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The Application of Nanotechnology for Micronutrients in Soil-Plant Systems

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Contents

List of Acronyms and Abbreviations

$AgNO_3$	Silver nitrate
B	Boron
Ca	Calcium
CNT	Carbon nanotube
Cl	Chloride
Cu	Copper
CuO	Copper oxide
Diam	Diameter
DNA/RNA	Deoxyribonucleic acid/ribonucleic acid
DOM	Dissolved organic matter
DTPA-TEA	Diethylenetriamine penta-acetic acid + triethanolamine
EDTA	Ethylenediaminetetraacetic acid
ENPs	Engineered nanoparticles
ENMs	Engineered nanomaterials
FAO	Food and Agriculture Organization of the United Nations
Fe	Iron
Fe_3O_4	Tri-iron tetroxide, or Iron(III) oxide, or magnetite
HS	Humic substance
INF	Intelligent nanofertilizer
IPNI	International Plant Nutrition Institute
K	Potassium
Mg	Magnesium
MN	Micronutrient
MUE	Micronutrient use efficiency
Mn	Manganese
Mo	Molybdenum
MWCNT	Multi-walled carbon nanotube
N	Nitrogen
NFDC	National Fertilizer Development Center
Ni	Nickel
NM	Nanomaterial
NP	Nanoparticle
P	Phosphorus
PE-MCM-41	Pore-expanded mesoporous silica CM-41
POP-MN	Polyphosphate-micronutrient
Pi	Inorganic phosphorus
PS	Phytosiderophore
S	Sulfur
SGA	Silica gel
SOM	Soil organic matter
SWCNT	Single-walled carbon nanotube
TiO_2	Titanium oxide

USGS	United States Geological Survey
Zn	Zinc
ZnO	Zinc oxide
$ZnSO_4$	Zinc sulfate

Abstract

Micronutrients (MNs) are important to world agriculture and human health. Over 3 billion people across the world suffer from micronutrient deficiencies. Zinc (Zn), iron (Fe), manganese (Mn) and copper (Cu) have become yield-limiting factors and are partly responsible for low food nutrition. Although crops use low amounts of MNs (<2.4 kg/ha), about half of the cultivated world's soils are deficient in plant bioavailable MNs, due to their slow replenishment from the weathering of soil minerals, soil cultivation for thousands of years and insufficient crop fertilization. Relevant MN deficiencies occur more frequently in neutral to alkaline soils, under anaerobic conditions and in arid or semi-arid regions. The MN use efficiency (MUE) of most commercial fertilizers added to soils or foliage is 2.5% to 5% of applied, due to their rapid stabilization by soil components, low leaf penetration and low mobility in plants. In soil-plant systems, fertilizer-MNs interact with macronutrients resulting in synergistic, antagonistic or neutral response affecting yield and food quality.

Thus far, conventional and newer fertilizer technologies and products are unable to synchronize the MN release from fertilizer according to crop demand during the growing season, resulting in low MUE. New efforts to improve crop yield, food nutrition and fertilizer-MUE involve the use of micro- and nanoencapsulation, nanomaterials (NMs), nanodevices and nanoparticles (NPs) of Zn, Fe, Mn and Cu oxides. Fertilizer products appear to increase MUE as follows: soluble salts < chelates < microcapsules ≤ nanocapsules = nanoparticles. Many of the effects of the new fertilizer materials on crop yield and quality, human health and environmental risks remain largely unknown. Nanobiotechnology will occupy a prominent place in transforming agricultural systems and food production worldwide in the coming years. This report proposes that the development of a MN intelligent nanofertilizer (INF) delivery platform may result in significant increases of MUE and food quality by enabling the synchronization of MN release from fertilizers according to crop demand. The novel MN-INF product development needs adequate financial support and a multidisciplinary team of scientists.

1 Introduction

Agriculture systems have a crucial role in the provision of food, improved livelihoods and income for many, being the main occupation of about 80% of poor people in rural areas, including women (Pinstrup-Andersen, 2011). The world will need to meet the food needs of an estimated population of 9 billion by 2050 (FAO, 2011). The consumption of micronutrient (MN)-deficient food results in anemia and reduction of cognitive and physical performance in children (Swaminathan et al., 2013). Improved food production systems and access to quality food can help reduce undernutrition (Panwar et al., 2012). For example, an investment of U.S. $8 billion per year globally would reduce the number of underweight children by 10 million and of hungry people by 201 million by 2050 and will also help raise the income of many of the world's poorest people (Hoddinott et al., 2013).

Because human nutrition is directly linked to that of plants, the production of nutritious foods requires a balanced content of essential macro-, meso- and micronutrients. Macronutrients are required in large amounts and include nitrogen (N), phosphorous (P) and potassium (K). The meso- or secondary nutrients include calcium (Ca), magnesium (Mg) and sulfur (S). Micronutrients or trace elements are required in smaller amounts and include iron (Fe), zinc (Zn), copper (Cu), manganese (Mn), boron (B), chloride (Cl), molybdenum (Mo) and nickel (Ni). Soils are the main source of MNs for plants, and the soil bioavailability of MNs is influenced by many soil and other environmental factors (Panuccio et al., 2009).

Once fertilizer-MNs are added to soils, the trace elements react rapidly to form chemical precipitates, or interact with clay colloids and the organo-mineral matrix of soils, rendering them unavailable for synchronized uptake by plants during crop growth. Thus, the crop fertilizer-MN use efficiency (MUE) is low, <5%. Over the past two decades, experts have realized that current conventional agronomic technologies would not be able to enhance farm productivity any further. The agricultural applications of bio-nanotechnology has the potential of breaking yield barriers through pests and disease surveillance and control, greater understanding of molecular level mechanisms of host-parasite interactions, the development of next-generation pesticides and their carriers and also by improving the efficiency of nutrient use by crops (Sekhon, 2014). Nanotechnology is the manipulation of matter at the atomic or molecular level, usually at scales <100 nm. Nanotechnology promises to improve current agricultural practices through the enhancement of management and conservation of inputs in crops, animal production and fisheries (Thornton, 2010). Research work conducted in the last two decades has focused on metal nanoparticles (NPs), such as ZnO and CuO, metal chelates and controlled released fertilizer-micronutrients. There are incomplete and conflicting published reports about the effects of NPs and other commercial sources of MN on MUE. It is therefore paramount to understand how novel technologies may increase MUE and food quality, by tackling MN deficiency in soil-crop systems.

1.1 Objectives

This report reviews the current knowledge on conventional MN fertilizers and provides new insights on recent knowledge, novel materials, products and nanotechnologies in MN-fertilizers. The review identifies knowledge and technology gaps existing in the areas of MN delivery and crop use efficiency; and offers a new vision involving scientific and technological concepts, with a special emphasis on increasing the MUE of Zn, Fe, Mn and Cu by crops.

2 Importance of micronutrients in crops

2.1 Micronutrients and metabolic processes

Micronutrients play a significant role in plant growth and metabolic processes associated with photosynthesis, chlorophyll formation, cell wall development and respiration, water absorption, xylem permeability, resistance to plant diseases, enzyme activities involved in the synthesis of primary and secondary metabolites, and nitrogen fixation and reduction (Adhikary et. al., 2010; Vitti et al., 2014). Accordingly, Zn, Fe, Mn and Cu are involved in many processes controlling plant growth, and their content in grains and leaves determine the quality of food consumed by humans and animals. Micronutrient deficiencies in plants lead to reduced yields and, in severe cases, to plant death. Among the micronutrients, Zn deficiency is the most detrimental to crop yield, especially in calcareous soils.

2.2 Functions and deficiency symptoms of MNs in plants

This sub-section briefly provides a few examples of key functions and physical deficiency symptoms for Zn, Fe, Mn and Cu. When the amount of MNs removed by crops exceeds the amount supplied by soils and fertilizers, the result is MN deficiency in food products. MN deficiency in crops is reflected by different symptoms (Adhikary et al., 2010; Das, 2000) expressed in different forms, depending on the specific element (Marschner, 2012). Some of the specific functions and deficiency symptoms for the four MNs have been reported widely. In general, the published scientific literature indicates that MNs tend to be immobile in plants; however, MNs such as Fe are taken up from the soil solution and transferred by the plant internally for storage in grain (Figure 1). For more in-depth information on functions and deficiency symptoms of all MNs in plants, the reader is invited to consult publications by Barker and Pilbeam (2006) and Marschner (2012).

2.2.1 Zinc functions and deficiency symptoms

As a co-factor, Zn is involved in enzyme systems and metabolic reactions and is necessary for the production of chlorophyll and carbohydrates. Zn deficiency results in discoloration of the foliage and growth abnormalities, such as a drastic reduction in leaf area and necrosis of upper foliage. Zn is not generally translocated within the plant, but is partly mobile in wheat and barley; hence, the first symptoms of deficiency appear on the younger leaves. Deficiency symptoms differ among plant species, but they can be corrected by Zn fertilization (McKenzie, 2001).

2.2.2 Iron functions and deficiency symptoms

Fe is a catalyst to chlorophyll biosynthesis and acts as an oxygen carrier and aids in respiratory enzyme systems. Like Zn, Fe is not efficiently translocated within the plant, so deficiency symptoms first show up on younger leaves. The classic Fe symptom is interveinal chlorosis, a pale green to yellow leaf with sharp distinction between green veins and yellow interveinal tissues. The symptoms of Fe deficiency can be confused with those of Mn. In general, Fe deficiency is common for fruit trees, shrubs, ornamentals and strawberries, especially when grown in high pH and calcareous soils. Other factors, like very high P, cold and wet conditions, high lime and genetic differences in crops, may result in the expression of Fe deficiency symptoms (McKenzie, 2001).

2.2.3 Manganese functions and deficiency symptoms

Mn activates several important metabolic reactions, aids in chlorophyll synthesis, in photosynthesis, accelerates germination and maturity and increases the availability of P and Ca. Manganese is not translocated in the plant, so symptoms first appear on younger leaves, as with Zn and Fe; however, there appears to be some translocation of Mn in oat (Vose, 1963). Inadequate Mn results in chlorosis of new leaves and slower growth. Yellowing between the veins is the main deficiency symptom and can be confused with Fe deficiency. Gray speck of oat is the most common symptom, which appears in interveinal areas. Severe Mn deficiency in oat can cause significant loss in yield (McKenzie, 2001).

