EC NUTRITION
Editorial

Nanotechnology-Enabled Agriculture is the Future?

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Received: June 07, 2017; **Published:** June 17, 2017

Human health is intrinsically connected to the environment we live in. Among others, plants serve as a basal component of our biosphere and support life of animals and humans alike, offering many essential nutrients. For example, vitamins, carbohydrates, minerals, amino acids and fatty acids are among the critical nutrients that plants and plant-derived foods provide, serving either as the energy source, or promoting growth and maintaining homeostasis [1].

While humans have been growing crops for the past 10,000 years [2], modern agriculture has become heavily reliant on the use of crop protection and retention products, such as high-volume, high-dose chemical pesticides and fertilizers [3]. In the United States alone, the use of chemical pesticides has almost tripled in the last half century: an increase from 196 million pounds of active ingredients in 1960 to 516 million pounds in 2008 [4]. While this increased use of pesticides has been vital in our ability to improve crop production and to feed the growing population, there are concerns regarding the crop and soil quality, however. Potential human health and ecological risks from exposure to these high-volume, high-dose agrochemicals have also been realized [5]. There is thus a growing need for innovative, sustainable, and safer technologies in modern agriculture.

In this context, Nanotechnology, nanofertilizers and nanopesticides have emerged as novel technology and products, showing tremendous potential for growth in modern agriculture which is in the quest for: (i) enhancing global food production; (ii) improving food quality and health; (iii) improving targeted and controlled/efficient distribution and delivery of pesticides and fertilizers, reducing ecological footprint; (iv) promoting waste minimization and sustainability; (v) implementing better crop management and conservation techniques; and (vi) developing disease resistant crops [6,7]. Albeit what potential impacts such new technology or products might have on the environment and human health are narrowly explored and are far from clear.

Plant diseases and infestations are caused by a multitude of factors including bacteria, fungi, viruses, and parasites, which significantly impact crop yield and food quality. The USDA estimates billions of dollars lost annually due to plant diseases, and hundreds of millions more spent on pathogen control and fungicides use [8]. While there has been research and experimentation to increase plant disease resistance via genetic manipulations, there is also lingering public concern regarding the perceived risk and acceptance of genetically modified crops [9]. An alternative method includes disease suppression, or the development of disease resistance, in crops via proper management and controlled supply of nutrient elements, including micronutrients (MNs), as needed by a crop species during different growth stages [8].

MNs including copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), and zinc (Zn) are essential for optimal plant growth and protection against diseases [10]. Disease resistance can be conferred by maintaining higher MNs levels as they induce enzymes and coenzymes in plants [8,10]. Improving MNs content in the edible portions of crop and produce, through the application of engineered nanomaterials

(ENMs) as additives or carriers of MNs, seems technically plausible. With adequate and timely supply of nutrients to the root system, the need for excess fertilization can be minimized, thus saving time and resources. However, these MNs are not adequately absorbed by plants due to fluctuating soil permeability, pH levels, and disease or pest infestations [11]. Nanoencapsulated pesticides allow for targeted application and slow chemical-release to crops as compared to the widely used large-scale pesticide spraying techniques, which often lead to non-targeted pesticide drift with implications to human health and ecological safety [6,12]. Enclosing pesticide substances within a shell/capsule is believed to better withstand external forces and increase the efficacy of pesticide delivery and thereby its potency [13]. Nanoencapsulation further allows farmers to reduce overall pesticide burden in soils in both the short- and long-term.

A conceptual rendition of nanocapsule as a carrier or delivery platform with potential for controlled release of MNs and macronutrients (N, P, K) is shown in figure 1. Controlled release of plant nutrients directly at the root interface is envisioned to occur in multiple ways: (i) pH responsive nanocapsule (a nano capsule that becomes permeable releasing nutrients at a specific soil pH can be designed); (ii) biodegradable nanocapsule (a nanocapsule that disintegrates at a specific time frame releasing nutrients at a given soil condition); or (iii) redox responsive nanocapsule (a nanocapsule with polymeric shell that can dissociate under reducing or oxidizing condition within the rhizospheric microcosm).

