

Responsible use of nanofertilizers and nanocarriers in agriculture

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Nanotechnology is a promising field in every aspect of modern life including agriculture. Nano-agriproducts like nanofertilizers and nanocarriers are becoming a cynosure due to their proposed role in precision agriculture. Nutrients mainly in their nanoforms are used as nanofertilizers and nanoporous materials are helpful for the controlled release of fertilizers, pesticides and semiochemicals. The use of these products is still in its infancy due to the harmful effects of their dissemination in the environment and probable health hazard to all the life forms including human beings. There is an urgent need to develop strict and legislative control strategies for the manufacture of nano-agriproducts in line with general nanomaterial safety guidelines; specific regulation is required for the agriproducts developed with the help of nanotechnology as their use is likely to greatly increase in the near future. Governmental and nongovernmental organizations should work together to augment the use of nanoproducts to enhance crop production.

Keywords: nanomaterials, nanotechnology, regulation

Introduction

World population is projected to grow to 9300 million by 2050 (Hillebrand, 2009). Due to the limited availability of agricultural land, crop production worldwide is not expected to meet the requirements of this increasing population (part of which even today is considered to be inadequately nourished). In order to adequately feed this larger population, food production must increase by 70% in order to have an average food consumption of 3130 kcal per person per day by 2050 (Bruinsma, 2009). The rate of increase in yields of several crops has been noted to have dropped at the threshold of the 21st century (Miflin, 1999). Also, for the past decade, improvements in conventional technologies for crop production do not seem to be satisfactory.

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The impact of long-term use of chemical fertilizers on agro-ecosystems is well documented (Savci, 2012). Most fertilizer run-off (leaching from fields) enters water bodies and food chains and webs. Furthermore, the unchecked use of insecticides and other pesticides entail detrimental effects on various life forms other than those targeted. In this regard, precision agriculture should be helpful in the future.

To increase crop production new technologies have to be incorporated into agriculture. With the advent of nanotechnology, various nano-enabled products are making their way into different fields; some nanoproducts are currently being used in agriculture, although their use is not established. Nanofertilizers and nanocarriers possess immense potential for applications in agriculture. These often revolutionary products of nanotechnology enhance production and delivery of a variety of compounds, including drugs, pesticides and fertilizers. Macro- and micronutrients in nanosized form can be applied as nanofertilizer, while mesoporous silica can be used as a nanocarrier of active substances.

To stimulate industry's involvement in the development of nanofertilizers and nanocarriers, technology validation that is nondisruptive to existing bulk production systems is needed (Dimkpa et al., 2017). It should, however, be borne in mind that the environment and human beings are directly exposed to these nanomaterials in the production area, through field application and through food webs. Once released into the environment, there is no means to recall such materials. Hence there is an urgent need to predict their fate and develop nanotechnologies employing safe nanomaterials in food and agriculture. To achieve the controlled and safe use of nanomaterials in agriculture, strict legislation must be implemented. The nano-enabled strategy first has to be compared with what can be achieved with current conventional methods (Kah et al., 2019). The safe and reasonable use of nanomaterials in agriculture will be helpful for mankind without disturbing the environment.

Nanofertilizers: nanotechnology in fertilizers

A nanofertilizer is a product of nanotechnology that can deliver nutrients to crops by encapsulating them inside a nanoporous material, coated with a thin protective polymer film, or by delivering the nutrients as particles or emulsions of nanoscale dimensions (DeRosa et al., 2010). Due to their high surface area:volume ratio, nanofertilizers are expected to be more effective than their conventional counterpart (Dimkpa and Bindraban, 2017). More sophisticatedly, the dynamics of soil bacterial populations associated with root exudates and nitrogen uptake by crops should be monitored extensively in order to develop intelligent nanofertilizers (Ghalamboran et al., 2009; Monreal et al., 2016). In this regard, new perspectives for integrating nanotechnology into fertilizers should be explored, keeping in mind potential risks to the environment or to human health. Nanotechnology could be highly transformative in this field, not least through the efforts of governmental organizations and research associations in developing such innovative agro-products.

Numerous studies have reported the effects of nanoparticles (NPs) on crops. However, most of the experiments have been done under controlled conditions. Both carbon-based engineered nanoparticles (ENPs) as well as metal and metal oxide ENPs have been the subject of these studies. Carbon nanomaterials such as single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), carbon buckyballs etc. are finding applications in

