Chapter 7
Nanofertilisers, Nanopesticides, Nanosensors of Pest and Nanotoxicity in Agriculture

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Abstract Food security in the world is challenging due to the limited available resources for the rising population. Various efforts are being practiced by governments, organisations and researchers to mitigate the demand and supply gap in human food chain. Agriculture took the roots of growth prior to industrial revolution, in around 90 countries. Though nanotechnology has already found industrial applications, the use of nanotechnology in agriculture is much more recent.

Here we review nanotechnology applications in agriculture such as plant production, protection, and detection of pathogen. We also discuss the environmental risk associated with nanotechnology. The major points are: (1) research funding for nanoresearch is highest in USA, followed by Germany and Japan, whereas China published the highest number of publications, and USA obtained the highest number of patents. (2) Nanofertilizers based on carbon walls, metal and metal oxide increase germination, photosynthesis, nutrient use efficiency and plant growth (3) The metal oxide-based nanomaterials such as ZnO, TiO_2, Cu and SiO_2 are increasingly used in pesticides and fungicides to protect crops from bacterial disease and control microbial activity. (4) Silver, copper and gold nanoparticles are used as bio-nanosensors and electrical-nanosensors to detect a potential pathogen problem in plant and postharvest foods. (5) The level of nanotoxicity in soil, plant and water mainly depend on the composition, size and concentration of the nanoparticles. (6) Nanoparticles of size lower than 50 nm usually adversely affect human health and the potential routing could be through inhalation, ingestion and dermal exposure. Overall, nanotechnology has the potential to increase agricultural production, but there is very limited knowledge about its long term adverse effect on soil, plants and ultimately on human. An intelligent use of nanotechnology may help to achieve food security with the qualitative and sustainable environment.

Keywords Nanotechnology • Agriculture • Agroecology • Nanofertilizer • Nanosensors

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E. Lichtfouse (ed.), *Sustainable Agriculture Reviews*, Sustainable Agriculture Reviews 19, DOI 10.1007/978-3-319-26777-7_7

7.1 Introduction

Food security becomes a fundamental human right and implies that all people, at any socioeconomic and geographical level, whenever they require, must have access to enough, affordable and healthy food that suffice people dietary requirement and food choice for active and healthy life (FAO 2009). Achieving the economic food with the optimum nutritional and calorific values from upper to very last chunk of the population is a hard task for any country due to the population rise. The world's population was about 7 billion in 2013 and it is estimated to attain about 9.6 billion by 2050 and 10.9 billion by 2100 with Asia being the largest contributor, of 60 % of this population (UN World Population Prospects 2013). The net increase of 230,000 people each day in the world increases the demand of food, shelter, and other resources (UN Population Division 2007). With so much of projected population of the world, there comes a very viable social problem of food security. World cereal production including wheat, rice and coarse grains estimated at 2525.4 million tonnes in 2013-2014 and projected to reach about 3 billion tonnes by 2050 (FAO 2009). Of this, 50 % of cereals is used as animal feed to achieve the world's meat demand. The current estimation of 50 % increase in food production is essential to maintain the demand of food grains and cereals by 2050 but due to compounding damaging effects by climate change, land degradation cropland losses, water scarcity and species infestation induce 5–10 % additional food demand (UNEP 2009).

