CHAPTER

10 Holistic view for the safe use of nanomaterials at permissible level for plant production

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Chapter Outline

10.1 Introduction

There are a variety of nanomaterials in use by numerous industries. Generally, nanomaterials can be classified into several categories such as nanoparticles, nanotubes and nanofibers, nanofilms, nanoblock, nanocomposites, and

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nanocrystalline solids (Aslani et al., 2014). The terminology "nanomaterial" was recommended and proposed by European Commission in October 2011. Based on the terminology by The International Organization for Standardization (ISO) TS 80004-1, materials that possess at least one of the external dimensions or internal structure within the size range of 1–100 nm (1 nm = 10^{-9} m = 0.000000001 m) is called nanomaterials. In the ISO 80004-1 standard, two families of nanomaterials, namely nano-objects and nanostructured materials, were identified. Nano-objects, usually applied in the form of powder, liquid suspension, and gel form, referred to the materials having one to three nano-scaled dimensions. Materials that are classified under nano-objects are (1) nanoparticles; (2) nanofibers, nanotubes, nanofilaments, or nanorods; and (3) nanoplates. Meanwhile, another class of nanomaterial called nanostructured materials are the materials that possess nano-scaled internal structure. The examples include (1) aggregates and agglomerates of nano-objects; (2) nanocomposites; and (3) nanoporous materials. The detailed classification of both nano-objects and nanostructured materials are summarized in Table 10.1.

Table 10.1 Classification of nanomaterials based on ISO TS 80004-1.

Class	Example	Description
Nano-objects	Nanoparticles • Nanoparticles of latex, zinc, calcium carbonate, etc.	Materials that have three nano-scaled dimensions
	Nanofibers, nanotubes, nanofilaments, or nanorods • Carbon and boron nanotubes, polyester nanofibers, etc.	Materials, normally elongated, that have two nano-scaled dimensions and a significantly larger third dimension
	Nanoplates • Clay and cadmium selenide nanoplates	Materials that have one nano-scaled dimension and significantly larger second and third dimensions
Nanostructured materials	Aggregates and agglomerates of nano-objects	Nanomaterials that exist in individual or aggregates and agglomerates form
	Nanocomposites	Nanomaterials that are specifically used as a reinforcement to improve mechanical and thermal properties of a matrix
	Nanoporous material • Silica aerogels	Materials that have nano-scaled pores and possess high thermal insulation properties

10.2 Global market of nanomaterials

According to Wise Guy Reports (2018), in the year 2015, a total amount of USD 4.79 billion was recorded for the global nanomaterials market. This amount is expected to be increasing steadily in the next few years and anticipated to reach USD 19.83 billion by 2022, growing at a compound annual growing rate (CAGR) of 22.5% from 2015 to 2022. Meanwhile, some pessimistic expectation of 15.5% CAGR of global nanomaterials has also been reported (Inshakova and Inshakov, 2017).

North America is the leading consumer of nanomaterials, followed by Europe. In 2015, USD 2.54 billion of revenue was generated by the European nanomaterials market and it is expected to reach USD 9.1 billion by 2022 with a CAGR of 20.0% during 2016−22 (Allied Market Research, 2016). The expansion of European nanomaterials market is mainly attributed to the increased usage of nanomaterials in healthcare and electronics industries. On the other hand, Asia Pacific also witnessed a significant growth in nanomaterials market during the last few years due to the increasing awareness toward environmental issues, favorable government initiatives and the rising demand for specialty materials. Two manufacturing powerhouses, China and India, had the fastest growth in nanomaterials demand throughout the year 2016.