agriculture and food packaging (Prasad et al., 2017)—the latter playing an important role in delaying spoilage and, by preventing food waste, thereby contributing to effective yields. The high reactivity of these nanomaterials has raised eyebrows regarding the safety of using such ENPs in agriculture. Reported effects of ENPs on crops are somewhat contradictory (Nair et al., 2010; Lee et al., 2013; Kah, 2015). Nanocalcium was found to be more easily absorbed by Tankan leaves as compared to colloidal calcium (Hua et al., 2015). Zinc oxide nanoparticles showed absorption in the root tissue of ryegrass (Lin and Xing, 2008) suggesting that new nutrient delivery systems that exploit the nanoscale porous structures on plant tissue surfaces can be developed. TiO₂ NPs have been found to improve light absorbance and promote the activity of rubisco activase thus accelerating spinach growth (Zheng et al., 2005; Hong et al., 2005; Gao et al., 2006; Xuming et al., 2008). Nano-anatase (TiO₂) treatment increased the activities of nitrate reductase, glutamate dehydrogenase, glutamine synthase and glutamicpyruvic transaminase during the growing stage of spinach (Yang et al., 2006). This has prompted attempts to develop nanofertilizers that can deliver nutrients encapsulated inside NPs like nanotubes or nanoporous materials. They might advantageously be coated with a thin protective polymer film, or the nutrients delivered as particles (including emulsions) of nanoscale dimensions. Carbon nanotubes (CNTs) can penetrate seeds and were found to noticeably enhance germination and growth rates in tomato (Khodakovskaya et al., 2009). Due to their high surface:volume ratio, their effectiveness (efficiency in use) would far exceed the most innovative polymer-coated conventional fertilizers (DeRosa et al., 2010). Presently, metal and metal oxide NPs of Ag, Au, Fe, Si, Zn, Cu, Ti etc. are being investigated for their potential as delivery vehicles for pesticides, herbicides and fertilizers. For instance, Si NP are being tested to deliver pesticides like avermectin and validamycin, and have been shown to afford protection against UV degradation; release control is dependent on pore diameter and shell thickness (Li et al., 2006; Liu et al., 2006). Mesoporous nano-Si has been reported to provide insecticidal activity (Popat et al., 2012) and nano-Si-Ag composites have been found to control a variety of plant diseases (Park et al., 2006). Nanoscale ZnO can be effectively foliarly-sprayed at low concentration (1.5 ppm) to improve biomass production of chickpea seedlings (Burman et al., 2013). Similarly, in *Glycine max* (soybean) the chlorophyll content was increased by Fe NPs at 30-60 ppm concentration (Ghafariyan et al., 2013). Synthetic apatite nanoparticles were used as a phosphorus fertilizer to increase the yield of *Glycine max* by Liu and Lal in 2014. Enhanced production of pearl millet (Pennisetum americanum) by foliar application of nanozinc particles as fertilizer was reported by Tarafdar et al. (2014). Nanosize Ca-based fertilizer application leads to vine growth and enhanced yield, berry quality attributes and leaf nutrient content of grapevines (Sabir et al., 2014). Delfani et al. (2014) noted a 7% increment in seed weight and a 10% increment in chlorophyll content in leaves of black-eyed pea with the use of Mg NP and Fe NP, respectively. Fe₂O₃ NPs might be an ideal substitute for traditional Fe fertilizer (Rui et al., 2016). Fe₂O₃ nanoparticles at 30 mM concentration were found to significantly increase growth parameters, photosynthetic pigments and total protein content in Catharanthus roseus compared to untreated plants (Askary et al., 2017). ZnO nanoparticles synthesized using soil fungi showed enhanced mobilization of native phosphorous in the mung bean rhizosphere (Raliya et al., 2016). Dimkpa et al. (2017) reported that under conditions of low NPK fertilization, both nanoparticle and ionic Zn promote nutrient loading of sorghum

grains. Exposure of soil with weathered and fresh nanoparticles or ionic Zn promotes grain yield and modulates nutrient acquisition in wheat (Dimkpa et al., 2018). The nanofertilizers mentioned in the text and their references are summarized in Table 1.

Nanofertilizer	Effect	Reference
TiO ₂ NPs	Promote the activity of rubisco activase, thus accelerating spinach growth	Zheng et al., 2005; Gao et al., 2006; Xuming et al., 2008
Nano-anatase (TiO ₂)	Increases the activities of various enzymes during the growing stage of Spinach	Yang et al., 2006
ZnO NPs	Enter the root tissue of ryegrass	Lin and Xing, 2008
Carbon nanotubes (CNTs)	Penetrate tomato seeds and noticeably enhance their germination	Khodakovskaya et al., 2009
ZnO NPs	Improve biomass production of chickpea seedlings	Burman et al., 2013
Fe NPs	Increase G. max chlorophyll content	Ghafariyan et al., 2013
Fe NPs	Increment chlorophyll content of Vigna unguiculata	Delfani et al., 2014a
Nano-Fe	Increases yield of wheat	Armin, 2014
Nanozinc	Enhances production of pearl millet	Tarafdar et al., 2014
Mg NPs	Increment Vigna unguiculata seed weight	Delfani et al., 2014b
Synthetic apatite NPs	Increase yield of G. max	Liu and Lal, 2014
Nanosized Ca-based fertilizer	Increases growth rate, yield, berry quality and leaf nutrient content of grapevines	Sabir et al., 2014
Ca NPs	More easily absorbed by <i>Citrus tankan</i> leaves than macro-Ca	Hua et al., 2015
Intelligent nanofertilizer	Enables soil bacterial populations associated with nitrogen uptake to be monitored	Monreal et al., 2016
Fe ₂ O ₃ NPs	Ideal substitution for Fe fertilizer	Rui et al., 2016
ZnO NPs	Enhance the mobilization of native phosphorous in mung bean	Raliya et al., 2016
Nanozinc particles	Promote nutrient loading of sorghum grain under low NPK fertilization	Dimkpa et al., 2017
Nano-iron fertilizer	Increases growth parameters in Catharanthus roseus	Askary et al., 2017
Nanozinc particles	Promote grain yield and modulate nutrient acquisition in wheat	Dimkpa et al., 2018

Table 1. Nanofertilizers and their effects on crop plants.