Uncertainty of food production, poor maintenance and distribution are the major challenges of food security. To control food security crises, the first priority is to increase food production by enhancing the resources and technology, and the second priority is to improve quality of available inputs (FAO 2009). Modern technologies that possibly enhance food production could be biotechnology (Ervin et al. 2010; Spiertz 2010), Deoxyribonucleic acid (DNA) (Devos et al. 2007), advance water management techniques such as micro irrigation, crop and soil sensors and modern farm mechanization. Food and agriculture organization (FAO 2000) reported that DNA and biotechnologies increase yield of sweet potato and cassava by 30 % and 27 %, respectively and income of small holder banana farmers by 25 %. Micro irrigation reduces nitrogen emissions and increases tomato crop yield by 78–119 Mg ha^{-1} (Kennedy et al. 2013). Zero tillage operations save 18–53 % energy and reduce 25–41 % cost of cultivation per hectare (Sorensen and Nielsen 2005). All these technologies improve crop production and reduce inputs, but require high skill and basic knowledge and regular monitoring. They are not sufficient to reduce the gap of demand and supply of food. Nanotechnology (Chen and Yada 2011; Sekhon 2014) has the ability to change entire agriculture and food industries and has potential solution to over-come all these problems and increase production. Scientist are working on nanotechnology to improve agriculture. Though nanotechnology can be very effective in making the agricultural production economic and resource efficient. But from the environmental point of view, it creates some unpredicted harmful effects (Bouwmeester et al. 2009; Nel et al. 2006) Therefore, it is essential to study all facets to nanotechnology from the agro-ecology perspective.

7.2 Nanotechnology

Nanotechnology is one of the rising technologies of the twenty-first century. Taniguchi (1974) first coined the term nanotechnology and stated that nanotechnology consists of the processing, separation, consolidation, and deformation of materials by one atom or one molecule. Nanoscience, nanotechnology and nanoengineering involve working under nanosize (one billionth of a meter) scale (NNI 2009). Engineering nano materials can be defined as the material that has single unit of size less than 100 nm (Taniguchi 1974). At nanoscale, the chemical and physical properties of material change and surface area of material is large compared to its volume. This makes material more chemically reactive and changes the strength and electrical properties of material compared to the bulk counterpart.

Application of nanotechnology in different fields anticipated to be beneficial for society and environment, reduce cost of input and increase production, improve quality of product, open opportunity for employment (Hansen and Maynard 2008). It covers a broad area, including medicine biology, electronics and instrumentation, cosmetics, defence, energy, environment, agriculture, information and communication technology. Nanotechnology in medicine involves application of nanoparticles in drug which is more effective than bulk material and directly attracted to the disease cell. (Ramsden 2011, 2013). Nanoparticles are used in sunscreens, abrasion-resistant coatings, barrier coatings, antimicrobial coatings, and fuel combustion catalysts (Ramsden 2013). Nanotechnology also used in high energy physics; carbon nanotube inside silica nano pores used as high resolution particle detector (Angelucci et al. 2003). Other uses of nanotechnology in electronics are to manufacture microchips and data storage devices. The small data storage device has potential to store 400–500 gigabyte/inch^2 data and can be used in wrist watches, mobiles and laptops (Mamalis 2007).

Governments of different counties have been spending millions of dollars on research and development of nanotechnology. The U.S.A government spent $862 million in 2003-2005 and proposed $1574.3 million to different agencies under national nanotechnology initiative (NNI) for year 2013-2016 (NNI budget, 2015). In Japan and china the total budget for nanotechnology were $810 and $280 million, respectively for the year 2003 (Jia 2005). According the Cientifica Ltd (2011) data source, only china spent $1.3 billion on nanotechnology research it is nearly close to U.S. budget for nanotechnology which is about $2.18 billion in 2011. India launched nano mission in 2007 with a budget of $250 million for 5 year with well-established research laboratories for nanotechnology development programme (6th Bangalore India Nano report 2013). The market of nanotechnology was around $147 billion in 2007 and predicted that would reach to $3 trillion by 2020 (Clunan and Hsueh 2014). Figure 7.1 shows the impact of nanotechnology on the economy of different countries. It is clear from the figure and data that contribution of nanotechnology to enhanced the economy of countries like U.S., China, Russia, Germany, and Japan increased. Many countries try to increase annual budget for research and development of nanotechnology to give a good competition in the market. With the