2.2.4 Copper functions and deficiency symptoms

Cu is involved in several enzyme systems, cell wall formation, electron transport and oxidation reactions. Deficiency of Cu results in slow growth, spotted and deformed leaves. Crop cultivars can respond differently to soil Cu deficiency. For example, wheat, barley, oats and canary seed are more affected than canola, rye, flax and forage grasses to soil Cu deficiency. Sandy soils in the Black and Gray soil zones and peaty soils are most likely to be deficient in Cu. Where Cu and Zn are both deficient, they both must be applied to obtain a yield increase. Cu deficiency usually occurs in irregular patches within fields (Jones, 2012).

2.3 Micronutrients removal by crops

McKenzie (2001) demonstrated that under adequate MN supply in soils, the total amounts of Fe, Zn, Mn and Cu removed in grain, straw, tubers, vines and pods by different crops range from 1.2 to 2.7 kg/ha. Among the seven reported crops, maize (*Zea mays*) removes large amounts of MNs. On average, Fe and Mn were removed in similar quantities (~0.5 kg/ha), and their removed amounts were more than double those of Zn (0.22 kg/ha) and Cu (<0.1 kg/ha). In comparison, most crops remove macronutrients, such as N and P, from 10 to 1,000 times greater amounts. For normal plant growth, the tissue concentrations of the four MNs range from 0.1 to 2 μmol/g shoot dry weight (Kirby, 2012).

2.4 Micronutrients and crop yield

There are numerous examples of the positive effects of MN addition to crops growing in MN-deficient soils. Information on the effects of MN fertilizers on crop yield and quality, as well as their interaction with macronutrients, is available (Malakouti, 2007; Malakouti et al., 2005; Malakouti et al., 2000). The use of fertilizer-MNs in crops can increase grain yield up to 50% as well as increase macronutrient use efficiency (Malakouti, 2007). Published information reporting agronomic performance data from different countries, soils and climate indicates that MNs applied alone or together with macronutrients have a significant effect on crop yield and MN content in grain (Imtiaz et al., 2010). Thus, when MNs are in short supply, the growth and yield of crops is severely depressed (IPNI, 2014). The exact effects of applying MN alone or in combination with NPKS or with each macronutrient to different crops in MN deficient soils and specific climate conditions need to be better established.

Table 1 shows the relative yield increases for various crops as influenced by the soil addition of MNs. 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 MN were added together to a soil planted with wheat (Malakouti, 2000). 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% (Adhikary et al., 2010; Welch, 1986; Moraghan, 1980). In general, rice, maize, sorghum bean and fruit trees are among the most sensitive crops to inadequate supply of the four MNs. Barley, cotton, lettuce, potatoes and soybean have a medium level of sensitivity to MN deficiency, and grasses, asparagus, wheat and oat are among the least sensitive (Martens and Westermann, 1991).

Table 1. *Effect of micronutrient-fertilizer application on relative grain yield increases*[a]

Micronutrient Added	Crop	Relative Yield Increase (%)	Control Treatment	Country-Reference
Zn	Rice	12	No Zn[b]	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	Malakouti, 2000

a. From Imtiaz et al., 2010; Malakouti, 2000.
b. The specific use of NPKS not reported.

2.5 Interactions of micronutrients with macronutrients in plants

The interaction of a MN with a macronutrient when added together results 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. So far, important efforts have been made to improve macronutrient (N, P, K, S) and MN (Zn, Fe, Mn, Cu) nutrition in crops, based on determining how plants respond to deficiencies of these nutrients at the agronomic, physiological and molecular levels. This section updates earlier published reviews on MN and focuses attention on crop yields and molecular control of the interactions between micro- and macronutrients as they have important implications to novel fertilizer technology.

Macronutrient fertilizers of N, P and K and MN-fertilizers of Zn, Fe, Mn and Cu can have significant effects on the accumulation of nutrients and yield in edible plant products. In general, both solid granular and liquid macronutrient fertilizers are commonly used as “carriers of micronutrients.” The mixing 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; and (e) mixing MN with fluid fertilizers has become a popular method of application, although it is necessary to check for compatibility of mixing and suspension.

Micronutrient-N interactions occur frequently, and mostly synergistically, in crops. 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 grain yield increases (i.e., 30% increase) of rice (Roshan et al., 2011). In a separate study, increasing levels of fertilizer-N addition increased the uptake and storage of Fe, but not of Zn, in rice grain (IRRI, 1999). In general, MN-N interactions stimulate plant growth. However, such stimulation may cause MN deficiency under limited supply of the microelements in soils (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 from fertilizers can interact 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 P at 180 mg P kg^{-1} to a siliceous and ferruginous sand matrix decreased the concentration of Zn in clover (Loneragan et al., 1979). P can also interact with Fe to decrease their plant uptake by forming precipitates of Fe-phosphates near the root surface (Murphy et al., 1981) or in the grain. Micronutrients are also stored in a few cellular structures of the grain in cereals. For example, Figure 1 shows that Fe is stored as granules in the aleurone and scutellum structures of wheat and oat grains where it is usually complexed by phytic acid, thereby reducing its bioavailability in food.

High concentrations of P (>1000 kg/ha) can induce Cu deficiency in citrus and avocados and in common crops such as corn, beans, tomatoes (Bingham and Garber, 1960). Verma and Minhas (1987) investigated the Zn-P interaction on wheat and its residual effect on maize. 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. Conversely, 20 kg ha^{-1} of Zn added in the absence of fertilizer-P resulted in a significant increase in maize grain yield planted in a silty clay loam soil of India. In a different study, the application of Mn and Zn (among other MNs) in combination with 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).

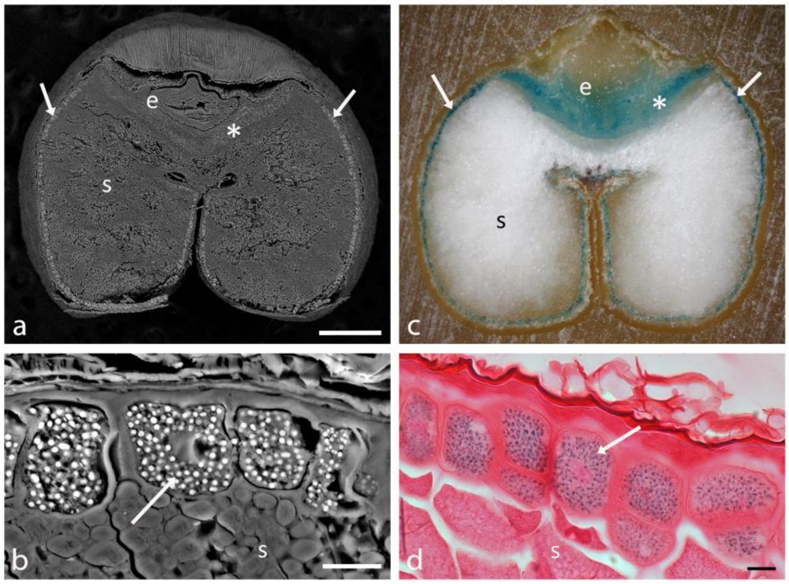

Figure 1. *Micronutrients in cereal grains*

*(a,b) Scanning electron micrographs of transversely cut wheat kernel, using back scattered electron detection to demonstrate areas containing elements with higher atomic numbers (e.g., minerals) in the aleurone layer. Minerals, including calcium and iron, are known to be complexed with phytic acid in "aleurone granules" in the aleurone layer and also in the scutellum region of the embryo. (a) bar = 500 µm; (b) bar = 20 µm. (c) Surface of transversely cut wheat kernel embedded in resin, stained with Perl's stain to demonstrate ferric iron in the aleurone layer and scutellum. (d) Thin section of oat stained with Perl's stain to demonstrate ferric iron in the aleurone layer (bar = 10 µm). Arrows, aleurone layer; e, embryo; *, scutellum; s, starchy endosperm. Scanning electron microscopy images courtesy of D. Chabot, AAFC-ECORC. Images of ferric iron staining in wheat and oat courtesy of S.S. Miller, AAFC-ECORC. Figure prepared by S.S. Miller.*

Potassium is essential for plant metabolism, and its cationic species, K^+, is very dynamic in the soil solution. From a plant physiological viewpoint, K is considered close to N in importance. For example, K is key in the synthesis of organic acids in the Krebs cycle during carbohydrate metabolism. Evidence is also emerging from molecular biology studies that K may play a regulatory role in plant stress responses (Ashley et al., 2006; Wang and Wu, 2010). In general, addition of K-fertilizer appears to decrease the uptake of Fe, but increases that of Zn, Mn and Cu. A synergistic relationship exists between K and Fe and Mn, elements that play a fundamental role in photosynthesis, chlorophyll synthesis, in N metabolism and oxidation-reduction reactions, among others (Ranade-Malvi, 2011). Humans, plants and animals have specific ratios of nutrients, such as K/Na, that are required for balanced nutrition (Römheld and Kirkby, 2010). This ratio of elements is often more critical than the actual concentration of the individual elements. Nutrient balancing in micronutrients is important and yet more difficult than balancing between macronutrients (Ranade-Malvi, 2011).

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, potatoes fertilized with K reduced Fe deficiency symptoms (Bolle-Jones, 1955). It is also known that K, Ca and Mg regulate Mn absorption in plants. The latter cations either promote the 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, the interactions between K and MN have not been well characterized.

2.5.1 Molecular aspects of micronutrient interactions and deficiencies

Under soil inorganic P (Pi) or Zn deficiency, root architecture changes and increases its capacity for nutrient import (Jain et al., 2013). A neglected interaction between Pi and Zn (and other MN) nutrition in plants is the interconnection between the homeostasis of these two nutrients occurring in many crop species. These interconnections have been summarized as follows: Zn-deficient plants overaccumulate P in the shoot and, conversely, Pi-deficient plants overaccumulate Zn in the shoot (Bouain et al., 2014; Khan, 2014). Also, in most soil-plant systems, symbiotic associations are formed between plants and mycorrhizal fungi (Schachtman et al., 1998), where mycorrhizae play an important role in the acquisition of P for the plant (Smith and Read, 2008), while facilitating the transport of Zn and other MNs from the soil into the plant (Chen et al., 2003). Numerous genes control and regulate the internal plant transport of P and Zn/Fe and other macro-micro nutrient interactions (Nussaume et al., 2011; Sinclair and Kramer, 2012; Hindt and Guerinot, 2012). In spite of the current progress, the molecular basis of the P-Zn, P-Fe and of other macro- and micronutrient interactions in plants remains poorly understood in both mycorrhizal (Watts-Williams et al., 2013) and non-mycorrhizal crop species (Khan et al., 2014).