10.3 Application of nanomaterials in agriculture

Over the past few years, nanotechnology has been identified as a potential tool in agricultural sector to regulate plant growth and improve its genetics as well as its use as pesticides and biosensors (Hong et al., 2013). Nanomaterials are commonly applied in agricultural sector to improve the efficacy of nutrient distribution as well as the controlled release of pesticides and other agrochemicals. Nanomaterials are often used to detect pathogens and identify preservation. Normally, the usage of nanomaterials in agriculture are by means of nano-encapsulations, nanoparticles, nano-emulsions, etc. (Amenta et al., 2015). Advancement of nanotechnology has created unique properties of nanomaterials with different sizes and shapes targeted toward specific applications. The development of nanotechnology has significantly expanded the application domain of nanomaterials in various fields. Agriculture is amongst that expected to be benefited from nanotechnology. The unique properties of nanomaterials have been employed to improve plant production via nano-sensors, nano-fertilizers, and nano-pesticides. Like many others new inventions, nanomaterials can be exciting from a scientific perspective; however, the potential risks and toxicities of nanomaterials will likely take decades to evaluate. The incident of “Silent Spring” is one of the best lessons that history has taught us, and it suggests the wisdom of taking a precautionary approach toward this new technology.

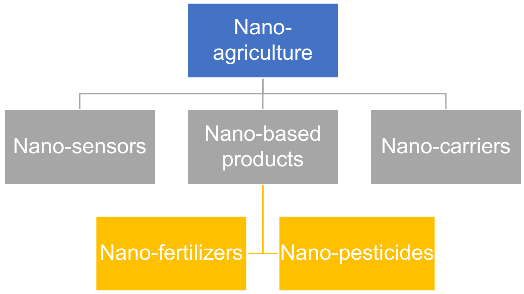

FIGURE 10.1

Nanotechnologies used in agricultural practices.

Nanomaterials are generally materials with a particle size less than 100 nm in at least one dimension. This emerging technology has withdrawn ample attention in the past decade and was valued at USD 11.7 billion globally in 2009. Rapid advance of this technology has engaged diverse industry sectors and not being left out, the food and agriculture industry. Agriculture is the only sector that feed the world population directly and indirectly. As world population is increasing, agricultural productions have to catch up with the growth. It is thus becoming necessary to use the modern technologies such as nanotechnologies in order to achieve this goal. Variety of carbon-based, metal, and metal oxide-based dendrimers (nano-sized polymers) and biocomposites nanomaterials are being used in agriculture production and crop protection (Bouwmeester et al., 2009; Nair et al., 2010; Sharon et al., 2010; Emamifar et al., 2010).

The evolving major role of nanomaterials in agriculture sectors is illustrated in Fig. 10.1. It is believed to be one of a solution for the pertinent issues in sustainable production and food security, which will lead to reduction in the production costs and maximize the output. Precision farming by employing nano-sensors to measure and manage variabilities such as yield, soil, pest, and weed across the fields can enhance efficiency in the management of agricultural practices in the cropping system; smart delivery systems on either using engineered fertilizer/nutrient in nanoscale size in order to increase uptake may result in greater nutrient use efficiency or incorporating with nano-carriers for the delivery of active ingredients to reduce losses and increase yields through optimized and sustainable nutrient uptake and water transport (Gogos et al., 2012; Martínez-Fernandez et al., 2016).

10.3.1 Nano-sensors

Sensors that have been developed in miniature size are being incorporated in precision farming by sprinkling it across a field to sense light, temperature, vibration, magnetism, or chemicals through radio frequency identification. This tiny microelectromechanical systems that linked directly to a computer through wireless are called "smart dust." Besides, sensors based on TiO_2 or nanocrystalline SnO_2 can serve as indicators for O_2, gases, pH changes, or the formation of metabolites due to microbiological growth (Peters et al., 2016). Permanent field characteristics are being established by recoding at precise locations over time to enable the study of spatial and temporal variabilities. This precision can only be achieved by retrieving the data in real-time and translate them into information and knowledge for use in improving the production system. Nano-sensors that are able to cover large area thereby offer significant improvements in selectivity, speed, and sensitivity to retrieve changes on the information maps of temperature distribution (or any other essential data) on the spot and can help in developing a strategy to prevent or control the disease (Joyner and Kumar, 2015). Overall, the goal of precision farming is to define a decision support system for whole farm management with the goal of optimizing returns on inputs while preserving resources (Reina, 2018), and this can be better achieved by incorporating nanosensors for precise data collection.