Nanocarriers: nanoscale carriers

Nanoporous materials—nanocarriers—have a network of channels and pores with well-defined sizes in the nanoscale range suitable for hosting a broad variety of compounds in a range of applications including drug, pesticide and nanofertilizer delivery. Such nanocarriers (e.g., so-called

mesoporous silica) are nowadays used for the slow and controlled release of drugs (in nanomedicine), but their analogous application in agriculture (for delivering pesticides and fertilizers) is still is in its infancy.

Nanotechnology in the field of agriculture has recently gained much popular interest because of one of its application is the controlled release of agrochemicals including fertilizers, pesticides and semiochemicals. In particular, silica-based nanoparticles have garnered interest as a potential delivery agent for agrochemicals to plants. This is mainly due to the flexibility in fabrication methods for forming nanoparticles of various sizes and shapes, and also silica's ability to form pores for carrying biomolecules (Campbell et al., 2011; Shi et al., 2010). The study of ordered mesoporous silica materials has greatly expanded since their discovery by Mobil researchers more than two decades ago. The most common types of mesoporous nanomaterials are MCM-41 and SBA-15. Mesoporous silica nanocarrier (MSN) possesses a well-defined structure and a high density of surface silanol groups, which can be modified with a wide range of organic functional groups (Kwon et al., 2013). Nowadays, mesoporous silica nanoparticles are functionalized by the introduction of surface groups; the modification depends on the application. Hence, they can serve as a nanocarrier in a wide range of fields, including agriculture. MSN has been used to deliver DNA and chemicals into plants (Torney et al., 2007). Controlled release of urea using mesoporous silica nanoparticles was reported by Wanyika and co-workers in 2012. Hussain et al. (2013) reported that MSNs are internalized by wheat roots during seed germination and that they can be taken up by the roots of lupin and transported in the vascular system. They also showed that 20 nm MSN can be synthesized with a large surface area; the pore diameter is suitable for the accommodation of biomolecules. The insecticidal effect of silica nanocapsules containing fipronil against economically important subterranean termites could be controlled by tuning the shell thickness (Wibowo et al., 2014) in vitro and in vivo. A study of functionalized MSN by Yi and co-workers (2015) showed that their use with redox-responsive gatekeepers can be an efficient technique to deliver agrochemicals into plants in a controllable fashion. Zhao et al. (2017) synthesized pyrimethanil-loaded MSN and showed pyrimethanil distribution in as well as excretion by cucumber plants, a landmark for evaluating the possibilities of pesticide-loaded MSN accumulation in fruits or grains that form part of the food chain connecting to human beings. The delivery of abscisic acid to arabidopsis seedlings using glutathione-responsive MSN was demonstrated by Sun et al. (2018); controlled release of the encapsulated phytohormone markedly prolonged the expression of the ABA-inducible marker gene (AtGALK2) and, importantly, improved the drought resistance ability of the seedlings under drought stress.

Beside MSN various other nanomaterials have been used as a nanocarrier for the controlled delivery of various substances in agriculture. Surfactant-modified zeolite (SMZ) as fertilizer carriers to control nitrate release showed that slow release of nitrate is achievable (Li, 2003). Hussein et al. (2005) found that the release of the herbicide anion 2,4-D (2,4-dichlorophenoxyacetate) from the lamellae of an organic–inorganic nanohybrid material, Zn–Al-layered double hydroxide nanocomposite, could be controlled by adjusting the type and the concentration of anions in the (aqueous) release medium. Slow-release sulfur-coated fertilizer was analysed by Wilson et al. (2008) in the laboratory. The coating thickness ranged from a few to 100 nm—improved uniformity of thickness would doubtless improve efficacy. Fluorescent