Under Fe limitation, plants employ a set of responses to boost Fe mobilization and uptake from soil. Fe absorption by plants is based on two strategies (Kobayashi and Nishizawa, 2012). Non-grass crops like bean use the first strategy, which is based on the reduction of Fe via the release of protons through the root membrane to acidify the surrounding environment and solubilize Fe, and also via the reduction of Fe^{+3} to Fe^{+2} by ferric reductase present in root membranes, an enzyme that also catalyzes the reduction of Cu (Santi et al., 2005; Kim and Guerinot, 2007). One unit drop in pH increases the solubility of Fe by 1,000-fold (Guerinot and Yi, 1994). Graminaceous plants use the second strategy involving the chelation of Fe by phytosiderophores (PS), such as mugineic acids, which are exuded by roots to bind Fe with high affinity for plant uptake (Conte and Walker, 2011). The chelated complex of Fe+3-PS is transported into the root through a family of transporters, named YS1 in maize or OsYSL15 in rice (Curie et al., 2009; Lee et al., 2009; Inoue et al., 2009).

Published information indicates that the interactions of MN with macronutrients create positive and negative effects on the agronomics of crop growth and yield. The reasons for different responses to the micro-macronutrient interactions remain largely unknown. However, recent published information indicates that the homeostasis of Zn and Fe (and likely other MNs) is highly regulated by complex processes in plants. Critical to our knowledge of Zn and Fe homeostasis in plants is determining how MNs are sensed and how the associated components of signal networks are transmitted and integrated into a cell response. The evidence of a Fe sensor in plants and a summary of recent findings on hormones and signaling molecules that contribute to Fe deficiency are discussed by Hindt and Guerinot (2012). Nevertheless, despite the fundamental importance, the molecular and chemical basis and biological significance of these interactions remain largely unknown, especially the mechanistic processes (Bouain et al., 2014; Hindt and Guerinot, 2014). Thus, in the future, it will be essential to elucidate the homeostasis interconnections between macro and MNs, as soil-plant homeostasis appears to be an important area of knowledge gap responsible for the shortcomings of current agronomic practices. Reducing this knowledge gap by developing novel nanotechnologies offers opportunities to increase MUE by crops for greater food security and a sustainable agriculture.

3 Soil micronutrient deficiency

Two main reasons help explain MN deficiency in cultivated soils of the world: (1) Farm soils have been cropped over long-periods (i.e., hundreds to thousands of years). In comparison, few long-term research plots have a soil-crop management and production history of less than two hundred years in which to base agronomic decisions. (2) As higher yielding varieties and hybrids have been developed starting last century, crop yields and nutrient removal through harvest have continued to increase, but inputs of fertilizer-MNs have not kept pace with their rates of crop removal. Sillanpää (1990) published a detailed evaluation on the effects of MNs on yields of economically important food and cash crops in 15 countries. This section briefly highlights the known distribution of MN deficient soils at the world level by key countries, with a specific focus on Asia and Africa. Our literature review and discussion with soil experts show the lack of adequate chemical information in most national soil databases to better analyze MN deficiency at regional or local level. Yet, corrections of MN deficiency using soil-plant biofortification strategies must be implemented at the local level for balanced crop and food nutrition (Patel and Singh, 2010).

3.1 Soil MN deficiencies in the world

As key evaluation of global soil MN deficiency has focused on Zn and few other trace elements (i.e., Alloway, 2008a,b), this report will provide a summary of the geographical distribution of Zn deficiency at the global and country level, with a special focus on Africa, India and China (Figures 2, 3, 4). Deficiencies of other soil MNs are assumed to follow a similar pattern as shown by Zn. For instance, it is estimated that 40% of the world's cultivated soils is low in available Fe (Shorrocks, 1984). Soil MN deficiency is widespread in soils of highly populated countries, in calcareous soils with high pH, low organic matter, salt stress, continuous drought and high bicarbonate content. Imbalanced application of fertilizers in semi-arid and desert areas, but also under irrigation contributes to widespread MN deficiency. Deficiencies of Zn and other MNs have been reported in soils of all five continents (Alloway, 2008). In Africa, widespread Zn deficiency extends from the sub-Saharan region all the way to the southern tip of the continent. India and China present widespread Zn, B and Mo deficient soils, affecting approximately 50% of their soils. In China, the order of importance for potential deficiency was reported to be: Zn 51% > Mo 47% > B 35% > Mn 21% > Cu 7% > Fe 5% (Yang et al., 2007; Zou et al., 2008). In India, analysis of 14,863 soil samples from all over the country showed that 49% of soils were potentially deficient in Zn, 33% in B, 12% in Fe, 11% in Mo, 5% in Mn and 3% in Cu (Singh, 2008). Significant deficiencies are also known to exist in soils of Turkey, Iran and Pakistan and Australia. In Europe, countries of the Southern region present medium deficiencies of soil Zn, and widespread Zn deficiency is noted for western France. Micronutrient deficiencies reported for soils of the world are paralleled by level of associated element deficiency risks reported for human health around the world (section 1.3.1.8).

In the Americas, the Northern Great Plains of Canada and the USA have lower frequency of soil MN deficiency relative to other regions of the world, due the occurrence of geologically young soils (<10,000 years old) and a temperate climate with low precipitation that result in slow rates of weathering. However, Zn deficiency extends from cultivated land in the northern USA-Canada border all the way through Central and few countries of South America. In Brazil, a trace element geochemistry study in Oxisols and Ultisols found that Zn, Cu, Mn and other lower valency cations are leached and depleted, while tri-, tetra- and pentavalent elements accumulate (Márques et al., 2004; Leon et al., 1985). A study conducted in the Cerrado soils of Brazil showed that the availability of Fe, Cu and Mn in a pasture related to the presence of crystalline iron and pH in water. Available Zn and Mn in

Cerrado soils appear as the most frequent limiting MN in pasture and other crops (Siqueira Vendrame et al., 2007; Teixeira et al., 2004).