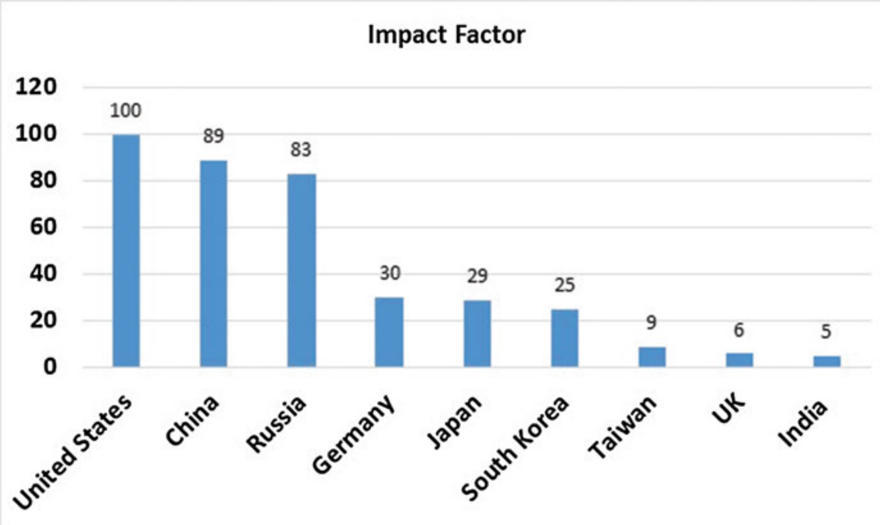

Fig. 7.1 Impact of nanotechnology on the economy of different countries (Source: Cientifica Ltd, 2011)

awareness of government of different countries, publications in nanoscience and technology are increasing rapidly. Figures 7.2 and 7.3 show the trends of research publications and patents available till date. World-wide research publications and patents in different fields of nanotechnology were about 70,000 and 30,000, respectively in the year 2012 (Figs. 7.2 and 7.3). China published large number of articles in 2012 and the USA being the second largest. European Patent Office (EPO) and United State Patent and Trademark Office (UPTO) have been registered worldwide 4994 and 35,081 patent respectively. The number of patents is continuously highest for USA during last 5 years followed by Germany, Japan, France and South Korea. The following sections explain the applications of the nanoparticles in agriculture and the associated risks to agroecology.

7.3 Nanotechnology Applications in Agriculture

Nanotechnology contribution in agriculture is increasing day by day to achieve higher and more stable yield of food grains based on optimizing water and nutrient supply. Application of nanomaterial in agriculture getting a wide space because of its positive response in food production. In agriculture two types of nanomaterials are mostly used: (1) carbon based single and multi-walled carbon nanotubes, (2) metal based aluminium, gold, zinc, and metal oxide based ZnO, TiO_2, and Al_2O_3. Single and multi-walled carbon nanotubes are used as nanosensors and plant regulator to enhance plant growth (Khodakovskaya et al. 2012). Nanosilver is used in