starch nanoparticles were prepared to carry not only exterior (phenotypic) genes (DNA) but also a GFP-expressing gene so that the course of exterior genes' movement could be investigated by observing the nanoparticles' trace and the expressed GFP under a fluorescence microscope (Liu et al., 2008). In a preliminary study of the incorporation of NPK fertilizer into chitosan nanoparticles, Corradini et al. (2010) used biodegradable, polymeric chitosan NPs (~78 nm) for controlled release of NPK sources such as urea, calcium phosphate and potassium chloride. High DNA delivery efficiency into plants by gold nanoparticles embedded in sharp carbonaceous carriers was demonstrated by Vijayakumar et al. (2010); the carbon-supported gold nanoparticles were produced by simple heat treatment of intracellular biogenic material and proved to be a better carrier than commercially available micrometre-sized gold particles. Hussein et al. (2012) demonstrated the potential application of a single zinc-layered hydroxide as host for the controlled release of two herbicides, namely DPBA (4-(2,4-dichlorophenoxy) butyrate) and CPPA (2-(3-chlorophenoxy) propionate), simultaneously. The impact of host structure on urea release rate and function in the field of urea nanocomposites associated with an exfoliated clay mineral prepared using various concentrations of hydrophilic or hydrophobic polymers was studied by Pereira et al. (2015) while developing a novel slow-release nanocomposite nitrogen fertilizer. These workers found that nitrous oxide (N₂O) emissions in the field were reduced substantially in the case of the nanocomposites, whether composed of polyacrylamide hydrogel or polycaprolactone, compared with no nanocarrier. The controlled release system enables regulated delivery of agrochemicals, maintaining their activity in the soil throughout a desired interval. This means that less agrochemical than otherwise needs to be applied, with concomitant savings in the manpower and energy (e.g., fossil fuel) needed to operate the application device (Aouada and Moura, 2015). Urea-hydroxyapatite (HA) nanohybrids for the slow release of nitrogen were developed by Kottegoda et al. (2017). Their work was a further demonstration of how nanotechnology can be used to develop slow-release fertilizers, which can significantly reduce the amount of chemicals used while maintaining crop yield. Laboratory data for the release of urea from nanohybrids with a 1:6 (HA): urea ratio released urea twelve times more slowly compared to pure urea (Chhowalla, 2017). Farmer-led trials in rice fields revealed that by using half as much nitrogen from the urea-HA nanohybrids, the same fertilization could be achieved under alluvial soil conditions.

Polymer nanoparticles and inorganic nanoparticles can be used as nanocarriers for pesticide delivery systems (Athanassiou, 2017). The controlled release and targeted delivery of nanoscale active ingredients can realize the potential of sustainable and precision agriculture (Raliya et al., 2017). The nanoscale carriers mentioned in the text to deliver agriproducts are summarized in Table 2.

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Nanocarrier	Attribute	Reference
Surfactant-modified zeolite (SMZ)	Controlled nitrate release	Li, 2003
Zinc aluminium layered hydroxide nanocomposite	Controlled release of the herbicide 2, 4- dichlorophenoxyacetate	Hussein et al., 2005
Mesoporous silica nanoparticles	Delivery of DNA and chemicals into plants	Torney et al., 2007
Sulfur-coated fertilizer	Slow release of fertilizer	Liu et al., 2008
Chitosan nanoparticles	Controlled release of NPK fertilizer	Corradini et al., 2010
Gold nanoparticles embedded in sharp carbonaceous carriers	High DNA delivery efficiency into plants	Vijayakumar et al., 2010
Single-layered zinc hydroxide	Controlled release of two herbicides simultaneously	Hussein et al., 2013
Mesoporous silica nanoparticles	Controlled release of urea	Wanyika et al., 2012
Mesoporous silica nanoparticles	Suitable for accommodation of biomolecules	Hussain et al., 2013
Biocompatible silica nanocapsules	Fipronil carrier against economically important subterranean termites	Wibowo et al., 2014
Zinc layered hydroxide (ZLH) nanocomposite	Release of chlorprop	Hashim et al., 2014
Functionalized mesoporous silica nanoparticles	Potential and efficient technique to deliver agrochemicals	Yi et al., 2015
Exfoliated clay mineral nanocomposite	Controlled urea release	Pereira et al., 2015
Mesoporous silica nanoparticles	Pyrimethanil loading	Zhao et al., 2017
Urea-HA nanohybrids	Controlled release of urea	Chhowalla, 2017
Urea-hydroxyapatite nanohybrids	Slow release of nitrogen	Kottegoda et al., 2017
Polymer and inorganic nanoparticles	Pesticide delivery system	Athanassiou, 2017
Glutathione-responsive mesoporous silica nanoparticles	Delivery of abscisic acid to arabidopsis seedlings	Sun et al., 2018

Table 2. Nanocarriers and their use for agrochemical release.

Regulation and legislation related to nanomaterials

Plants, animals and the environment are exposed to nanomaterials directly or indirectly (Ray et al., 2009). Due to possible hazardous effects, risk assessment of these new materials is compulsory for safety purposes (Reijnders, 2006). As such, there is no specific regulation or legislation related to nano-agriproducts, but the legislation dealing with nanomaterials is applicable to nano-agriproducts. Various regulations are being implemented in different jurisdictions for the safe use of nanomaterials as a whole. In the USA, risk assessment of nanotechnology is the joint responsibility of the Environmental Protection Agency (EPA) and the Food and Drug Administration (FDA) (Duvall and Wyatt, 2011). The EPA follows the Toxic Substances Control Act (TSCA), which encompasses new uses of chemicals before they enter the market, imposes restrictions and then adds the chemicals to the toxic list if appropriate. The relationship between nanotechnology and the EPA's statutory mandate includes providing recommendations related to potential environmental benefits, or indicating research needs associated with nanotechnology risk assessment. Under EPA norms, it is mandatory for nanomaterial manufacturers to provide information about the production volume, methods of manufacture, exposure and health & safety data. The main focus of the EPA is on single-walled

and multi-walled CNTs and on nanoscale clays and silica. The EPA also devises tests for nanomaterials in commerce, particularly those not already being tested by other international organizations. Nanomaterial users are not required to supply information to the EPA; they may be asked for information given by the suppliers, especially data related to exposure in use. The FDA does not automatically categorize all products that involve nanomaterials as harmful. Regulation of nanotechnology products is done in accordance with the specific legal standards applicable to each type of product. The FDA addresses issues including regulatory status, quality, performance, effectiveness, occupational safety and public health impact of nanotechnology products through product-specific guidance documents. Beside the EPA and FDA, the Consumer Product Safety Commission (CPSC), the Occupational Safety and Health Administration (OSHA) and the National Institute for Occupational Safety and Health (NIOSH) look after the nanosafety of nanomaterials in the USA.