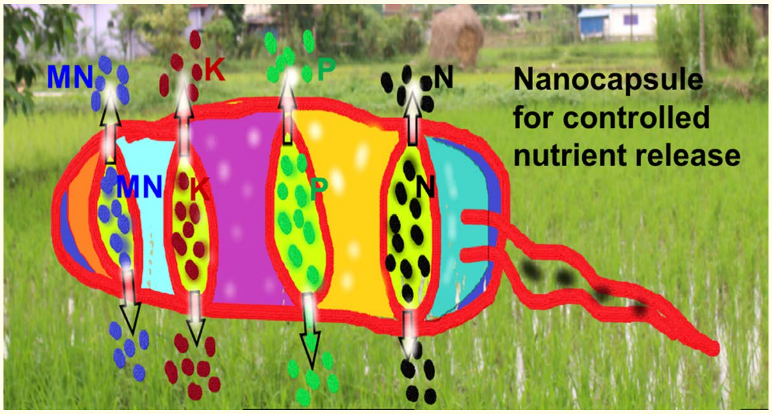

Figure 1: *A conceptual rendition of nanocapsule as a carrier or delivery platform with potential for controlled release of micronutrients (MNs) and macronutrients (N, P, K). A flagellum-like propeller is shown (to the right) envisioning that the nanocapsule can be made mobile within the soil delivering nutrients where needed. Potential mechanisms of controlled release of the nutrients are described in the text.*

Studies have indicated potential hermetic effects, especially at low concentrations (low ppb level), of the metal and metal oxide nanoparticles applications as they enhance crop biomass, while simultaneously inhibiting pathogenic growth and survival. Some nanomaterials, such as silver nanoparticles, could control crop disease due to their prominent antimicrobial properties [14]. Additionally, nanofertilizers could offer more controlled release of key nutrients over time, thereby facilitating improved growth and development in plants [8]. In a study, Zhao., *et al.* [15] showed Cu-based nanopesticide ($Cu[OH]_2NP$) could enhance K^+ and Cu^{2+} concentrations in lettuce. In bitter melon, fullerol ($C_{60}[OH]_20$) bioaccumulation promoted crop yield, plant growth, and water content, including its potential phytomedicinal properties [16]. ENMs may competitively inhibit toxic elements uptake by the plants, or via complex formation render them less bioavailable and thus confer protection against toxic heavy metals and other elements in soils. Applying nanoparticles of Al, Fe, Cu, Mn, Ni, or Zn to tomato or eggplant before inoculating each plant with a soil fungus, *Fusarium* or *Verticillium* wilt, Elmer [10] reported that Cu- and Mn-based nanoformulations provided greater protection against the fungal infections in both plants as compared to their bulk counterparts or other nanoformulations tested. When atrazine was applied as a nanoformulation in soils, Kah., *et al.* [11] found that its degradation rate was slowed down suggesting potential for nanoformulation of the standard pesticide to confer extended protection to crops against pests and fungal pathogens. These data suggest that the use of select nanomaterials may improve food quality by increasing phytonutrients content, while also conferring plant protection and improving crop production.

Another growing application of nanotechnology outside of farm is in the food and packaging industry, which aims to: (i) reduce food wastes and foodborne illnesses; (ii) improve shelf-life; and (iii) maintain the nutritional content in packaged food for extended period. For example, recently a canola oil based “nanodrop” has been developed, which carries nutrients such as vitamins, minerals, and phytochemicals to targeted sites within the human body [6]. Additionally, the use of nanobiosensors in food packaging may help reduce food waste by informing consumers when the product is about to rot [17]. Although silver nanoparticles are currently in high demand, magnesium and zinc oxide nanoparticles are also being considered for protection against pathogenic food-borne microorganisms within the food packaging industry due to their ease of synthesis, low-cost, and effective antimicrobial properties [17].

As the above studies underscore the importance of nanotechnology and nano-based products’ applications in modern agriculture benefitting the society, there are also studies indicating potential negative effects of ENMs to crops and other organisms in the ecosystems. Presence of gold nanoparticles (AuNPs) within the xylem vessels in the leaf indicated that the NPs were transported during nutrients and water uptake [18]. 3.5 nm size AuNPs exposure led to leaf necrosis culminating in plant death, which, however, did not occur with the larger 18 nm size AuNPs exposure [19]. A size threshold has also been suggested for NPs translocation to the leaves which is reported to be < 36 nm; while accumulation of TiO_2NPs in the wheat root could only occur if NPs were < 140 nm in diameter, with higher accumulation occurring with smaller size NPs (size range 14 - 22 nm) [20].