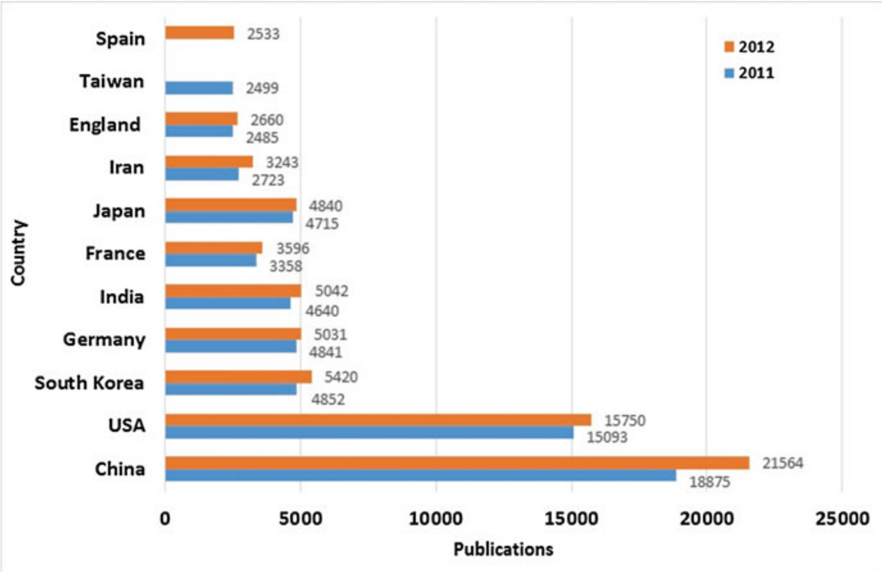

Fig. 7.2 Research publications on nanotechnology related fields during the years 2011 and 2012

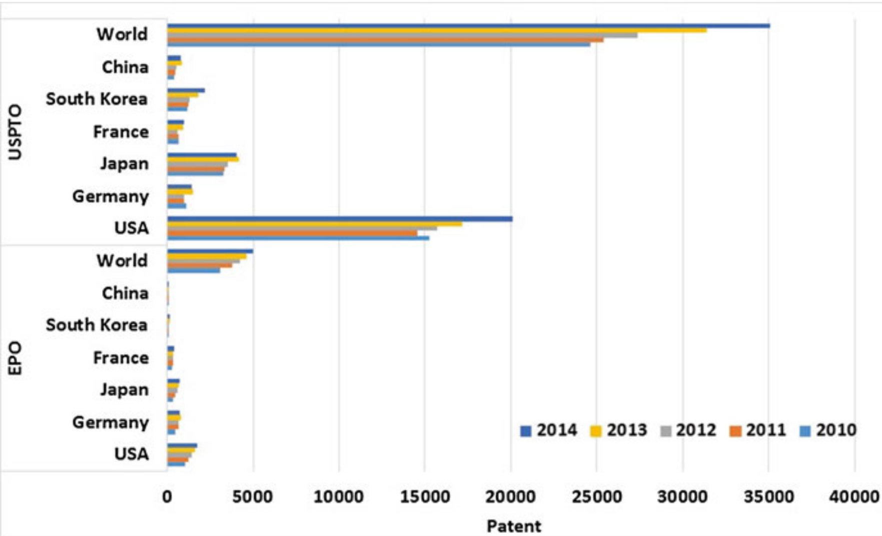

Fig. 7.3 Nanotechnology related patents at the United State Patent and Trademark Office (UPTO) and European Patent Office (EPO) (Source: http://www.statnano.com/)

packaging food material for killing bacteria from stored food (Food Safety Authority FSA of Ireland 2008). Nanosilica is used in filtration of food and beverages and packaging. Metal oxides like ZnO, TiO_2, and Al2O3 are used in nanofertilizers to boost the crop growth (Gogos et al. 2012; Sabir et al. 2014). The applications of nanomaterial as fertilizers, pesticides, sensors have been described in the following sections.

7.3.1 Crop Production

Nanomaterials like TiO_2, multi walled carbon nanotubes and ZnO are reported to be increased crop growth and quality of crop. It is also found that some nanomaterials could absorb water and nutrient more than their bulk size, it helps to enhance vigor of root system and breakdown activity of organic substance (Harrison 1996). Carbon nanotubes have the ability to augment germination and plant growth. Khodakovskaya et al. (2012) found that multi walled carbon nanotubes have potential to increase the growth of tobacco cell culture by 55–64 %. The interaction of nanoparticles with plant cell, modify the plant gene expression and biological pathways, which affect the plant growth and development (Nair et al. 2010). The carbon nanoparticles help to enhance photosynthesis process and transform plant leaves into biochemical sensors. Single walled carbon nanotubes able to monitoring of nitric oxide using near-infrared fluorescence, this function convert plat leave to a photonic chemical sensor (Giraldo et al 2014). To find the phytotoxicity of alumina nanoparticles on corn, cucumber, soybean, cabbage, and carrot, Yang and Watts (2005)) investigatedthat uncoated alumina particles reduce root elongation and the surface characteristics of the nanoparticles are very important for phytotoxicity of alumina nanoparticles. The effect of different types of nanoparticles on the growth of different crops is presented in Table 7.1.