In Europe, the REACH (Registration, Evaluation, Authorisation & Restriction of Chemicals) and Classification, Labelling & Packaging (CLP) frameworks control nanosafety measures. the Asia–Pacific region has its own agencies for controlling the safety of nanomaterials. In Japan, the Ministry of Economy, Trade and Industry (METI) and the National Institute of Advanced Industrial Science and Technology (AIST) looks after nanosafety regulations. In China, the National Centre for Nanoscience and Technology (NCNST) and the National Steering Committee for Nanoscience and Nanotechnology (NSCNN) prepare drafts essential for nanotechnology standards including terminology, methodology and safety in the fields of nanoscale measurements, materials and nanoscale biomedicine. In Thailand, the National Nanotechnology Centre (NANOTEC) puts a "Nano Q" standard nanomark for selected Thai nanoproducts to identify the types, sizes and properties of nanoparticles contained in them. In Australia, the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) controls nanosafety measures. In India, there is no such company or agency dedicated toward the risk assessment or looking after the safety of nanomaterials, despite a plethora of nanotechnology initiatives (Dutta, 2007).

International agencies and organizations also contribute towards the biosafety of nanomaterials. The Organization for Economic Co-operation and Development (OECD) formed a Working Party on Manufactured Nanomaterials (WPMN) to check nanomaterial biosafety. The International Organization for Standardization (ISO) has established a technical committee (ISO/TC 229) to develop international standards for nanotechnology (Hatto, 2007). The International Agency for Research on Cancer (IARC) operates under the auspices of the World Health Organization (WHO) and the American Society for Testing and Materials (ASTM) for evaluating nanomaterials and developing nanosafety measures. Internationally renowned national laboratories such as the UK's NPL are heavily involved in developing metrology suitable for nanotechnology (Peggs, 2005; Minelli and Clifford, 2012). Nanomaterial manufacturers (nanofacturers) provide guidance on safety, health and environmental matters in product-specific safety data sheets (SDSs) for substances classified as manufactured nanomaterials and for chemical products containing manufactured nanomaterials. Finally, the efforts of the Integrated Nano Science & Commodity Exchange (INSCX) to develop international commercial trading of nanomaterials along the lines of those long established for metals, grains etc. should be noted (McGovern, 2010); concomitant development of standards and globally uniform regulation is part of this effort (McGovern, 2014). The state of legislation concerning the use of nanomaterials in different countries is summarized in Table 3.

Agency/Organization	Origin	Role
Environmental Protection Agency (EPA), Food and Drug Administration (FDA)	USA	Undertake risk assessment and recommend regulation/legislation related to nanotechnology
Consumer Product Safety Commission (CPSC), National Institute for Occupational Safety and Health (NIOSH)	USA	Ensure safety of nanomaterials
REACH (Registration, Evaluation, Authorization & Restriction of Chemicals) and Classification, Labelling & Packaging (CLP)	European Union	Control nanosafety measures
Ministry of Economy, Trade and Industry (METI)	Japan	Control the safety of nanomaterials
National Center for Nanoscience and Technology (NCNST) and National Steering Committee for Nanoscience and Nanotechnology (NSCNN)	China	Draft essential standards including terminology, methodology and safety in the fields of nanoscale measurements, materials and nanoscale biomedicine
National Nanotechnology Centre (NANOTEC)	Thailand	Put "Nano Q" standard nanomark for selected Thai nanoproducts to indicate types, sizes, and properties of nanoparticles
National Industrial Chemicals Notification and Assessment Scheme (NICNAS)	Australia	Control safety measures
Working Party on Manufactured Nanomaterials (WPMN)	OECD	Issue guidance documents on characterization, dosimetry and risk assessment issues related to nanomaterials
International Organization for Standardization (ISO)	ISO member countries	Develop standard terminology and metrology procedures for substances classified as manufactured nanomaterials and chemical products containing manufactured nanomaterials

Table 3. Governing bodies regarding the use of nanomaterials.

Future challenges

Exposure to nanofertilizers and nanocarriers is likely to increase in the near future because of their wide applications in the advancement of agriculture. Large gaps in knowledge exist regarding the fate of nanofertilizers and nanocarriers once they have been used for their designed purposes or after unintentional releases. Repercussions on the environment and health ramifications for human beings as well as to other life forms are still largely a mystery, albeit intensively studied in the context of medicine (Revell, 2006). It is therefore imperative to frame legislation for nanomaterials employed in crop production, generate comprehensive nanosafety data and, most importantly, direct the relevant industries to follow the new rules for the safe use of nanomaterials in agriculture once they are enacted. There is the utmost need to assess the safety of these new nano-agriproducts before their large-scale practical application in agriculture for crop production.