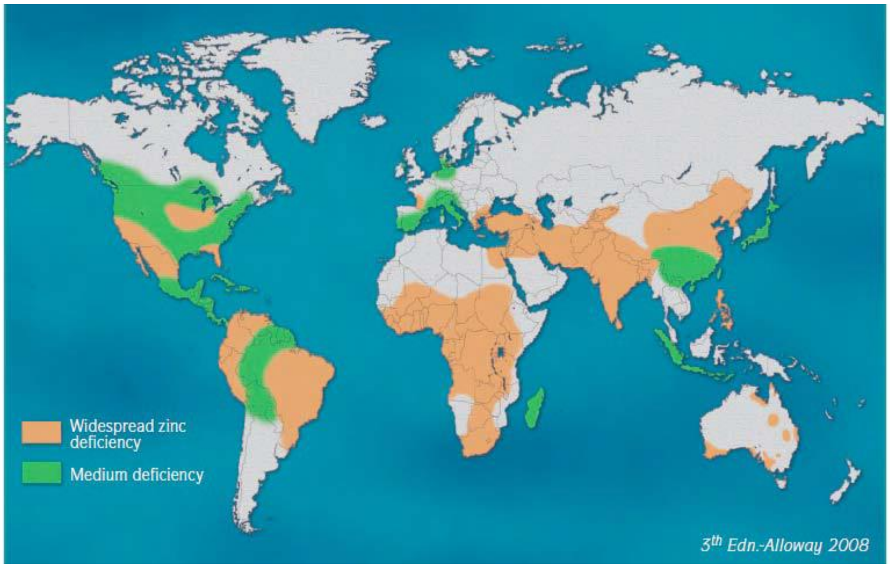

Figure 2. *Areas with Zn deficiency in the world (from Alloway, 2008b)*

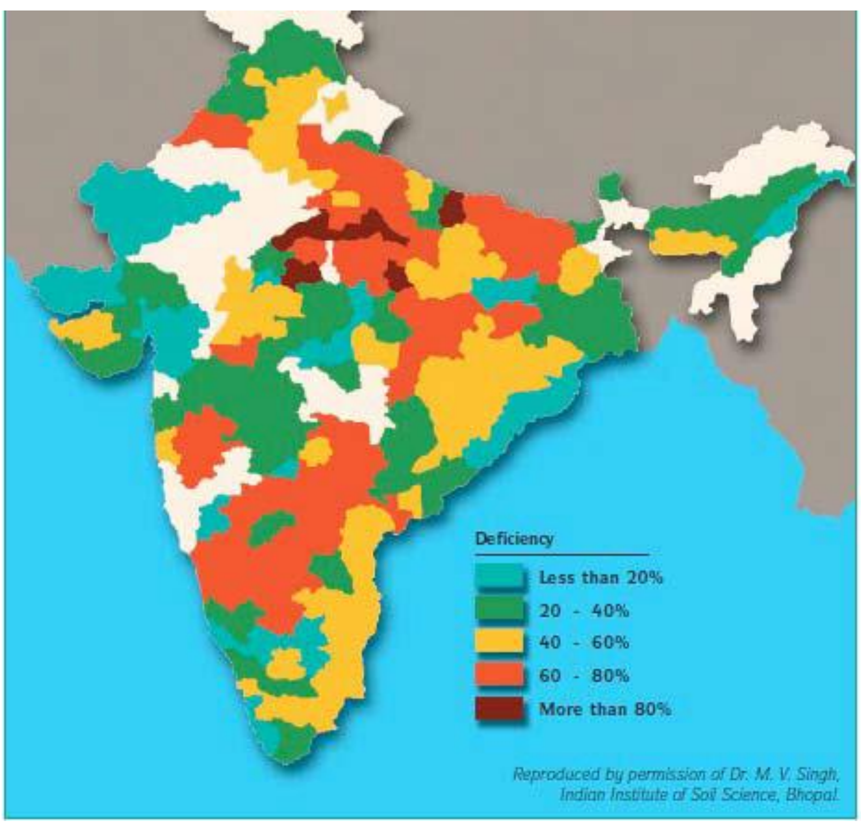

Figure 3. *Soil zinc deficiency in soils of India (from Alloway, 2008b)*

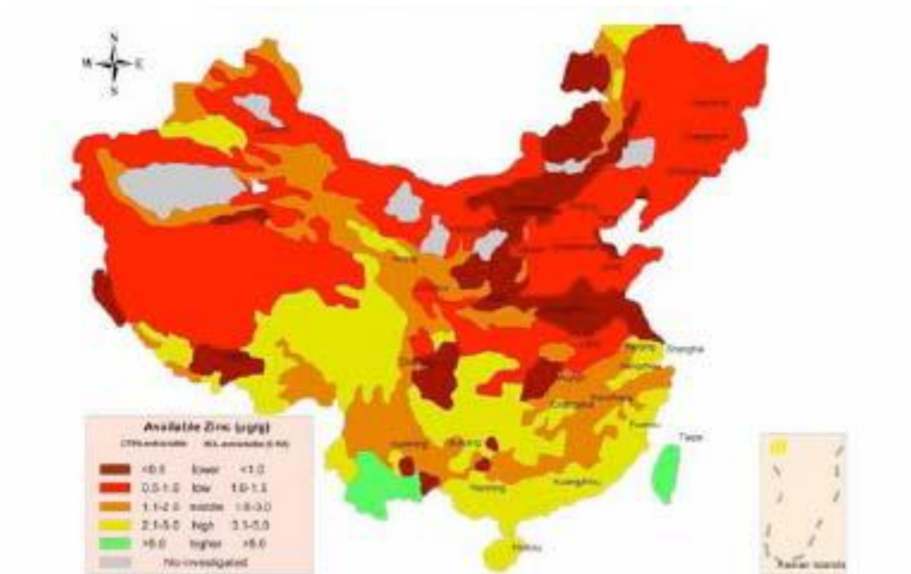

Figure 4. Soil zinc deficiency in soils of China (from Alloway, 2008b)

3.2 Total versus bioavailable micronutrients

Information presented in Figures 2, 3 and 4 on total Zn deficiency at the country and global scales are useful for policy and decision making processes. For a better understanding of nutrient deficiency in plants, the global, large scale (1:1,000,000 scale) needs to be complemented with the determination of the spatial distribution of plant available soil MNs and regional patterns of plant MN deficiencies. In addition, the relation of MNs with soil parent materials, genesis and surficial geology, and the consequences of land disposal of MN wastes become important information in the evaluation (White and Zasoski, 1999; Singh et al., 1987). Overcoming MN deficiency in soil and plants requires the acquisition of knowledge on the bioavailable content of MN in soils and plants and the application of remedial measures at the local level. Education of field agronomists and crop advisers increases the awareness and ability to look for and diagnose possible MN deficiency (PAIS, 2012). At the farm level, soil and foliar chemical tests to determine the content of bioavailable MN are useful tools to diagnose and correct their limitations during crop growth. Use of chemical extractants such as diethylenetriamine penta-acetic acid + triethanolamine (DTPA-TEA) and the Mehlich extractant solution for determining soil MN content have proven to be useful and reliable for predicting the response of crops to Zn and other MN fertilization and for determining critical levels of these nutrients for cereal crops (Sharma et al., 2006).

4 Commercial fertilizer-micronutrient sources

This section briefly discusses the main types of commercial fertilizer-MNs. The three main classes of commercial fertilizer-MNs are inorganic, synthetic chelates and organic. The inorganic sources include water-soluble sulfate salts of Fe, Zn, Cu and Mn. Other inorganic products comprise of commercial oxysulfates (i.e., mixture of ZnO and $ZnSO_4$) and oxides of MN that are less readily available to plants relative to sulfate salts. Synthetic chelates of ethylenediaminetetraacetic acid (EDTA) consist of a ring-type structure that binds Fe, Zn, Mn and Cu or other elements within its structure. Organic acids, such as citric acid, are also used to chelate MNs. Chelated MN sources stay available for plant uptake over long periods by preventing rapid reactions of the elements with soil clay colloids. Other forms of organic-MN complexes include animal manures, which, when applied to cultivated soils, constitute a method of recycling macro-and MN added to animal feeds in cultivated land. Finally, other forms of MN involve phosphites, carbonates and nitrates, but these are seldom used in crop production. For further details on the plant availability and solubility, chemical forms, concentration and agronomic use of fertilizer-MNs, the reader is referred to excellent publications by Havlin et al. (2013), Gowariker et al. (2009) and Stewart et al. (2005).

4.1 Production and demand of MN-fertilizers

Depending on the element, the total annual world production of Fe, Zn, Cu and Mg range from a few million metric tons to a few billion metric tons. In 2013, the total production of Fe ore was 2,950,000 x 10^3 metric tons, that of Zn was 11,200,000 metric tons and that of Cu was 17,900,000 metric tons (U.S. Geological Survey [USGS], 2013). Similarly, the world production of Mn was 31,200,000 metric tons in 2009 (USGS, 2009). In the last six decades, MN production increased steadily and linearly due to increased industrial demand (IHS Inc., 2014; USGS, 2013). The demand of MN in agriculture accounts for only a small percentage (<4%) of the total element production. Estimates made by IHS (2014) indicate that the global demand for Zn-derived chemicals (including fertilizers) will be 1.8 million metric tons by 2018, of which 400,000 metric tons (or 22%) will be used in agriculture. Depending on the market supply-demand of the four elements, there is a high risk that demands from agriculture will be outcompeted by industrial demand based on its greater purchasing power (PAIS, 2012). Unfortunately, global and country data on specific fertilizer-MN production and consumption is not easily available in the public domain.

4.2 Fertilizer-MN use efficiency (MUE)

Micronutrient use efficiency by crops can be defined as the yield of biomass per unit input of fertilizer or nutrient content (Hawkesford et al., 2014). Alternatively, MUE can be defined as the relative proportion of fertilizer-MN added to the soil or leaves that is absorbed by crops. In this report, we define MUE as the amount of the added fertilizer-MN that ends up in the crop, as biomass yield may be influenced by other factors, such as plant genetics and weather. The MUE also is associated with the transport, usage and storage within the plant and indirectly with MN fate in the environment.

4.2.1 Fertilizer-MN use efficiency (MUE) – soil addition

Iron, Mn, Zn and Cu rapidly react in soil components via oxidation and/or precipitation. Applying these nutrients directly to the soil is inefficient because in soil solution they are present as positively charged metal ions and will readily react with oxygen and/or negatively charged hydroxide ions. Accordingly, the MUE of inorganic MN fertilizers ranges from 2.5% to 5% (Singh, 2008; Samra, 2006). Soil applied MN reach root via diffusion or root interception and move about 0.1 inches during the growing season. Higher rates of addition are required when MN are broadcasted relative to band application (Kaiser, 2011). An important practical issue associated with MUE deals with the application of small amounts of MN (from a few g to <5 kg per hectare) resulting in large uneven spatial distribution of the elements. Thus far, chelated fertilizers appear to help improve MUE (Liu et al., 2012b). Low MUE increases crop production costs for farmers and adversely influences their content in crops, in addition to its negative effect on environmental health. In general, soil applied Fe is ineffective except for Fe-sequestrine (Imtiaz et al., 2010).

4.2.2 *Fertilizer-MN use efficiency (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. The leaf cuticle is the first major obstacle in that chain of event. For Fe, Zn and Mn applied either in chelated or sulfate-salt form, an extensive nutrient fixation by cuticle may occur at the point of application (Ferrandon and Chamel, 1988). Foliar absorption of these three elements 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). A number of studies where different fertilizers had been applied foliarly at various rates did not include measurement of MN concentration in grain (see Berg et al., 1993; Fawzi et al., 1993). Information for increasing MUE via foliar fertilization of macro 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 soil or foliar application of Zn. The foliar Zn application was more effective in a wheat crop than a rice crop (Srivastava et al., 2014). On the other hand, foliar application of Mn with glyphosate results in antagonistic effects and reduced their effectiveness in the plant (Bott et al., 2008). Ferric reductase is required for iron absorption in plants. Glyphosate reduced the activity of ferric reductase in plants by 50% within six hours of application (Ozturk et al., 2008). The repeated use of glyphosate appears to tie up the MNs in the plant as glyphosate acts as a chelating agent for Ca, Mn, Mg, Fe and other metals such as Al (Cakmak et al., 2009). The latter type of chelation reaction appears to have important implications to plants and human health (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 upper (adaxial) surface and not on the lower (abaxial) 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 ratio ~0.73 (Teare et al., 1971). Rain on leaf surface or rapid leaf drying affect the absorption of MNs in foliar applications (Kaiser, 2011).

5 Dynamics of MNs in soil-plant systems

5.1 Soil factors and chemical species of micronutrients

In soils, the chemical interactions important in the partitioning of MN are those species bound to soil surfaces (i.e., organic and inorganic), to the soil solution phase and those allocated to the plant pool (Allen, 2002). Important factors controlling partitioning of MN between soil and soil solution include pH, inorganic ligands (e.g., HCO_3 and Cl), organic ligands (e.g., labile soil organic matter, plant or microbially produced ligands) and competing cations such as Ca^{+2} and excluded ligands. Other soil factors involve element concentration, organic matter content, redox conditions, soil moisture status, microbial activity, concentrations of other trace elements, the levels of macronutrients and also climate (Guala et al., 2010; Panuccio et al., 2009; Schulin et al., 2008; Alloway, 2008b). Soil pH affects exchangeable Fe, Mn, Cu and Zn similarly (Imtiaz et al., 2010). Several soil properties influence the bioavailability of iron, including high soil pH, high bicarbonate content, plant species and abiotic stresses (Takáč et al., 2009). Plants typically utilize iron as ferrous iron (Fe^{+2}). Ferrous iron can be readily oxidized to the plant-unavailable ferric form (Fe^{+3}) when soil pH is greater than 5.3 (Morgan and Lahav, 2007).The availability of MNs to plants is also influenced by both parent material and soil development, but soil properties can operate differently for different trace elements. Organic complexes can be important sources of slow MN release for plant uptake especially during soil organic matter decomposition (McKenzie, 2001). Only a small proportion of the total soil MN content is made available for plants. Uptake of metal by soil organisms may be physiologically moderated by pH and competing cations such as Ca^{+2}. Some inorganic and organic MN complexes may be directly taken up, while other ligands may compete with soil organisms for the MN (Allen, 2002).

