (2009).

Under various soil nutrient conditions, roots are able to respond via changes in morphology and architecture and through molecular signaling components to local deficiencies or high levels of P (Niu et al. 2012), and N (Peng et al. 2008).

Among other benefits for plants, plant growth-promoting rhizobacteria (PGPR) are known for their abilities to increase the amount and solubility of plant-available macronutrient and MNs, possibly through effects at the physiological and molecular levels. The molecular mechanisms underlying these positive effects, the signals involved, and the potential application of PGPR in sustainable agriculture remain uncertain (Pii et al. 2015). Recent publications by Monreal (2015) and Monreal and Schnitzer (2015) provide evidence that the communication between roots and microorganisms is an integral part of chemical signaling networks in crop rhizospheres, and that part of this signaling networks is associated with soil nutrient cycling processes and plant defense-pathogen infection factors as indicated by key metabolites identified in the soil solutions of wheat rhizosphere. The abundances of some of these metabolites in soil solutions vary according to the phenology of a wheat crop (Monreal and Schnitzer 2013). Functional roles for some chemical components of labile SOM in soil solutions have been reported (Monreal and Schnitzer 2013, 2015). As a result of the plant-soil microbial communication under MN deficiency, metabolites, such as siderophores, or other organic molecules are released into the soil solution to facilitate plant MN uptake. Dependent on the plant and soil microorganisms, the identities of several of these communication metabolites have been determined (see, for example, Monreal and Schnitzer 2015; Martineau et al. 2014), including metabolites involved in nutrient mobilization (Keuskamp et al. 2015).

The coupling of knowledge on chemical signals under MN limitation to new advances in nanotechnology and root-microbial communications can be a major factor shaping modern agriculture (Monreal 2015). Hence, the interspecies chemical communication may become a key pillar in the development of new nanobiotechnology-based intelligent MN fertilizers. For example and from a technology viewpoint, MNs loaded in NMs incorporating molecular recognition agents, such as aptamers (Zhang et al. 2013), to detect plant signals denoting MN deficiency in soil environments, could be delivered into crop rhizospheres or plant foliage to increase plant MUE and nutrition. Figure 2 shows that the chemical communication concepts represent a promising approach for developing a model intelligent nanofertilizer delivery platform for MNs, such as Zn and Fe. This nutrient delivery model platform is based on the recognition of specific plant metabolites by a nanobiosensor system. The plant metabolites are exuded in response to deficiencies of specific MNs in soils. In this nanobiotechnology strategy, the main mechanism of nutrient release is based upon the recognition and binding of a specific plant signal by a nanobiosensor housed in a polymer film which coats Zn fertilizer NPs or soluble Zn salts (or MN-NPs or salts of Cu, Fe, and Mn). Upon binding, the fertilizer Zn NPs are released in a synchronized fashion in response to a root signal indicating the deficiency of Zn. Zinc is used to illustrate this model because it is one of the most limiting MNs in agriculture, globally. The development and use of this type of technology have a great potential for enhancing MUE and food quality, producing economic savings to farm producers, and reducing adverse environmental impacts. Ultimately, this nanobiotechnology approach is consistent with the plant homeostasis regulating MN nutrition and toxicity in soils. Noteworthy, nanobiotechnology approaches to enhance MUE in soil-crop systems need to be accompanied by research dealing with the interactions of not only NPs, polymer films, and nanodevices with heterogeneous soil phases, such as electrically charged humic substances and clay colloidal surfaces, but also with active soil microorganisms and fauna.