10.3.2 Nano-fertilizers

Applications of nanotechnologies in agrochemicals products can be either on the chemicals itself or integrating with other components. In other words, the nutrients can be encapsulated inside nanoporous materials or delivered as particles or emulsions of nanoscales dimensions (Rai et al., 2012). These implications are aimed for targeted delivery and sustainable release of nano-agrochemicals products in response to environmental stimuli and biological demand in order to increase nutrients use efficiency, reduces soil toxicity, minimizes the potential negative effects of over dosage, and reduces the cost on frequent application (Naderi and Danesh-Shahraki, 2013). Chitosan, liposomes, and dendrimers are among the few organic nanoparticles being used for nano-encapsulation that serve to increase the stability, delivery, and bioavailability of nutrients (vitamins, minerals) and agrochemicals (Anu Puri et al., 2009). Inorganic nanoparticles such as clays, zeolites, ZnO, SiO_2, and TiO_2 are also widely employed in this smart delivery system (Lei et al., 2007; Chinnamuthu and Boopathi, 2009; Burman et al., 2013; Mahmoodzadeh et al., 2013; Zhao et al., 2014).

10.3.3 Nano-pesticides

Reducing the amount of pesticide consumption via effective targeted delivery to the pests is very much concerned to reduce the cost and lost in plant production and relieve the impact of pesticide to the environment (Sharon et al., 2010). This could be achieved by extending the release time with better contact due to high surface area to volume ratio (Allen, 1994; Kim et al., 2007). For instance, nanoparticles derived from clay, silica, biodegradable polymers (e.g., chitosan, alginates, and starch) and polyesters (e.g., poly-ε-caprolactone and polyethylene glycol) are being used or in the stage of development in order to produce less harmful plant protection products in combination with biodegradable polymers (Dwivedi et al., 2016). Certain natural substances, which exhibit pesticidal properties but are unstable after application (Macías et al., 2004), can now be improvised through nano-formulations in the form of nano-spheres, nano-gels, or nanofibers applied in organic crop production without chemical toxicity concern. The examples of eco-friendly matrices with biological origin such as beeswax, corn oil, ecithin (Nguyen et al., 2012), or cashew gum (Abreu et al., 2012) are in rising demand concurrent with the trend of organic farming.

10.3.4 Nano-carriers

Nano-carriers have been mentioned previously under nano-based products as one of the crucial elements in smart delivery system. In this section, nano-carriers are being discussed as whole in every application they may be involved to achieve the smart delivery. It can be broadly categorized into two main groups, organic and inorganic nanoparticles. While the inorganic nanoparticles have attracted more attention due to their superior material properties with versatile functions, the organic nanoparticles have gained much interests from the aspects of biodegradable and lower toxicity concern.

The use of nano-carriers has a huge scope in agriculture and not being restricted for only fertilizers and pesticides delivery (Liu et al., 2002; Cotae and Creanga, 2005). For instance, inorganic particles such as gold and silica have been used in molecular level to deliver DNA to plant cells (Torney et al., 2007). Other narrow-spectrum agrochemicals have also employed nano-gels to improve the loading and release profiles of the chemicals such as pheromones and essential oils to control or trapping plant pests (Paula et al., 2011; Bhagat et al., 2013). Pure chitosan nano-gels was suggested to deliver copper for a better performance of antifungal treatments. The combination of both inorganic and organic nanoparticles in this case improved distribution and the long-term release of copper on the leaves or into the soil without compromising its antifungal properties. This successful synergistic effect between chitosan and copper in inhibiting the growth of *Fusarium graminearum* has been reported (Brunel et al., 2013).

10.4 Potential harmful effects of nanomaterials to the environment

Nanomaterials are very useful and vital owing to their unique physicochemical properties and wide range of applications in numerous sectors. Nevertheless, at the same time, it may impose some hazards and negative effects to human health, plants, and even environment. Thorley and Tetley (2013) has emphasized the importance of the evaluation and balancing on the efficacy and toxicity of nanomaterials before these nanomaterials were used. Numerous studies have been reported on the behavior of naturally occurring nanoparticles in the environment. These natural nanoparticles in the environment are now accompanied by those that have been released intentionally and unintentionally through the industrial application of various, extremely polymorphic synthetic nanoparticles in unknown amounts.