The ions of Fe, Zn, Cu and Mn are transported from soil solutions into the plant roots after they form chelates with labile organic compounds, which also helps intracellular mobility. Zinc is immobile in soil and its deficiency may occur on calcareous, high pH, sandy texture, high P and eroded soils. Zinc deficiency usually shows up under cool, wet conditions in early spring when root growth is slow. Poorly drained and eroded soils may also be Zn deficient. Zinc is not generally translocated within the plant (but is partly mobile in wheat and barley). Under soil aerobic soil conditions, Fe^{+2} is oxidized to Fe^{+3} that has a low water solubility resulting in precipitates of FeO, FeOH and Fe-phosphate, thus making Fe less mobile in soils and plants. As with Zn, factors like very high soil P content, high soil water and lime contents, cold temperatures and genetic differences in crops may result in the expression of Fe deficiency symptoms (Marschner, 2012). Manganese tends to be immobile in soil and plants, although there is intracellular translocation of Mn in oat (Vose, 1963). Peat soils deficient in Mn with a high pH and/or good drainage, may respond to Mn fertilization. Copper also tends to be immobile in soil, with its solubility and plant availability highly dependent on soil pH. Copper solubility increases approximately 100-fold for each unit decrease in soil pH. Sandy soils are most likely to be deficient in Cu; Cu deficiency usually occurs in irregular patches within fields.

Unlike total concentration of MNs, indices of their bioavailability can change overtime because of changes in the factors that control phytoavailability (Allen, 2002). Under MN deficiency, plants secrete phytosiderophores (PS) that chelate Fe and Zn into the soil solution from where they are taken up by plants. The uptake rate of PS-Fe and PS-Zn is 100 and 5 to 10 times higher than that of free Fe and Zn, respectively (Dotaniya et al., 2013).

Two soil properties that deserve attention when examining the dynamics of soil MNs are soil pH and soil organic matter.

5.1.1 Soil pH

Soil pH is the soil property that most influences MN availability, and for all but Mo, the higher the soil pH, the lower the plant availability (Imtiaz et al., 2010; Marschner, 2012). Liming can prevent Mo deficiencies. In basic soils, the acidity caused by the addition of many fertilizers or from small quantities of elemental sulfur to a portion of the root zone can often provide adequate MN to plants. Solubility of Fe decreases a thousand-fold for each unit increase in soil pH in the range 4 to 9 (Lindsay, 1979), and consequently, most Fe deficiency occurs on calcareous soils. The bioavailability of Mn, Cu and Zn decreases 100-fold for each unit increase in soil pH (Imtiaz et al., 2010). At low pH, soil humic substances (HSs) for aggregates and complexes with metals via the carbonyl and nitrogen-containing groups from the HS (Alvarez-Puebla et al., 2004; Frenkel et al., 2000). In the medium to long term (10 to >15 years), the addition of ammonium-based fertilizers, such as ammonium sulfate, decreases soil pH with potential increases on MN availability.

5.1.2 Soil organic matter (SOM)

In general, the reaction of MNs, such as Cu, Fe, Zn and Mn with SOM significantly affects their bioavailability (Stevenson, 1991; Shuman, 1988). For example, Cu reacts with SOM to form very stable complexes with carboxylic, carbonyl and phenolic groups. Due to these stable complexes Cu deficiency is often associated with organic soils. Reaction of Zn with SOM is also important in providing bioavailable Zn, but the strength of these bonds are not as strong as that of Cu. The importance of the chemical quality of SOM and HS on the content and bioavailability of MNs is largely unknown. Chen and Kenny (2007) indicated that the complexation of metal ions with functional groups of soil HS can easily result in HS-metal aggregation. The general order of affinity of heavy metals and metalloids for organic matter is as follows: Cu^{2+} > Hg^{2+} > Cd^{2+} > Fe^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+} > AS(V) > AS(III) (Park et al., 2011).

5.2 Plant uptake and transport of micronutrients

Most of the MNs are taken up mainly as ion-organic chelates from the soil solution but also as ions. For example, Zn^{+2}, Fe^{+2}, Fe^{+3}, Mn^{+2} and Cu^{+2} are the predominant ionic forms taken up by plants. MNs are acquired from the soil solution by plant roots via diffusion or active transport (Grotz and Guerinot, 2006; Briat et al., 2007). MNs of Fe, Zn, Mn and Cu are transferred form the soil solution through the root or leaf cell membranes into the xylem for transport, utilization, internal recycling and storage in the plant (Marschner, 2012). The uptake of mineral elements by plant roots and their subsequent transport within the plant have been the subject of many studies and publications (Karley and White, 2009; Miller et al., 2009; Miwa et al., 2009; White and Broadley, 2009; Mengel et al., 2001). Some characteristics that may cause MN deficiency-induced stress in plants include morphological structure such as scattered leaf stomata and imperfect and fewer xylem vessels of small size. Widespread infestation of various diseases and pests and also low activation of phytosiderophores are also important factors (Alloway, 2008b). Under soil MN deficiency, plants have a self-regulated mechanism that secretes the PS to mobilize MNs into roots. PS production is a general response of plants to Fe and Zn deficiency. The uptake rate of PS-Fe and PS-Zn is 100 and five to 10 times higher than that of free Fe and Zn (Dotaniya et al., 2013).

6 Novel technologies for fertilizer micronutrients

Most fertilizer technologies are close to 100 years old. The use of enhanced efficiency fertilizer-N products in many countries of the world has led to a modest 5-7% increase in yield and 8% in N uptake (Linquist et al., 2013). It is also known that the fertilizer-MUE efficiency is low (<5%) when added to cropped soils. The authors of this report did not find exact quantitative information on MUE when MN-fertilizers are applied to plant foliage. The addition of conventional fertilizer-MNs to crops according to soil and plant tissue tests resulted in small increases of nutrient use efficiency (White and Brown, 2010). Low MUE adversely influences their elemental content in crops, increases crop production costs to farm producers and possesses adverse risks to the environment.

Chapter 3 reviewed what is considered to be old and conventional commercial fertilizer-MNs, such as soluble fertilizer salts and chelated products. In this Chapter, we discuss the use, fate and effects of novel products and technologies for MN encapsulation, nanomaterials (NMs), nanoparticles (NPs) and nanodevices mostly in plants and a few in soils. Subsequent chapters (6 and 7) examine the potential of nanobiotechnology to enhance MUE and strategies that result in the design and development of efficient new nanofertilizer delivery platforms for use at the farm level. In these chapters, published information has been summarized and grouped according to the nature, composition and functional capacity of novel products to control the release rate of MNs. This report provides selected information published in the areas of nutrient delivery, crops and food products, medicine and pharmacy that may be useful in enhancing the MUE of fertilizer and food quality. We emphasize here that occasionally the boundary for separating the new and old technologies and products is somewhat blurry, as new advances are frequently based and linked to past technologies, products and knowledge.

6.1 Controlled-release of micronutrients

6.1.1 Micro-encapsulation and low solubility products

This section focuses on products and technical aspects of controlled-release microencapsulation and low water solubility products that may help increase MN bioavailability in crops and humans. To date, little work has been published on microencapsulation of fertilizer-MNs. Published information exists, however, for the agronomic, environmental and polymer efficacy of encapsulated macronutrient sources, such as urea (i.e., Blackshaw et al., 2011; Venterea et al., 2011; González et al., 2015). Microencapsulation of MNs produces tiny capsules (i.e., µm diam.) that have several nutritional advantages: (1) enhancement of the contact surface for absorption and, thus, increase in bioavailability; (2) low cost of production; and (3) biodegradability and biocompatibility with food and the environment (Moslemi et al., 2014). Noteworthy, most research and development work on encapsulated MNs are in the areas of food and medicine (Moslemi et al., 2014; Majeed et al., 2013; Dubey and Windhab, 2013; Choi et al., 2009). 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 (Moslemi et al., 2014; Wang et al., 2013; Abedi-Koupai, 2012; Han et al., 2008). In medical research, a cocktail of MNs of ferrous fumarate and of ascorbic acid and beta-carotene were delivered in microcapsules to the gastrointestinal track (Han et al., 2008). Functionalization by acylation of the matrix polymers alginate and chitosan increased their elasticity and water impermeability. This study demonstrated the potential to protect the bioactive molecules from temperature, moisture and acidic conditions in the gastrointestinal area. Most importantly, encapsulation strongly increased the stability and absorption of MNs (Han et al., 2008).

Little published information exists on the encapsulation of MN-fertilizers and their effects on crop growth, yield and quality and MUE (Abedi-Koupai et al., 2012). The encapsulation of commercial fertilizers uses polymer films to protect the nutrients from rapid stabilization reactions in soils and control their release into the soil solution during plant growth. Nutrient release of coated fertilizer-MNs occurs according to soil moisture content and/or temperature, pH and ionic content, among other factors. The nutrient release mechanism is based on either direct diffusion through a polymer film or by decreasing the rate of product hydrolysis, such as urea. The properties and structure of polymers together with the architecture of microcapsules influence the release of encapsulated MN-fertilizer, such as Fe (Abedi-Koupai et al., 2012).

A controlled-release MN-fertilizer containing Zn, Fe, Mn and Cu was prepared after reacting and polymerizing phosphoric acid, zinc oxide, hematite, pyrolusite, copper sulfate and magnesium oxide, followed by neutralization of the polyphosphate (P-O-P) chain with ammonium hydroxide (Bandyopadhyay et al., 2014). This polyphosphate-MN product had low solubility in water but was almost completely soluble in organic acids, suggesting good plant bioavailability. The multi-MN product was tested in different field trials and showed that the slow-release POP-MN fertilizer increased rice yield from 10% to 55% over the control treatment (no MN added) and up to 17% over the conventional MN-sulfate salts. There were significant increases in total accumulation of Zn, Fe and Mn in the rice grain. The same authors reported significant increases in the yield and vitamin C content of potato. The latter fertilizer product may be an alternative to other coated control release fertilizer-MNs (Bandyopadhyay et al., 2008). In the rhizosphere, the pH near the root surface is acidic due to the presence of carbonic acid and organic acids exuded by roots, which may help improve the supply and uptake of MNs from the polyphosphate source to increase MUE. The exact mechanisms on how yield was increased are unknown but may be associated with the presence of P or interactions between P and the added MN sources in the plant.