To increase the growth of plant and control disease, huge amount of chemical fertilizers and pesticide are being used. About 90 % of the fertilizer applied is being wasted through runoff and other processes and causes downstream surface and ground water pollution. Nano fertilizers are more environmental friendly and more effective with little amounts. Kottegoda et al. (2011) used modified hydroxyapatite nanoparticles coated urea fertilizer, encapsulated into cavities of soft wood '*Gliricidiasepium*' and found that nanoferilizer releases nitrogen slowly and uniformly upto 60 days compared to commercial fertilizer which losses the fertilizer upto 30 days with uneven release rate. Milani et al. (2012) compared solubility and dissolution kinetics of nano and bulk ZnO coated monoammonium phosphate and urea fertilizers. They found that coated monoammonium phosphate granules with nano ZnO showed slow release of Zn and more solubility in sand columns and help to improve Zn use efficiency of plant. Nano sulphur coated urea fertilizer was mostly used to control nutrient release where soil is low in sulphur (Wilson et al. 2008).

The growth of crop depend upon concentration of nanomaterial used. Zheng et al. (2005) found that photosynthesis rate of spinach was increased by 3.13 times

Table 7.1 Effect of different types of nanoparticles and their size on the crop growth

NPs	Size (nm)	Crop	Effect	Reference
Titanium dioxide (TiO_2)	N.A.[a]	Spinach (*Spinaciaoleracea*)	Photosynthesis rate (~3 times), chlorophyll-a (~45 %) and chlorophyll-b (~28 %) was increased	Zheng et al. (2005)
MWCNTs	N.A.[a]	Tomato (*Solanumlycopersicum*)	Water absorption of seed was increased by 58 % and germination was increased by 90 %	Khodakovskaya et al. (2009)
Iron (Fe) and Copper (Cu)	7.5–20.5	Potato (*Solanumtuberosum*)	Weight of sprouts was increased by 50 % with Fe and it was not significant with Cu	Chalenkoa et al. (2010)
MWCNTs	~30	Mustard (*Brassica juncea*)	Seed germination was increased by 99 %	Mondal et al. (2011)
Carbon nanotubes (CNTs)	10–30	Gram (*Cicerarietinum*)	Water absorption was increased by 50 % through Xylem	Tripathi et al. (2011)
Zinc Oxide (ZnO)	~25	Peanut (*Arachishypogaea*)	Crop yield was increased by 25–30 %	Prasad et al. (2012)
ZnO, FeO, and ZnFeCu-oxide	20 (ZnO) 100 (FeO) and 40 (ZnFeCu)	Mung (*Vignaradiata*)	Root and shoot biomass ware increased by 40 % and 44 % with ZnO, 68 % and 48 % with FeO, 42 % and 84 % with ZnFeCu, respectively	Dhoke et.al. (2013)
Hydroxyapatite ($Ca_5(PO_4)_3(OH)$)	<200	Rice (*Oryzasativa*)	Sugar level in rice straw and rice husk was reduced by 21–41 %	Dutta et.al. (2014)

[a]N.A. is not available

at 2.5 % TiO_2, and decreased beyond 4 % of TiO_2 concentration. Metal oxides like TiO_2, FeO and ZnO can be apply directly by foliar spray because it able to penetrate directly from pore spaces of leaves of plant and affect the growth, but the maximum results was shown at 50 ppm of ZnFeCu-oxide, FeO oxide and 20 ppm of ZnO concentration (Dhoke et.al. 2013). Multiwalled carbon nanotubes penetrate in seed coat and affect the biological activity mostly increased the water uptake inside the seed. But mechanism of water uptake by nanoparticle inside the tomato seed is yet not clearly understand by the researcher but in gram seed water uptake through xylem by capillary motion and increase growth of every part of plat (Khodakovskaya et al. 2009; Tripathi et al. 2011). Therefore, it is observed that carbon walled, metal and metal oxide based nanofertilizers successfully helped in increasing germination, photosynthesis, nutrient use efficiency and plant growth in the laboratory studies. However, systematic and rigorous experimentation is essential to study the nanofertilizers effect at the field scale.