In the 21st century, products and applications involving nanomaterials is expected to be the basis of many innovations in the environmental and climate protection sectors. With the increasing use of nanomaterials, the hazard potentials and possible risks to the environment and consequent causes on ecosystem health are increasingly becoming a concern (Oberdorster et al., 2002; Oberdorster et al., 2004; Lam et al., 2004; Lee et al., 2007; Warheit et al., 2007; Sharma and Sharma, 2007; Mortensen et al., 2008; Zhang and Monteiro-Riviere, 2008). Because of these concerns, there is a need to understand the characteristics and life cycle analysis of the nanomaterials when being put in use.

There are four major ways that nanoparticles or nanomaterials may make their entry to the environment, toxify, and harm the surrounding: (1) hydrophobic and hydrophilic nanoparticles, (2) mobility of contaminants, (3) solubility, and (4) disposal (Hofmann and Von der Kammer, 2009). TiO_2 powder has been studied by nanocoating researchers to reduce the weathering effects, such as salt rain degradation on composite materials. However, Fenoglio et al. (2009) expressed their concern of the effect of TiO_2 nanoparticles when leaked into the environment where further studies on the impact was suggested before application was made.

During the manufacturing of nanomaterials, solid or liquid waste streams and atmospheric emissions containing nanoparticles may enter the environment through intentional releases as well as unintentional releases. Some may enter the environment relatively during application, with nanoparticles containing products such as paints, fabrics, and personal and health care products, including sunscreens and cosmetics. Eventually, these discharged nanomaterials will deposit on land and water surface. Nanoparticles attained on land are likely to pollute soil and drift into water resources. Nanoparticles in solid wastes, waste water effluents, direct discharges, or accidental spillages can be transferred to aquatic systems by wind or rainwater runoff. The highest possibilities of nanoparticles entering the environment are from accidental spillages during manufacturing and transporting of nanomaterials, intended releases for environmental applications and dispersed from the nanomaterial itself during utilization due to deterioration and disintegration process.

Several factors including pH value, salinity, concentration, existence of organic or inorganic matter are able to influence the series of chemical processes and transformation of nanomaterials in the environment. Nevertheless, synthetic nanomaterials vary in certain aspects from those occurring naturally. The features and properties of a nanomaterial also play a major role. Some experiments have shown that nanomaterials could have harmful effects on aquatic and land animals, including changes to their behavior, development, and reproduction (Table 10.2).

Table 10.2 Harmful effects of nanomaterials on the environment.

Nanomaterials	Possible risks	References
Carbon nanotubes	Accumulate heavy metals, influence transport in water bodies and in biological systems, pulmonary inflammation, granulomas, and fibrosis	Schierz and Zänker (2009), Oberdorster et al. (2002), Warheit et al. (2007), Chou et al. (2008), Lam et al. (2004)
Nano-TiO_2	Damage the cell membrane of microorganisms, skin penetration	Mortensen et al. (2008), Rouse et al. (2007)
Nanosilver	Highly toxic to microorganisms such as bacteria, fungi, and algae, distribution into organs, including central nervous system	Lapied et al. (2010), Oberdorster et al. (2002, 2004), Semmler et al. (2004)

Table 10.3 The mediators of the toxicity of particles.

Characteristics of nanoparticles	Toxicity of particles	References
Size (reduction in size to the nanoscale level results in an enormous increase of surface to volume ratio)	More molecules of the chemical are present on the surface of nanomaterials than larger particles of the same insoluble material when compared on a mass dose base, thus enhancing the intrinsic toxicity	Donaldson et al. (2004)
Chemical composition and surface characteristics	Toxicity of nanoparticles depends on their chemical composition, but also on the composition of any chemicals adsorbed onto their surfaces	Donaldson et al. (2004)
Shape (shape of nanotubes: few nanometers in diameter but with a length that could be several micrometers)	In relation to inhalation, where the physical parameters of thinness and length appear to determine respirability and inflammatory potentialSingle-walled carbon nanotubes were demonstrated to induce lung granulomas after intratracheal administrationOn a dose per mass basis the nanotubes were more toxic than quartz particles	Lam et al. (2004), Warheit et al. (2004)

In recent studies, scientists studying nanoscale processes and products identified and reported the exact size, shape, parent material, and coating of their manufactured nanoparticles (Ali et al., 2015; Rahimi et al., 2016; Patra et al., 2017; Patra and Baek, 2017). This is critical when sharing experimental evidence and predicting their behavior. Parent material, surface characteristics, particle size, and shape are related to the toxicity of nanomaterial as shown in Table 10.3.