Despite the latter agronomic and nutritional potentials, the economic cost and energy intensity for the industrial production of the polyphosphate-MN product is unknown relative to the production of encapsulated soluble MNs. The release mechanisms of MNs from controlled-release products (e.g., microcapsules and low water solubility products) do not appear to respond to the temporal differential needs of MNs required by crops during the growing season. In spite of the latter, the encapsulation approach to deliver MNs in cultivated soils may offer significant advantages to increase plant bioavailable MNs over the limitations presented by the use of conventional water-soluble salts. Still, more research is needed on the development and testing of MN encapsulated products for use in agricultural crops.

6.1.2 Nanoencapsulated micronutrients

The synthesis of ordered and functionalized mesoporous materials of silica alone or in combination with Al in aluminosilicates (to increase the acidity of the material) has been an active area of research for practical applications. 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 (Wu et al., 2008; Xu et al., 2009; Zhao et al., 1996). As nutrient delivery systems, mesoporous aluminosilicates appear to have the potential for delivering macronutrients and MNs to soils or plant leaves as they have been used as carriers of nanoparticles (NPs) of CuO (Huo et al., 2014). Previously, 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. The in vitro urea hydrolysis reaction on urease and different urease-loaded catalysts showed that the rate of hydrolysis reaction is significantly slower on PE-MCM-41 compared to that of bulk urease and urease on MCM-41 and SGA. The authors suggested the latter technique could be used as an alternative to urease inhibitors to control the ammonia release from urea fertilizer in soil-plant systems. We envisage that, in soils, these mesoporous materials of silicate may also help reduce the rate of release of macronutrients and MNs to plants. Indeed, the industrial preparation of mesoporous materials as fertilizer carriers may be possible, as various types of natural silicates (such as saponite, bentonite, metakaolin, imogolite) are abundant in nature and the structural similarity of the natural material to those of synthetic mesoporous materials (Yang et al., 2010a,b).

In the last few decades, hollow core shell NMs and nanostructures have become an important research area due to their potential applications in the fields of agriculture and biomedicine (Burda et al., 2005). A nano-sized Mn-carbonate hollow-core shell loaded with $ZnSO_4$ regulated Zn release in solution, but also in a Black Inceptisol sample placed in a percolation reactor (Yuvaraj and Subramanian, 2014). These authors suggested that the hollow-core shell could serve as an excellent plant growth medium for supplying plant roots with additional nutrient ions and demonstrated that the nano-formulated material released Zn more slowly that the $ZnSO_4$ salt, satisfying plant root demand through the process of dissolution and ion exchange reactions. When rice plants were fertilized with the Zn-fortified core magnesium carbonate shell, there were significantly increased growth, nutrition and grain yield under submerged and aerobic moisture regimes, respectively. The encapsulation of Zn using the Mn-hollow core shell appear to improve Zn use efficiency by rice while reducing the loss of nutrients.

Relative to micro-encapsulation and on a weight-by-weight basis, nanoencapsulation can only load a fraction of catalytic proteins or crop nutrients into the mesoporous structures of silica or aluminosilicates (i.e., 1% to 10%, 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). The latter implies important practical issues from the viewpoint of the cost and energy use during production and for the transportation of products. Because the rates of loading in microcapsules are much higher, smaller amounts of carrier material per amount of nutrient units are needed. Conversely and due to their low MN load efficiency, nano- or mesosilicates and aluminosilicates result in fewer nutrients transported per unit weight of product. Moreover, relative to microcapsules, nano-, meso- and macro-porous silicates and aluminum silicates used for soil and foliar applications are not biodegradable, thus, they will accumulate in the soil environment and may impact nutrient cycling processes in the rhizosphere.

6.1.3 Nanomaterials and nanoparticles

Nanomaterials (NMs) are atomic or molecular aggregates with at least one dimension between 1 and 100 nm (Ball, 2002; Roco, 2003a). The physico-chemical properties of NPs can be drastically modified compared to the bulk material (Nel et al., 2006). NPs have all three dimensions on the nanoscale and can be produced from a variety of bulk materials, and the chemical composition as well as the size and/or shapes of the particles govern their main properties and reactivities (Brunner et al., 2006).

There are three types of NMs depending on their origin: natural, incidental and engineered (Ruffini Castiglione and Cremonini, 2009). Natural NMs have existed from the beginning of the earth's history and still occur in the environment (i.e., soil clay colloids, remnants of DNA strands). Incidental NMs occur as a result of industrial or mining processes. On the other hand, engineered nanomaterials (ENMs) and engineered nanoparticles (ENPs) can be grouped into four types: (1) carbon-based materials, such as fullerene, single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotubes (MWCNT) (a carbon nanotube [CNT] is a honeycomb carbon lattice rolled on to itself, with diameter of the order of nanometers and length of up to several micrometers); (2) semiconductor, metal and metal oxide-based materials such as quantum dots, nanogold, nanozinc, nanoaluminium and nanoscale metal oxides like TiO_2, ZnO and Al_2O_3; (3) polymer NPs, e.g., dendrimers which are nano-sized polymers built from branched units, capable of being tailored to perform specific chemical functions; and (4) composites which combine NMs with other NMs or NPs or with larger bulk-type materials (Lin and Xing, 2007). These composites present different morphologies such as spheres, tubes, rods and prisms (Ju-Nam and Lead, 2008). Some of the unique properties of ENPs include magnetism, very large specific surface area, high surface energy and quantum confinement (Peddis et al., 2009). These unusual properties may result in substantially different environmental fate and behaviors than their bulk counterparts. Engineered NMs have received special attention for having positive impacts on many sectors of the economy and industry, including consumer products, pharmaceutics, cosmetics, energy and agriculture. Still, the production of ENMs for a wide range of applications within industry continues to increase (Nowack and Bucheli, 2007; Roco, 2003b). Given the rate of production and use, the delivery, effects and safe use of NMs for the improvement of crops have also been discussed (Nair et al., 2010).

6.2 Nanomaterials and nanoparticles in soil-plant systems

The application of nanotechnology in agriculture is nascent. However, NMs and NPs can provide the basis of constructs and macroassemblies for developing new tools and technological platforms for the study and transformation of MNs in soil-plant systems. As stated earlier, NMs and NPs may become part of intelligent technological systems to efficiently apply production inputs, such as fertilizers and pesticides for specific temporal and spatial scales. Accordingly, the main aim of this section is to provide information on the potential effects and interactions of NMs and NPs in soil and plants and provide insights on how NMs, NPs and nanotechnology may be used to enhance the amounts of nutritious food, while reducing the environmental footprint of MN fertilization practices associated with crop production.

6.2.1 Growth promoters and micronutrient sources

An increasing number of studies have focused on the effects and mechanisms of NPs and NMs on plants (Rico et al., 2011; Miralles et al., 2012a,b). The probability of plant exposure to the ongoing production and use of ENMs has increased (Pan and Xing, 2010). Synthetic NMs and/or ENPs closely interact with biotic and abiotic components in terrestrial ecosystems. As a result, ENPs will inevitably interact in soils with plants via plant uptake, and their intracellular accumulation in plants will greatly affect their fate and transport in the environment. The ENPs may also adhere to plant roots and exert physical or chemical toxicity on plants, depending on their properties and concentration. Publications have emerged recently concerning the interactions of ENPs with plants (see Battke et al., 2009; Lin and Xing, 2007; Lin et al., 2009). For example, the effects of MWCNTs on the growth of tomato seedlings in soilless growth media have been studied (Khodakovskaya et al., 2009). Relative to a control treatment (no MWCNTs added), tomato seedlings increased their growth after a three-day incubation with MWCNTs added at a concentration of 10 and 40 g ml^{-1} of the growth solution. The MWCNTs induced 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).

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 (Miralles et al., 2012b). On the basis of these findings, Mastronardi et al. (2015), in a recent review article, considered CNTs as plant growth promoters as they stimulate plant growth in spite of them not being transferred into the plants. Thus, stimulation of plant growth may occur through indirect mechanisms as indicated by Khodakovskaya et al. (2011). Noteworthy, Lin et al. (2009) found that rice plants accumulated CNTs in stems, leaves and seeds. These contrasting findings suggest both systemic and non-systemic effects of CNTs on plants. With metal-based NMs, a metal oxide solution of anatase-TiO_2 NPs (4-6 nm diam, 0.25% TiO_2) was used to immerse spinach plants (*Spinacia oleracea*) for 48 h at 10°C under light. Seedlings were also sprayed with 0.25% solution at the 2 leaves stage. 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., 2007b). The NPs of TiO_2 also increased the fresh and dry weight of spinach during 45 days of growth in the soilless growth media. The study was conducted in a greenhouse using perlite instead of soil.

Collectively, reviews of carbon based NMs and NPs, their applications and implications in the environment and food chain have been published (Mauter and Elimelech, 2008; Gardea-Torresdey et al., 2014; Rico et al., 2011). These reviews indicate that in soil-plant systems, the penetration mechanisms, uptake, bioaccumulation, biotransformation and risks for food crops and soils of NM and NP are still largely unknown and not well understood. Some of the effects and interactions of selected NMs and NPs and plant species have been studied, mainly at the very early plant growth stages.

Our literature review points out that many of the published studies on nanotechnology in plants have been conducted with industrial grade NMs and NPs, where plants have been grown in soilless media, and that unknown nanoproduct impurities can also influence plant metabolic responses. Also, many studies lack rigorous characterization of the NMs, which could lead to reproducibility problems. In addition, studies using artificial light exposure to plant growth media and roots appear to influence the reported bioavailability of MNs and N metabolism, such as the case reported for TiO_2 that reacted through photocatalysis resulting in stimulus to plant development. The light stimulation of roots will not occur in cultivated soil systems.