7.3.2 Crop Protection

Fabrication and characterization of nanomaterials have the advantage to know the mechanism and interaction between plant and pathogen. It helps researcher to establish a relation between plant cells and plant pathogen fungi like F. oxysporum, C. lunata, A. alternata, and P. destructiva. Nanoscale material help to reduce degradation of pesticide and fungicide and increase the effectiveness of application with reduce amount. Application of nanoparticles and nanocapsules in pesticides and fertilizers distribute it in a control manner and reduce plant damage (Nair et al. 2010). Cucurbits family is very sensitive for powdery mildew disease; nano silver (100 ppm) inhibits the growth of fungal hyphae and germination of conidia (Lamsal et al. 2011). Table 7.2 describes the use of nanoparticles for protection of different crops.

The metal oxide nanomaterials like ZnO, TiO_2, Cu and SiO_2 are increasing their presence in pesticide and fungicide to protect plant from bacterial disease and control microbial activity. ZnO nanoparticle inhibit the growth of human pathogen like Escherichia coli, Listeria monocytogenes and plant pathogen like Botrytis cinerea, Penicillium expansum, and Botrytis cinerea by its antifungal and antibacterial activity, affecting the cellular function of fungi. Nanoparticles inhibit the development of conidiophores and conidia also called mitospores of fungi which causes the death of fungus hyphae. Hyphae is the main root of vegetative growth of fungi (He et al. 2011; Kairyte et al. 2013). TiO_2 photocatalysis technique is more effective to control litchi fungal disease than conventional fungicide (Lu et al. 2006). Silica nanoparticle use in drug and DNA delivery in animal cells and tissue, but its use in plant is limited because of cell wall present in plant that restrict delivery system. The current research by Torney et al. (2007) shows that mesoporous silica with end cap of nano gold particle can be used as gene gun to deliver chemicals, protein and necessary nutrient directly into the plant in control condition.

Table 7.2 Effect of different types of nanoparticles for protection of various crops

NPs	Size (nm)	Crop	Application type	Effect	Reference
TiO_2	32	Lychee (*Litchi chinensis*), maize (*Zea mays*), and Rice (*Oryzasativa*)	Fungicide	Litchi downy blight, rice blast and maize southern leaf spot were reduced by 80 %, 38 % and 67 %, respectively	Lu et al. (2006)
Silica (SiO_2)	100–200	Tobacco (*Nicotianatabacum L.*)	Gene gun	Successfully delivered Genetic material (DNA), and chemical to plant cell	Torney et al. (2007)
Imidacloprid (C9H10ClN5O2)	30	Rice (*Oryzasativa*)	Insecticide	About 95 % effective than conventional imidecloprid on Martianusdermestoides insect	Guan et al. (2008)
ZnO	70–80	N.A.	Fungicide	Growth of Botrytis cinerea and Penicilliumexpansum was reduced by 63–80 % and 61–91 %, respectively	He et al. (2011)
	~200	Gram (*Cicerarietinum*)	Fungicide	About 58 % of colony growth was inhibited with a concentration of 5×10^{-3} Moles	Kairyte et al. (2013)
Cu	3–10	N.A.	Fungicide	The activity was superior to bavistin (commercial fungicide) against plant pathogenic fungi *F.oxysporum*, *C.lunata*, *A.alternata*, and *P. destructiva*	Kanhed et al. (2014)