References

Aouada FA, de Moura MR (2015). Nanotechnology applied in agriculture: Controlled release of agrochemicals. In: *Nanotechnologies in Food and Agriculture* (eds M. Rai et al.), pp.103–116. Springer International.

Askary M, Amirjani MR, Saberi T (2017). Comparison of the effects of nano-iron fertilizer with ironchelate on growth parameters and some biochemical properties of *Catharanthus roseus*. *J Plant Nutr*. **40**, 974–882.

Athanassiou CG, Kavallieratos NG, Benelli G, Losic D, Rani PU, Desneux N (2017). Nanoparticles for pest control: current status and future perspectives. *J. Pest Sci.* **91**, 1–15.

Bruinsma J (2009). The resource outlook to 2050: By how much do land, water and crop yields need to increase by 2050? In: *FAO Expert Meeting. How to Feed the World in 2050*. (24–26 June 2009 in Rome, Italy), pp. 2–16. Economic and Social Development Department, Food and Agriculture Organization of the United Nations.

Burman U, Saini M, Kumar P (2013). Effect of zinc oxide nanoparticles on growth and antioxidant system of chickpea seedlings. *Toxicol. Environ. Chem.* **95**, 605–612.

Campbell JL, Arora J, Cowell SF, Garg A, Eu P, Bhargava SK, Bansal V (2011). Quasi-cubic magnetite/ silica core-shell nanoparticles as enhanced MRI contrast agents for cancer imaging. *PLoS ONE* **6**, e21857.

Chhowalla M (2017). Slow release nanofertilizers for bumper crops. ACS Central Sci 3, 156–157.

Corradini E, De Moura MR, Mattoso LH (2010). A preliminary study of the incorporation of NPK fertilizer into chitosan nanoparticles. *Express Polym. Lett.* **4**, 509–515.

Delfani M, Baradarn Firouzabadi M, Farrokhi N, Makarian H (2014). Some physiological responses of black-eyed pea to iron and magnesium nanofertilizers. *Commun. Soil Sci. Plant Anal.* **45**, 530–540.

DeRosa MC, Monreal C, Schnitzer M, Walsh R, Sultan Y (2010). Nanotechnology in fertilizers. *Nature Nanotechnol.* **5**, 91.

Dimkpa CO, Bindraban PS (2017). Nanofertilizers: new products for the industry? J. Agric. Food Chem. 66, 6462–6473.

Dimkpa CO, Singh U, Bindraban PS, Elmer WH, Gardea-Torresdey JL, White JC (2018). Exposure to weathered and fresh nanoparticle and ionic Zn in soil promotes grain yield and modulates nutrient acquisition in wheat (*Triticum aestivum*). *J Agric. Food Chem.* **66**, 9645–9656.

Dimkpa CO, White JC, Elmer WH, Gardea-Torresdey J (2017). Nanoparticle and ionic Zn promote nutrient loading of sorghum grain under low NPK fertilization. *J. Agric. Food Chem.* **65**, 8552–8559.

Dutta DK (2007). Nanoscience and nanotechnology initiatives in India. *Nanotechnol. Perceptions* **3**, 25–33.

Duvall MN, Wyatt AM (2011). *Regulation of Nanotechnology and Nanomaterials at EPA and Around the World: Recent developments and context.* Washington, DC: Beveridge & Diamond.

Gao F, Hong F, Liu C, Zheng L, Su M, Wu X, Yang F, Wu C, Yang P (2006). Mechanism of nano-anatase TiO_2 on promoting photosynthetic carbon reaction of spinach: inducing complex of rubisco-rubisco activase. *Biol. Trace Element Res.* **111**, 239–253.

Ghafariyan MH, Malakouti MJ, Dadpour MR, Stroeve P, Mahmoudi M (2013). Effects of magnetite nanoparticles on soybean chlorophyll. *Environ. Sci. Technol.* **47**, 10645–10652.

Ghalamboran MR, Ramsden JJ, Ansari F (2009). Growth rate enhancement of *Bradyrhizobium japanicum* due to magnetite nanoparticles. *J. Bionanosci.* **3**, 1–6.

Hatto P (2007). Standardization for nanotechnology, Nanotechnol. Perceptions 3, 123–130.

Hillebrand E (2009). Poverty, growth and inequality over the next 50 years. In: *Expert Meeting on How to Feed the World in 2050* (24–26 June 2009 in Rome, Italy), pp. 1–22. Economic and Social Development Department, Food and Agriculture Organization of the United Nations.

Hong F, Zhou J, Liu C, Yang F, Wu C, Zheng L, Yang P (2005). Effect of nano-TiO₂ on photochemical

reaction of chloroplasts of spinach. Biol. Trace Element Res. 105, 269-280.

Hua KH, Wang HC, Chung RS, Hsu JC (2015). Calcium carbonate nanoparticles can enhance plant nutrition and insect pest tolerance. *J. Pesticide Sci.* **40**, 208–213.

Hussain HI, Yi Z, Rookes JE, Kong LX, Cahill DM (2013). Mesoporous silica nanoparticles as a biomolecule delivery vehicle in plants. *J. Nanoparticle Res.* **15**, 1676.