6.2.2 *Bioavailability of micronutrient nanoparticles in soils*

As stated in section 4.1, the plant availability of MNs depends on several soil properties, especially soil pH and SOM; this is also true for MN-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). An increasing number of studies have been conducted to assess the effects of NPs on plants; however, most of these studies have been conducted with plants growing in soilless media, such as pure nutrient solutions and sand. Intact CuO NPs were adsorbed on root surfaces and taken up into aboveground plant tissues from the sand growth matrix (Dimkpa et al., 2013; Wang et al., 2013). Wheat growth increased dissolution of both CuO and ZnO nano- and microparticles in a sand growth matrix 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). It was noted that the average size of CuO and ZnO NPs increased from their nominal size <50 nm and <100 nm to 317 nm and 483 nm, respectively, after 14 days of incubation in the sand-wheat system (Dimkpa et al., 2013). The formation of larger size NP aggregates was attributed to unknown factors associated with the sand and/or plant, or to dissolution of NPs and subsequent formation of larger size particles in solution that may be associated with the Ostwald ripening effect (Ostwald, 1897). Due to their small size and huge surface energy, NPs are prone to aggregation in aqueous phase, which may influence their bioavailability and toxicity (Lin and Xing, 2008). The nominal negative surface charge (a property influencing particle stability in an environment) of NPs incubated in sand was also reduced by the presence of wheat (Dimkpa et al., 2013). The uptake and transformation of ZnO NPs were studied in tissues of cowpea (*Vigna unguiculata* [L.] Walp.), either grown in a nutrient solution or soil (Wang et al., 2013). It was observed that nanoparticles of ZnO accumulated on the root surface, were dissolved in the rhizosphere and taken up as ions, to form various kinds of complexes with organic and inorganic ligands (Dimkpa et al., 2013; Wang et al., 2013). Watson et al. (2015) reported on the pH-dependent dissolution of ZnO NPs in soil, which was higher in acidic soil compared to alkaline soil. Jośko and Oleszczu (2013) reported no effects of NPs of ZnO, TiO2 and Ni on seed germination of *Lepidium sativum*. NPs displayed varied effect on inhibition of plant root growth in relation to soil type. The ZnO NPs and their bulk counterparts showed a dose-effect relationship on root growth in one out of three soils. These authors also reported that the interaction between ZnO with TiO2 or Ni had an antagonistic character, that was manifested in a reduction of the toxicity of ZnO.

Based on the available data, further research is warranted on several aspects influencing bioavailability of NPs in soils, especially those dealing with physico-chemical reactions in soils of different pedogenesis, dissolution of NPs in the soil solution of crop rhizospheres, and their interaction with macronutrients, but also their transport in soil profiles and landscapes. Pan and Xing (2012) reviewed some of the potential applications and implications of manufactured NPs in relation to their leaching and transport in soils. They concluded that the stabilization of MN-NPs by dissolved organic matter is of great environmental significance, but the mechanism of reaction is unclear. Also, there is important missing information for modelling the fate of manufactured NPs, such as the release of micronutrients from nanoproducts, proper characterization of NP properties to predict transport and the coefficients for biotransfer, biomagnification and bioaccumulation of NPs between different environmental media.

6.2.3 *Uptake and transport of NPs and NMs in plants*

The potential fate of NPs and NMs in plants and the environment has been proposed in several publications (Dimkpa et al., 2013; Ma et al., 2010; Zhu et al., 2008). In general, the main mechanisms for the reactions of NP in soil-plant systems involve the following: aggregation of individual NPs into larger size units and their dissolution in soils, chelation of NPs to root exudates or labile organic matter, adsorption to root surfaces and absorption of intact NPs or ions released from NPs by primary or lateral roots, followed by the transport from root through stem to leaves. Nanomaterials such as CNTs do not appear to be internalized into wheat and alfalfa root tissues, although some CNTs were found associated with the root epidermis, but not in the cell tissues of roots (Miralles et al., 2012b). The CNTs appear also to be adsorbed onto root surfaces of crops such as wheat, rice and cucumber (Wild and Jones, 2009; Cañas et al., 2008; Lin and Xing, 2007). Root exudates appear to contribute to the bonding of CNTs onto root surfaces. In comparison, CNTs and CNT-quantum dots were found in the leaves of exposed tomato and rice plants (Alimohammadi et al., 2011, Lin et al., 2009). Thus, the observed difference could have resulted from the NMs and species studied, or from variations in the experimental conditions.

Magnetite (Fe_3O_4) NPs are taken up, translocated and then accumulate 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; Gherardi and Rengel, 2003; Pittman, 2005), although recent data from Pradhan et al. (2013) indicate the potential for plants to accumulate nanoparticulate Mn. Manganese uptake by roots is characterized as a biphasic process. The initial and rapid uptake phase in plants is reversible and non-metabolic, with Mn^{2+} and Ca^{2+} or other cations being freely exchanged in the rhizosphere. Future studies will provide necessary scientific information to help answer the question on how significant plant uptake of intact NPs is as a potential transport pathway and its role in bioaccumulation through the food chain. Wang et al. (2013) reported that when cowpea was grown in a soil, there was no significant difference in plant growth and accumulation or speciation of Zn between soluble Zn and ZnO-NP treatments, indicating that the added ZnO-NPs underwent rapid dissolution following their entry into the soil and then moved from soil, root, to shoot as Zn ions and other Zn-organic ligand compounds.

Further research is warranted to better understand the behavior and fate of NPs and NMs in soil-plant systems. Also, the mechanisms of interactions of NPs in soil and plant systems deserve more attention, such as the NP uptake potential of different plant species, mechanisms of NP uptake and translocation in plants, and the interactions between the particles within plant tissues, and also the effects caused by NPs at the gene and molecular level. The interaction mechanisms influencing the dynamics and fate of MN-NPs needs to be studied in-vivo soil-plant systems, as their behavior appears to be different than when studied in plants alone.

6.2.4 Toxicity of NPs and NMs in plants

The high reactivity of NPs and NMs has continued to cause concerns about their potential toxicity in biological systems. This is based on the published evidence that materials and particles at the nanoscale have chemical, electrical, magnetic, mechanical and optical properties that are quite different from bulk materials. However, terrestrial ecosystems are important ecological receptors that have not received adequate attention with respect to potential toxicity of NPs and NMs, especially to microorganisms in soil-plant cosms. Publications on the phytotoxicity of NMs and NPs have increased rapidly starting in about 2005. As shown previously, engineered NPs can be potentially taken up by plant roots and transported to shoots through vascular systems depending upon the composition, dose, shape, size of ENPs and plant species (Ma et al., 2010). In planta, these materials can produce toxicity. For example, it has been reported that NPs of ZnO are toxic to wheat (*Triticum aestivum*), soybean (*Glycine max*), rye grass (*Lolium perenne*) and cucumber (*Cucumis sativus*). Other publications indicate that NPs of CuO are also toxic to wheat, ryegrass and cucumber, but also to maize (*Zea mays*), radish (*Raphanus sativus*) and duckweed *(Landoltia punctate*) (Shi et al., 2011; Wang et al., 2012; Atha et al., 2012). Nanoparticles of Cu were bioavailable, but agglomerated intracellularly resulting in greater toxic effects (inhibition of seedling growth) to mung bean (*Phaseolus radiates*) than wheat (Lee et al., 2008). In wheat, CuO NPs or NMs were more toxic than ZnO NPs (Dimkpa et al., 2012a,b, 2013) 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, but 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 or rhizosphere (Lin and Xing, 2008), suggesting the occurrence of nano-specific toxicity.

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 effects on chlorophyll and carotenoid contents (Nair and Chung, 2014; Dimkpa et al., 2013). However, few studies have focused on the plant gene and anatomic impacts caused by NPs and NMs to explain their toxic effects. Exposure of maize and cabbage seedlings (*Brassica oleracea* var. capitata L.) to citrate-nAg, nZnO, $AgNO_3$ and $ZnSO_4$ solutions for seven days revealed structural changes in the primary root cells of maize. Microscopic evidence showed 'tunneling-like effect' with nZnO treatment, while exposure to $AgNO_3$ led to cell erosion in the root apical meristem. 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). In both maize and cabbage, measures of germination and root elongation revealed lower NP toxicity compared to free ions.

The growth and balance of essential metals in beans exposed to ZnO or CuO NPs were influenced 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 et al., 2014, 2015). Studies on the toxic effects of NPs and NMs on soil microbial biomass (see review of Dimkpa, 2014) and macrofauna are emerging. A recent study indicates that root exudates have the potential to ameliorate the toxicity of MN-NPs towards 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). However, the effects of root carbon exudation on MN-NPs and NMs are unknown. Therefore, many questions remain to be answered, especially those concerning the fate and behavior of ENP-MNs in plant systems such as the role of surface area or surface activity of ENP-MNs on phytotoxicity, the potential route of entrance to plant vascular tissues and the role of plant cell walls in the internalization, transport and storage of ENP-MNs. Most of the research undertaken regarding the uptake and phytotoxicology of NPs and NMs has been performed using seed germination and incubation of plant seedlings over short periods in agar and pure nutrient solution cultures (Alidoust and Isoda, 2014).

Very few plant ecotoxicology studies (e.g., Wang et al., 2013; Watson et al., 2015) have been conducted in soil-plant systems, as these studies are very relevant to determine the fate of NPs in the environment (i.e., accumulation), but also its dissolution and transport in soils and plants during the growing season of crops and in crop rotations.

6.2.5 Nanofertilizer formulations

The outcomes from many of the discrete studies of NP-plant interactions suggest the potential use of commercial NPs of Zn, Fe, Mn and possibly Cu as nutrient sources in crop production. Nanoparticles of Fe, Zn, Mn and Cu oxides may have the potential for increasing plant growth MUE by crops when they are applied to soils or foliage. Reports indicate that ZnO NPs (<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, tomato (Singh et al., 2013) and common chickpea (Pandey et al., 2010) helped increase the Zn MUE of crops. *Moringa peregrine* plants sprayed with a Hoagland solution containing ZnO and Fe_3O NPs 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 N, P, K^+, Mg^{2+}, Mn^{2+}, Fe and Zn (Soliman et al., 2015).

Novel nanofertilizer formulations have been patented (see Naderi and Danesh-Shahraki, 2013). Recently, Mastronardi et al. (2015) presented and discussed the potential use of patented products for commercial applications in agriculture. The latter authors highlighted opportunities for the intervention of nanotechnologies in the area of novel fertilizers and the current status of nanotechnology in plant nutrition, but also expressed concerns about the fact that very little is known about the risks and fate in the environment of the patented products. There are several patents on nanofertilizer formulations with carbon-based NMs (see Biris and Khodakovskaya, 2011; Lewis, 2013; Zhang and Liu, 2011). However, little information on specific crop uses and responses to these patented formulations exist in the scientific literature.

6.2.6 Nanodevices

Nanoscience and nanotechnology encompasses three fields: nanodevices, nanomaterials 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.