7.3.3 Detection

Nanosensors are powerful tools to detect nutrient deficiency, toxicity, disease of plants and animals, also control health of plant, food quality and safety. It helps to improve agriculture production with increasing efficiency of input such as minimum loss of input like irrigation, fertilizer and pesticide. Mainly two types of nanosensors are being used in agriculture: (i) bio-nanosensors and (ii) electrical-nanosensors. Biological organism has sense to identify the environmental condition; combination of biology and nanoparticles into sensors has potential to increase sensitivity and could reduce the response-time to sense a potential problem (Scott and Chen 2012). Several biosensors are developed for accurate detection of toxicity of microcystins, which are produced by cynobacteria and threat to agriculture and animal's health (Singh et al. 2012). Table 7.3 shows the various nanosensors used for agriculture safety.

Wireless nanosensors give the precise time based information including pesticide detection in food material and environment, quality control, and environmental condition. Salicylic acid is a phenolic phytohormone present in plant, help to improve plant growth, photosynthesis and transpiration. It is an important part of plant and sensitively need to detect level of salicylic acid in plant. Wang et al. (2010) use electrical nanosensor with gold electrode modified with copper nanoparticle. Copper nanoparticles sense the electrocatalytic oxidation of salicylic acid and detect the electrochemical behaviour of salicylic acid. Nano gold electrode with copper nanoparticle accurately detect salicylic acid levels in oilseed rape infected with the fungal pathogen sclerotinia sclerotiorum (Wang et al. 2010). Electrochemical sensor with carbon nanotube electrode modified with deposition of gold nanoparticle used to detect triazophos insecticide present in postharvest vegetables (Li et al. 2012). Gold and silver nanoparticle also used in biosensor to detect level of organophorous pesticide in environment and postharvest food (Simonian et al. 2005; Wu et al. 2011). Surface enhanced Raman scattering (SERS) spectrum used in analytical chemistry and also used in agriculture to detect pesticide in food and environment. In a new study fabricated silver nanoparticle monolayer used to enhance sensitivity for Raman detection and help to detect concentration of methyl-parathion (Zhang 2013).

7.4 Agroecological Risks

Application of nanomaterials in agriculture is not always effective. It has number of negative effects on soil, plant, and aquatic life and most importantly human because of long food chain and easy motion of nanoparticles. Study of behaviour of nanoparticles at different size with different concentration in soil, plant and water are necessary to understand the agroecological toxicity.

Table 7.3 Application of nanosensors in agricultural safety

NPs	Size (nm)	Sensor type	Target	Detection limit	Reference
Gold (Au)	N.A.	Biosensor	Neurotoxic organophorous pesticide in environment	Not available	Simonian et al. (2005)
Liposome (enzyme)	300	Biosensor	Organophorous pesticide	10^{-6} mole	Vamvakaki and Chaniotakis (2007)
Calcium carbonate-chitosan ($CaCO_3$-chi)	N.A.	Biosensor	Methyl parathion pesticide	1 ng mL^{-1}	Gong et al. (2009)
Cu and Au	<100	Electrochemical	Fungal pathogen *Sclerotiniasclerotiorum*in oilseed rape	0.1 μM	Wang et al. (2010)
Au	4–7	Biosensor	Organophorous pesticide and immobilization of protein in food	0.8 pg/mL	Wu et al. (2011)
Au coated Carbon-nanotube (CNT)	30–60	Electrochemical biosensor	Triazophos in vegetables and food sample	9.3×10^{-8} M	Li et al. (2012)
Iron oxide (Fe_3O_4) coated CNT	N.A.	Biosensor	Organochlorine and organophosphate insecticide in food and environment	0.1 nmol L^{-1}	Chauhan and Pundir (2012)
Silver (Ag)	<50	Raman detector	Monolayer film to detect pesticide	10^{-7} M	Zhang (2013)
Cu	N.A.	Biosensor	Propineb fungicide detection in river and sea water	1 μM	Abbacia et al. (2014)
Ag	~16	Electrochemical	Organophorous pesticide, and dipterexfungiside	0.18 ng mL^{-1}	Li et al. (2014)