10.5 Regulatory aspects of nanotechnology in the agriculture sector

In a usual practice, the efficacy of pesticides and other agrochemicals can be enhanced by increasing their solubility through reducing their dimension. Sometimes, slower and more controlled release could also be achieved by mixing or encapsulating active substances in micro or nano-emulsions and nano-dispersions. In this way, the dosage of use could be reduced (Kah et al., 2012). Nevertheless, despite the lower dosage being used, there is still some possibilities to impose negative impacts to the environment. For example, higher persistence owing to its slow release nature might result in higher residues and impose higher risk to nontarget organisms (Kah and Hofmann, 2014). Therefore, specific legislation or guidance is necessary to make sure these materials will be applied safely.

Physiochemical properties of nanomaterials are unique, and they play a crucial role in plant production that cannot be ignored. However, the potential adverse effects to human health, plant, and environment that might arise caused by the usage of such nanomaterials also cannot be taken lightly. Thus, it is vital to find the balance between efficacy and toxicity of nanomaterials intended to be used in the various aspect of plant production (Thorley and Tetley, 2013). Lately, Jain et al. (2018) suggested through the review of various researches that nanomaterials that are intended to be used in food and food-related products must undergo scrupulous investigation and analysis before being used. European Union (EU) is among the first world region to establish regulations regarding the use of nanomaterials directly or indirectly in agriculture and related sectors. EU and Switzerland are the only two region and country that have established legislative provision for nanomaterials used in agriculture, food, and related sectors. On the other hand, other non-EU countries only provide non-mandatory frameworks binding and guidelines regarding the use of nanomaterials in agriculture (OECD, 2013). However, it is safe to assume that regulations and safety measures that should be taken for other nanomaterials used in sectors other than plant and food production are also applicable to the usage of pesticides in plant production.

In the EU, REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) is the main regulation concerning the safety of substances used on human health and the environment. The specific established regulation regarding the agriculture and food sector is the usage of nanomaterials in plant protection products (pesticides, etc.), food additives and supplement, and food contact materials. In the EU, pesticides are regulated by Plant Protection Products (PPP) Regulation (EC) 1107/2009 (European Parliament and Council, 2009a). According to the above-mentioned regulation, nanomaterials intended for the use of plant protection, such as pesticides, must first undergoe the authorization procedure before the substances are marketed and used. To ensure the safety of the substances used, assessment and analysis are required to be carried out on a case-by-case basis (RIVM, 2012). Through this procedure, potential risk of substances that are not specifically listed in the legislation can also be examined.

In Switzerland, a general "Action Plan for Synthetic Nanomaterials" has been launched by the Swiss Federal council. The action plan is a general chemical regulation and risk assessment which also includes the synthetic nanomaterials use in agriculture sector. Besides that, the risk concerning nanomaterials is also guaranteed by the existing regulations and procedures used by conventional non−nano-derived chemical. Swiss Ordinance required that nanomaterials to be used in pesticides must be submitted for registration (Schweizerischer Bundesrat, 2010). For the registration purposes of nanomaterials used in pesticides, characteristic and properties of the nanomaterials must be provided. Such information includes composition, shape, particle size, surface area, aggregation state, coatings, and functionalization. However, there was reported application of nanomaterials-derived pesticides till the year 2013 (Bucheli, 2014).