Recent developments show that novel sensor devices can also be incorporated into microbial cells. For example, microbial-based sensors have been used in 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; Maderova and Paton, 2013). For example, a 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 has 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 assessment of chemical availability, toxicity and bioavailability of soil Zn demonstrated that the biological responses could not be inferred from the quantitative measurements of various chemical Zn species in soil. They also concluded that the bacterial sensors responded to the bioavailable fraction of Zn in soils.

Synthetic nanodevices also hold some promise for MN sensing and delivery platforms. Biosensors of magnetic nanoparticles 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 pesticides sensing (Rocha Santos, 2014). Advances in research made on 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 (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 in crop rhizospheres.

In recent years, novel aptamer-based materials have been investigated for potential controlled released materials that may be applied in agriculture and medicine (Mastronardi et al., 2014). 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 may 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 macro- and MNs according to the temporal and spatial MN requirements of crops 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.

7 The future

New advances in nanotechnology can be a major factor shaping modern agriculture. The successful development and application of nano-platforms in medicine in vitro have generated interest in agri-nanotechnology (Nair et al., 2010). Among the latest line of technological innovations, nanobiotechnologies occupy a prominent position in transforming agricultural systems and food production worldwide. Micronutrients loaded and delivered in materials such as microcapsules and/or porous aluminosilicates, NMs and NPs may provide useful ways to use fertilizer-MNs in a controlled fashion with high site specificity, thus resulting in economic savings to farmers and reduced environmental impacts. The incorporation of molecular recognition agents, such as aptamers (Mastronardi et al., 2014; Sultan and DeRosa, 2011; Zhang et al., 2013) into crop rhizospheres or plant foliage, which may help in efficiently delivering specific fertilizer nutrients needed by crops, could be transformative in this regard.

Nevertheless, this literature review shows that significant research efforts are requimosred to fill gaps in knowledge, information and efficient MN-fertilizer technologies. To this end, capital investments are necessary to advance nanotechnology and nanobiotechnology for the development, testing and demonstration of novel nanofertilizer platforms that will significantly enhance MUE by crops and ultimately food quality.

7.1 Knowledge and technology gaps

Conventional soil and crop management systems and fertilizers have resulted in little improvements in crop yield amounts and quality, as well as low MUE in the past 100 years. Much financial investment in agriculture during the last few decades has been dedicated to efforts in plant genetics and breeding. This literature review report shows that knowledge on the exact spatial distribution of deficiencies and bioavailability of key micronutrients at the local level is deficient for most regions of the world, including the Americas. Most existing information relates to total content of MNs in large spatial scales (1:1,000,000), with unknown bioavailability levels. The response of crops to MN addition and their interactions with macronutrients need further research under different crops, soils and climates common to specific regions of the planet. Research efforts exploring the potential benefits of nanotechnologies, nanodevices, NMs and NPs as sources of MNs for crop production need to be strengthened. Much needs to be learnt about the potential use of micro- and nanoencapsulated MNs and NMs on the metabolism and growth of crops and plant rhizosphere soil microorganisms. New technologies and products for fertilizer-MNs need to be developed and tested under controlled conditions in greenhouses and in the field before they can be commercialized widely around the planet. Important efforts need to be made on the mechanisms of reaction and fate of NPs, NMs and nanodevices with in-vivo soil-plant systems, as the outcomes of research studies may be different than those reported in plants grown in agar, nutrient solutions or artificial soil media.

7.2 Nanobiotechnology for micronutrient delivery

Biotechnology and nanobiotechnology combined may result in rapid and significant progress in the areas of fertilizer-MN development for their efficient delivery and production of abundant nutritious food. In this section we attempt to identify and prioritize research directions for development of nanofertilizers for MNs. Increasing the MUE by crops requires urgent and significant support from governments and industry for increasing research activities in basic areas of nutrient cycling in soil-plant systems. Such research requires a multidisciplinary team effort including soil and plant scientists, chemists and engineers to understand basic processes affecting the cycling of MNs in soils, crop rhizospheres and plants, and the development of novel nanofertilizer products and technologies. In particular, future research focus will be to gain additional experimental evidence about how metal oxide NPs applied alone or in combination with macronutrients to leaves and/or deficient soils under different environments increase crop MUE, grain yield and food nutrition. Advanced research prospects for integrating nanobiotechnologies into fertilizers should be explored, cognizant of any potential risks to the environment or to human health.

New knowledge in soil-crop ecology and advances in nanobiotechnology can serve as the basis for significantly increasing MUE by crops in agriculture. Advances in nanotechnology, such as novel polymer film materials for nutrient encapsulation, NMs and NPs for MNs, identification of metabolites resulting from chemical communication between plant roots and soil microorganisms will permit better manipulation and synchronization of the release of fertilizer-MNs with their demand by crops during the growing season (Monreal, 2015). Research with a focus on the latter will contribute to the development of novel efficient MN-nanofertilizer platform delivery systems designed for specific soils, crops and agro-climates around the world.

7.3 A nanotechnology-based delivery platform for micronutrients

The recent R&D efforts to develop intelligent nanofertilizers (INF) for wheat and canola will be essential and useful for the development of a nanotechnology based delivery platform for MNs. The fundamental and practical research work conducted by the Canadian Nanofertilizer research group on INF has opened up new research avenues in nanobiotechnology for fertilizers in agriculture. Specifically, research conducted and experience gained by this group of scientists has focused on understanding the interactions between root exudates and root-microbial signals associated with soil N mineralization and its uptake by wheat and canola; the preparation of aptamer based biosensors to detect specific metabolites of communication signaling networks of plants with soil microorganisms; and the development of novel polymer films together with a nanocoating tool and process. 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 wheat or other crops rhizosphere. As a result of this communication, microbial or plant metabolites are released into the soil solution. Figure 5 shows that the chemical communication concepts represent a promising approach for developing model Intelligent Nanofertilizer Delivery Platforms for MNs, such as Zn and Fe. The main mechanism of nutrient release is based on the recognition and binding of a specific plant signal by a nanobiosensor housed in a polymer film which coats Zn-fertilizer NPs or salts. Upon binding, the fertilizer-ZnO-NPs (or other MN-NPs) is released in a synchronized fashion in response to root signal release, polymer permeability and MN crop needs.

Once an advanced prototype of this MN-nanofertilizer delivery platform is developed, it will need to be evaluated in different soils, crops, climate, agro-ecologies and field situations to improve MUE, thus mitigating fertilizer losses to the environment. Development of novel nanotechnology MN platforms will bring benefits to farmers and rural areas around the world. Finally, the use of a novel micronutrient INF technology will need complementary soil testing to evaluate micronutrient availability and the use of precision farming technologies at the field scale.

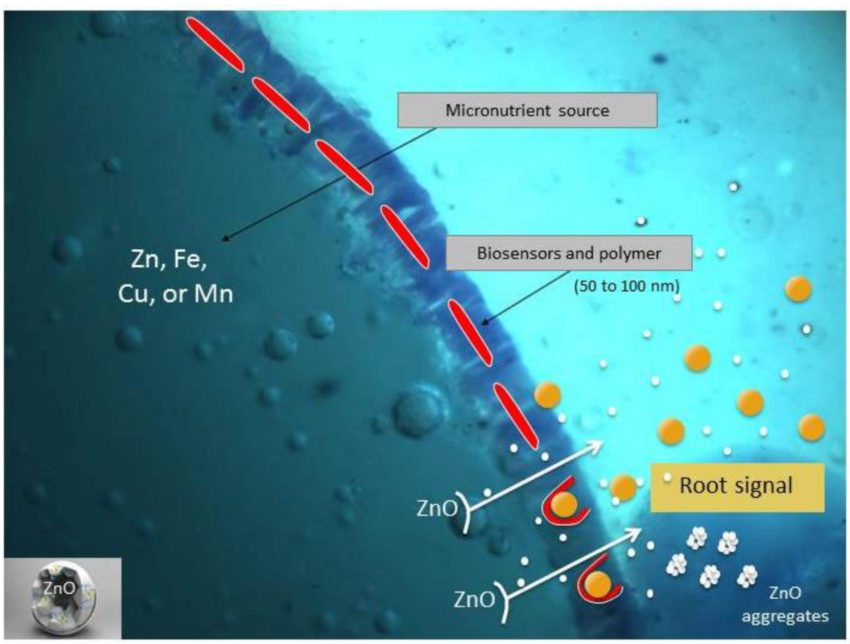

Figure 5. *A conceptual model for the synchronized release of ZnO nanoparticles according to crop demand*

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, plant uptake and aggregation of ZnO NPs (white spheres) in the soil solution of crop rhizospheres.*

8 Conclusions

Micronutrient deficiency in 50% of the world's soils and many crops greatly reduces the amount and quality of food. The low (<5%) MUE by crops adversely affects human health, the economic status of farmers and the environment around the world. Research on conventional MN-fertilizers conducted during the last 100 years has resulted in small increases in crop MUE. Technology differential appear to show that MUE increases among MN products as follows: soluble salts < chelates < microcapsules ≤ NPs ~ nanocapsules. However, the effects of incorporating nutrient sources in NPs, NMs, with nanodevices for increasing MUE in soil-plant systems, remains largely unknown and awaits further studying. Moreover, many of the studies on NPs and NMs on plants are conducted in nutrient rich media obviating important soil aspects.

An important reason for the low MUE is the lack of synchronization between the fertilizer-MNs release and their crop demand during the growing season. It is very difficult for current conventional technologies to enable synchronization of fertilizer-nutrient release according to crop demand. Modern research efforts are conducted to increase MUE, paying special emphasis on potential contributions of nanotechnology and nanobiotechnology; however, their application in fertilizer nutrient delivery is at a nascent stage. In Canada, a multidisciplinary team of scientists are attemptingto synchronize the release of urea-N according to crop demand. This approach uses knowledge from soil-plant ecology, together with tools, devices and materials from nanotechnology and nanobiotechnology to develop an intelligent nanofertilizer platform for efficient nutrient delivery. This developmental work can serve as the basis to develop a nanofertilizer technology platform for MNs, as is the interest of the International Fertilizer Development Center and its subsidiary, the Virtual Fertilizer Development Center. Such MN technology platform may help increase MUE from 5% upwards of 50%, ultimately resulting in improved crop yield and quality, enhanced human health, and environmental and economic gains for the poor around the world.

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