When ENMs are present in the environment (air, soil and water), they can be bioavailable to crop plants, and may potentially transfer across generations (e.g., CeO_2NPs in soybean; [21]). Although phytotoxicity of ENMs has often been associated with dissolved ions being released from the ENM surfaces, higher nanotoxicity has also been reported for multiple metal-based nanomaterials, regardless of whether they tend to release ions (e.g., ZnONP, AgNP) or not (e.g., CeO_2NP, TiO_2NP) [20,22].

Apparently, ENMs applications in modern agriculture and food industry appear promising, there are lingering concerns, however, which ought to be addressed in terms of overall public safety and food quality, including potential implications upon their release into the environment. Reports showing significant negative, positive or no observable adverse effects on plant growth and development are documented in the nanoliterature [23-26]. Thus, no consensus exists on whether the use of ENMs and/or nanopesticides in agriculture is harmful to crops and human health, including their potential long-term effects and fate in the environment [22]. Such conflicting and inconclusive results are likely a manifestation of methodologically inconsistent and unrealistic study designs. Doses applied in much of studies are often ecologically irrelevant (usually high g/L water, or g/kg soil) and test media compositions (filter paper vs. agar vs. sand vs. soil) also varied widely among studies [22,27,28], potentially altering particle behavior (colloidal stability, state of aggregation, transport, etc.) and thus differential nanotoxicity [29]. Owing to their nanoscale size, biouptake by crop plants can be expected to increase [22] but other factors such as surface charge and surface functionalizations might also play key roles to inhibit or promote ENM uptake (LRP personal observation). Toxicity investigation using high purity ENMs is critically important as impurities, excess ligands or heavy metal ions within the ENM suspensions could significantly contribute to ENM toxicity [22]. Techniques such as tangential flow filtration (TFF) [30,31], dialysis or washing (using suitable solvent) can offer high purity and high quality ENM products, but unfortunately, commercially procured ENMs are routinely utilized for toxicity testing, and with no knowledge of what and how much impurities the treatments contained, conclusions drawn from such studies can often be misleading.

Greater uncertainty remains regarding the realistic environmental exposure scenarios and exposure concentrations/doses since estimates on the ENMs concentrations in the environment vary widely depending on the model assumptions and ENM use data quality [32]. Furthermore, no studies to-date has concurrently tested for potential influence of background heavy metals, pesticides, and fertilizers on the fate and behavior of ENMs in the soils and in plants. Nano-bio interactions at soil-root interfaces (i.e., rhizospheric interactions) accounting for the role of soil microbes such as mycorrhizae have not been probed systematically; hence, a knowledge gap exists in understanding how interactions within the rhizosphere could influence ENM and other background pollutants' co-bioavailability and co-translocation into plants.

To date, studies have widely addressed acute toxicity (short-term, high-dose) at single plant species level and within controlled laboratory setting, providing valuable information on individual species responses to, and mechanistic understanding of, ENM exposure. However, research investigating ecosystem-level responses, including the field trials, to chronic (long-term, low-dose) ENM exposure have only been narrowly explored and must be the focus of future research. More realistic exposure conditions, such as augmentation of natural organic ligands (humic acid, fulvic acid, cysteine, carboxylates, thiols), mono-/divalent cations/anions, and pH must be routinely examined in future nanotoxicity testing to identify the key factors, and elucidate the underpinning mechanisms, of nanotoxicity [29,31]. Further, more focused research is needed to elucidate how biologic surfaces interact and influence the fate of ENMs *in vivo* leading to toxicity [33]. Above all, for sustainable growth of nanotechnology in modern agriculture, investigations should focus on biouptake in edible portions of produce/crop, effects on food nutrient attributes, crop yield, and public health and environmental risks before nanotechnology-based products (e.g., nanofertilizer, nanopesticides, growth stimulant, gene delivery, etc.) become increasingly common in modern agribusiness.

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