The scenario in Australia and New Zealand is that all food in the regions which includes those produced by the aids of nanomaterials, such as pesticides, must comply with the Australia New Zealand Food Standards Code (FSANZ). This is to ensure that the food is safe for consumption. Under the code, any food substances produced (nano-derived substances included) must be subjected to a thorough safety assessment with the appropriate standard for testing. Marketing of such nanomaterials can only be done after the appropriate standard testing have been carried out. FSANZ, which is the body accountable for the regulation of food and related products in Australia and New Zealand, has come out with various plans to manage the potential safety issues for human health and environment regarding nanomaterials used in food production. Recently, new regulations were added to the FSANZ *Application Handbook* under the various strategies to ensure food safety (Fletcher and Bartholomaeus, 2011). FSANZ also summarizes nanomaterials used in food production into two categories, that is those soluble in water or oil and those insoluble in water and oil and are not biodegradable. Owing to the nature of the materials, the insoluble type of nanomaterials is subjected to further regulations and analysis.

Currently in Canada, there are no specific regulations regarding the application of nanomaterials in plant and food production. Therefore, to address the potential health and environment issue of the use of nanomaterials, existing legislation and regulations guidelines are used by Health Canada instead. Health Canada classified nanomaterial as a structure within the nanoscale dimension and displays one or more nanoscale properties (Health Canada, 2011). Furthermore, Health Canada encourage the related party to communicate with the regulatory body from the initial stage of developing nano-derived products that will be used in food production. Besides that, Health Canada also require manufacturers to notify the related regulation authority before the submission process, so that a detailed discussion about the nanomaterials products and safety analysis procedures required can be conducted.

In the United States, related agencies follow the principles for regulation and oversight of emerging technologies due to the issue raised by nanomaterials (Holdren et al. 2011). National Nanotechnology Initiative was founded to leverage the research programs on nanotechnology (Tinkle and Carim, 2011). In terms of the safety of food and related products, the Food and Drug Administration (FDA) is responsible in this regard. The food products are subjected to the Federal Food, Drug, and Cosmetic Act (FFDCA) (US-FDA). Substances such as food additives and coloring are often subjected to the authorization by the FDA before marketing. However, for some food ingredients that are commonly considered as safe for consumption, no such premarketing authorization is mandatory. At the moment, FFDCA does not clarify the required specification for nano-derived products. FDA also does not have a clear definition of nanomaterials for regulation purpose. The FDA uses a rather general but comprehensive approach when dealing with nano-derived food products (Hamburg, 2012).

In Asia, there is currently no specific legislation about the application of nanomaterials in plant production and agriculture sectors. However, nanotechnology was stated as one of the main research areas in the third Science and Technology Basic Plan for 2006−10 by the Japanese government (Government of Japan Council for Science and Technology Policy, 2006). As a result of the plan, in 2007, "Food nanotechnology project" was successfully funded by Japanese Ministry of Agriculture, Forestry and Fisheries. Numerous researches were conducted concerning the nano-scale food products under this particular project, and the results were published in a scientific journal. Moreover, the Japanese Ministry of Health, Labour and Welfare also launched a six-year program (2009−14) entitled the "Research project on the potential hazards, etc. of nanomaterials." In other Asian countries such as Malaysia and India, the regulations are very much dependent on the Nation's Act such as "Food Safety and Standards Act 2006" for India and "The Nanotechnology Industry Development Act" and "The Nanotechnology Safety-Related Act" for Malaysia. On the other hand, the national standards in China for nanotechnology are developed based on the Food Safety Law.

10.6 Conclusion

Owing to the disparities of view across the world and the high uncertainty of regulatory frameworks, it is very difficult to impose a harmonized regulation on the permissible level of nanomaterials to be applied for plant production. A comprehensive risk assessment and risk management are of utmost importance and need to be taken into consideration in developing a regulatory policy for attending the biosafety matters of the application of nanomaterials. Apart from that to ensure an efficient regulatory measure, exchanging point of views with the community and public across the world are also equally important. Before application, the behavior of the nanomaterials and their potential retention in the environment have to be studied thoroughly. The findings could be served as a baseline data for framing regulatory guidelines for balancing the efficacy and toxicity of the nanomaterials. Regulations and risk management for nanomaterials used in plant production is still in its infant stage for many regions. Therefore, scientific community and regulation authorities from around the world alike must work together to come out with a more specific and comprehensive approaches when dealing with nanomaterials used in plant production and protection such as nano-derived pesticides. Permissible amount of nanoparticles pesticides has to be stated in future regulations for better management of various potential risk problems caused by the application of nanomaterials in agriculture sector.

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