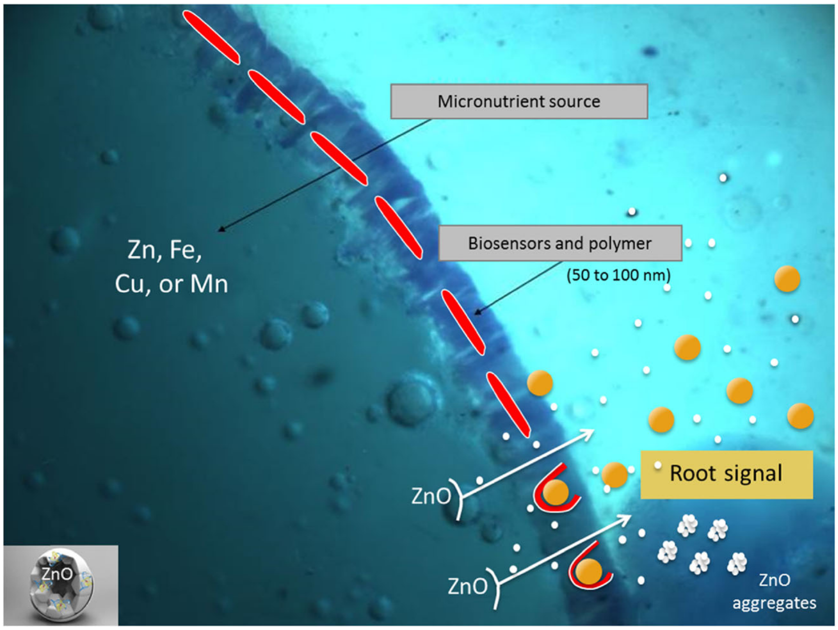

Fig. 2 A conceptual model for the synchronized release of ZnO nanoparticles according to crop demand. The binding of specific root chemical signals (*yellow*) with a nanobiosensor (*red*) housed in a thin polymer film (*blue*) coating ZnO fertilizer nanoparticles (*dark grey*). The selective signal-biosensor binding process results in the release, dissolution, and aggregation of ZnO NPs (*white spheres*) with their plant uptake from the soil solution

In summary, we need to be cognizant of the agricultural and environmental risks involved in the use of NMs and NPs as nutrient sources in MN-deficient soils. A thorough review of the literature indicates that most of the reported effects and interactions of selected NMs and plant species have been studied during the very early plant growth stages, mostly in vitro, with industrial-grade NMs, where plants have been grown using NPs in high doses, and in soil-less media rather than soil systems. Also, impurities present in NMs can also influence plant metabolic responses, and a majority of published studies lack rigorous characterization of these materials. The soil-less studies and lack of proper characterization of NMs represent serious limitations for establishing proper policies and regulations for the production and safe use of NMs and NPs as nutrient sources or growth enhancers in agriculture. Future research studies need to address these limitations before definite conclusions can be made for the use of nanotechnologies in vivo soil-crop systems.

Conclusions

MN deficiency in 50 % of the world's soils greatly reduces the amount and quality of food and adversely affects human health. In addition, the fertilizer-MUE by crops is low (<5 %), due to a lack of synchronization between the fertilizer-MN release and the crop demand during the growing season. Modern research efforts are conducted to increase MUE, paying special emphasis on potential contributions of nanotechnology; however, its application in fertilizer nutrient delivery is at a nascent stage. Published information from soil-less studies indicates that the addition of NMs and NPs to plants can enhance their biomass production and MN concentration. The effects for delivering MNs in nanocapsules and microcapsules, NMs, and NPs for increasing yield and grain quality and MUE in soil-plant systems remain largely unknown and await further research.

The successes recorded in the use of NMs in drug delivery and food sector indicate promising possibilities for the application of nanobiotechnology in fertilizer-MNs. A model of an intelligent nanofertilizer platform for efficient delivery of MNs in soil-crop systems is presented. Such a technology model is based on the understanding of communication signaling networks established between living cells in crop rhizospheres under MN deficiency, resulting in the synchronization of fertilizer-MN release according to crop demand. Such novel technology platform for MNs may help improve the economics of food production, enhance crop yield and quality, and reduce the environmental footprint of agriculture for improved human health worldwide.

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