Hussein MZ, Yahaya AH, Zainal Z, Kian LH (2005). Nanocomposite-based controlled release formulation of an herbicide, 2, 4-dichlorophenoxyacetate encapsulated in zinc–aluminium-layered double hydroxide. *Sci. Technol. Adv. Mater.* **6**, 956.

Hussein MZ, Abdul Rahman NS, Sarijo SH, Zainal Z (2012). Herbicide-intercalated zinc layered hydroxide nanohybrid for a dual-guest controlled release formulation. *Intl J. Molec. Sci.* **13**, 7328–7342.

Kah M (2015). Nanopesticides and nanofertilizers: emerging contaminants or opportunities for risk mitigation? *Frontiers Chem.* **3**, 1–6.

Kah M, Tufenkji N, White JC (2019). Nano-enabled strategies to enhance crop nutrition and protection. *Nature Nanotechnol.* **14**, 532–540.

Khodakovskaya M, Dervishi E, Mahmood M, Xu Y, Li Z, Watanabe F, Biris AS (2009). Carbon nanotubes are able to penetrate plant seed coat and dramatically affect seed germination and plant growth. *ACS Nano* **3**, 3221–3227.

Kottegoda N, Sandaruwan C, Priyadarshana G, Siriwardhana A, Rathnayake UA, Berugoda Arachchige DM, Kumarasinghe AR, Dahanayake D, Karunaratne V, Amaratunga GA (2017). Urea-hydroxyapatite nanohybrids for slow release of nitrogen. *ACS Nano* **11**, 1214–1221.

Kwon S, Singh RK, Perez RA, Abou Neel EA, Kim HW, Chrzanowski W (2013). Silica-based mesoporous nanoparticles for controlled drug delivery. Silica-based mesoporous nanoparticles for controlled drug delivery. *J. Tissue Engng* **4** (doi: 10.1177/2041731413503357).

Lee S, Kim S, Kim S, Lee I (2013). Assessment of phytotoxicity of ZnO NPs on a medicinal plant, *Fagopyrum esculentum. Environ. Sci. Pollution Res.* **20**, 848–854.

Li ZZ, Xu SA, Wen LX, Liu F, Liu AQ, Wang Q, Sun HY, Yu W, Chen JF (2006). Controlled release of avermectin from porous hollow silica nanoparticles: Influence of shell thickness on loading effiCiency, UV-shielding property and release. *J. Controlled Release* **111**, 81–88.

Li Z (2003). Use of surfactant-modified zeolite as fertilizer carriers to control nitrate release. *Microporous Mesoporous Mater.* **61**, 181–188.

Lin D, Xing B (2008). Root uptake and phytotoxicity of ZnO nanoparticles. *Environ. Sci. Technol.* **42**, 5580–5585.

Liu F, Wen LX, Li ZZ, Yu W, Sun HY, Chen JF (2006). Porous hollow silica nanoparticles as controlled delivery system for water soluble pesticide. *Mater. Res. Bull.* **4**, 2268–2275.

Liu J, Wang FH, Wang LL, Xiao SY, Tong CY, Tang DY, Liu XM (2008). Preparation of fluorescence starchnanoparticle and its application as plant transgenic vehicle. *J. Central S. Univ. Technol.* **15**, 768–773.

Liu R, Lal R (2014). Synthetic apatite nanoparticles as a phosphorus fertilizer for soybean (*Glycine max*). Sci. Rep. 4, 5686.

McGovern M (2010). Commoditization of nanomaterials. Nanotechnol. Perceptions 6, 155–178.

McGovern M (2014). Regulation of nanotechnology: developing a level regulatory playing field for emerging materials. *Nanotechnol. Perceptions* **10**, 24–28.

Miflin B (2000). Crop improvement in the 21st century. J. Exp. Bot. 51, 1-8.

Minelli C, Clifford CA (2012). The role of metrology and the UK National Physical Laboratory in nanotechnology. *Nanotechnol. Perceptions* **3**, 59–75.

Monreal CM, DeRosa M, Mallubhotla SC, Bindraban PS, Dimkpa C (2016). Nanotechnologies for increasing the crop use efficiency of fertilizer-micronutrients. *Biol. Fertility Soils* **52**, 423–437.

Nair R, Varghese SH, Nair BG, Maekawa T, Yoshida Y, Kumar DS (2010). Nanoparticulate material delivery to plants. *Plant Sci.* **179**, 154–163.

Park HJ, Kim SH, Kim HJ, Choi SH (2006). A new composition of nanosized silica-silver for control of various plant diseases. *Plant Pathol. J.* **22**, 295–302.

Peggs GN (2005). Measurement in the nanoworld. Nanotechnol. Perceptions 1, 18–23.

Pereira EI, Da Cruz CC, Solomon A, Le A, Cavigelli MA, Ribeiro C (2015). Novel slow-release nanocomposite nitrogen fertilizers: the impact of polymers on nanocomposite properties and function. *Ind. Engng Chem. Res.* **54**, 3717–3725.

Popat A, Liu J, Hu Q, Kennedy M, Peters B, Lu GQ, Qiao SZ (2012). Adsorption and release of biocides with mesoporous silica nanoparticles. *Nanoscale* **4**, 970–975.

Prasad R, Bhattacharyya A, Nguyen QD (2017). Nanotechnology in sustainable agriculture: recent developments, challenges, and perspectives. Frontiers in microbiology. *Frontiers Microbiol.* **8**, 1014.

Raliya R, Saharan V, Dimkpa C, Biswas P (2017). Nanofertilizer for precision and sustainable agriculture: current state and future perspectives. *J. Agric. Food Chem.* **66**, 6487–6503.

Raliya R, Tarafdar JC, Biswas P (2016). Enhancing the mobilization of native phosphorus in the mung bean rhizosphere using ZnO nanoparticles synthesized by soil fungi. *J. Agric. Food Chem.* **64**, 3111–3118.

Ray PC, Yu H, Fu PP (2009). Toxicity and environmental risks of nanomaterials: challenges and future needs. *J. Environ. Sci. Health C* **27**, 1–35.

Reijnders L (2006). Cleaner nanotechnology and hazard reduction of manufactured nanoparticles. J. Cleaner Production 14, 124–133.

Revell PA (2006). The biological effects of nanoparticles. Nanotechnol. Perceptions 2, 283–298.

Rui M, Ma C, Hao Y, Guo J, Rui Y, Tang X, Zhao Q, Fan X, Zhang Z, Hou T, Zhu S (2016). Iron oxide nanoparticles as a potential iron fertilizer for peanut (*Arachis hypogaea*). *Frontiers Plant Sci.* **7**, 815.

Sabir A, Yazar K, Sabir F, Kara Z, Yazici MA, Goksu N (2014). Vine growth, yield, berry quality attributes and leaf nutrient contentof grapevines as influenced by seaweed extract (*Ascophyllum nodosum*) and nanosize fertilizer pulverizations. *Scientia Horticulturae* **175**, 1–8.

Savci S (2012). Investigation of effect of chemical fertilizers on environment. *APCBEE Procedia* 1, 287–292 (ICESD, 5–7 January 2012, Hong Kong).

Shi YT, Cheng HY, Geng Y, Nan HM, Chen W, Cai Q, Chen BH, Sun XD, Yao YW (2010). The size-controllable synthesis of nanometer-sized mesoporous silica in extremely dilute surfactant solution. *Mater. Chem. Phys.* **20**, 193–198.

Sun D, Hussain HI, Yi Z, Rookes JE, Kong L, Cahill DM (2018). Delivery of abscisic acid to plants using glutathione responsive mesoporous silica nanoparticles. *J. Nanosci. Nanotechnol.* **18**, 1615–1625.

Tarafdar et al. (2014). Development of zinc nanofertilizer to enhance crop production in pearl millet (*Pennisetum americanum*). *Agric. Res.* **3**, 257–262.

Torney F, Trewyn BG, Lin VS, Wang K (2007). Mesoporous silica nanoparticles deliver DNA and chemicals into plants. *Nature Nanotechnol.* **2**, 295–300.

Vijayakumar PS, Abhilash OU, Khan BM, Prasad BL (2010). Nanogoldloaded sharpedged carbon bullets as plant gene carriers. *Adv. Functional Mater.* **20**, 2416–2423.

Wanyika H, Gatebe E, Kioni P, Tang Z, Gao Y (2012). Mesoporous silica nanoparticles carrier for urea: potential applications in agrochemical delivery systems. *J. Nanosci. Nanotechnol.* **12**, 2221–2228.

Wibowo D, Zhao CX, Peters BC, Middelberg AP (2014). Sustained release of fipronil insecticide in vitro and in vivo from biocompatible silica nanocapsules. J. Agric. Food Chem. 62, 12504–12511.

Wilson MA, Tran NH, Milev AS, Kannangara GK, Volk H, Lu GM (2008). Nanomaterials in soils. *Geoderma* **146**, 291–302.

Xuming W, Fengqing G, Linglan M, Jie L, Sitao Y, Ping Y, Fashui H (2008). Effects of nano-anatase on ribulose-I, 5-biphosphate carboxylase/oxygenase mRNA expression in spinach. *Biol. Trace Element Res.* **126**, 280–289.

Yang F, Hong F, You W, Liu C, Gao F, Wu C, Yang P (2006). Influence of nano-anatase TiO₂ on the nitrogen metabolism of growing spinach. *Biol. Trace Element Res.* **110**, 179–190.

Yi Z, Hussain HI, Feng C, Sun D, She F, Rookes JE, Cahill DM, Kong L (2015). Functionalized mesoporous silica nanoparticles with redox-responsive short-chain gatekeepers for agrochemical delivery. *ACS Appl. Mater. Interfaces* 7, 9937–9946.

Zhao P, Cao L, Ma D, Zhou Z, Huang Q, Pan C (2017). Synthesis of pyrimethanil-loaded mesoporous silica nanoparticles and its distribution and dissipation in cucumber plants. *Molecules* **22**, 817.

Zheng L, Hong F, Lu S, Liu C (2005). Effect of nano-TiO₂ on strength of naturally aged seeds and growth of spinach. *Biol. Trace Element Res.* **104**, 83–91.