Table 7.4 Adverse effects of nanoparticles on soil health

NPs	Size (nm)	Effect	Reference
C_{60} fullerene	50	Fast growing bacteria and protozoa were reduced by 20–30 %	Johansen et al. (2008)
Ag, CeO_2 and TiO_2	7–45	Growth (9–21 %), fertility (11–28 %) and survival (20–30 %) of Caenorhabditiselegans (species of nematode) was reduced	Roh et al. (2009, 2010)
TiO_2 and ZnO	10–20	Traces of ZnO (~50 μg g^{-1} weight) and TiO_2 (~32 μg g^{-1} weight) were found inside the earthworm	Hu et al. (2010)
ZnO, Zn and Zn^{2+}	50	Soil enzymes (dehydrogenase, phosphatise, and β-glucosidase) were reduced by 17–80 %	Kim et al. (2011)
Ag	9–21	The activity of nitrifying bacteria was reduced by 50 %	Okkyoung and Zhiqiang (2008)
	10	Culturability of beneficial soil bacterium Pseudomonas chlororaphis O6 was reduced	Calder et al. (2012)
Zero-valent iron (nZVI)	20–100	Mortality of eiseniafetida and lumbricusrubellus species of earthworm was 100 % at 750 mg/kg	Temsah and Joner (2012)
CeO_2, Fe_3O_4 and SnO_2	50–105 (CeO_2), 20–30 (Fe_3O_4) and 61(SnO_2)	Microbial stress was noticed	Antisari et al. (2013)
Cr_2O_3, CuO, Ni, and ZnO	<100	The activity of Enzyme (60 %), dehydrogenase (~75 %), and urease (44 %) was reduced	Josko et al. (2014)

7.4.1 Soil

Soil is prima facie receiver of fertilizers with nano-particles. There is harmful chemical reactions and contamination by these nanoparticles to soil ecosystem and change in soil structure due to their large surface area and Brownian motion. Nanoparticles used through fertilizers could be harmful to soil biota and fertility (Ranallo 2013). They affect microbes, micro fauna of soil and digestive system of earthworm. The properties of nanoparticles may change the structure of soil and default to detect contamination due to nanoparticles in soil and environment (Du et al. 2011; Mura et al. 2013). Table 7.4 shows the adverse effects of nanoparticles on soil health.

The potential harmful effects of nanoparticles Ag, TiO_2, ZnO, CeO_2, Fe_3O_4 include reduction in growth, fertility, survival and increase mortality of earth worm and soil bacteria. Size is the main factor for ecotoxicity. To find out the relationship between size and toxicity Roh et al. (2010) was started their investigation with TiO_2

and CeO_2 nanoparticle on Caenorhabditis elegans, it is a free-living, transparent nematode, about 1 mm in length, that lives in temperate soil environments. They found that smaller size of TiO_2 (7 nm) and CeO_2 (15 nm) nanoparticles are seems more toxic compared to larger size (TiO_2 of 20 nm and CeO_2 of 45 nm). If doses increased from certain amount ZnO nanoparticle become toxic for soil. Hu et al. (2010) were increase amount of ZnO from 1 g/kg of soil to 5 g/kg, ZnO nanoparticles were bioaccumulated inside the earthworm and causes DNA damage.

7.4.2 Plant

Toxicity of nanoparticles depends upon various factors like plant species, size and concentration of nanoparticles in different stages of crop. Toxic effect of nanoparticles also depends upon their composition and size. Small sized nanoparticles are more reactive and toxic compared to large sized and affect the respiration or photosynthesis process (Navarro et al. 2008). Hund-Rinke and Simon (2006) worked on different size of photocatalytic active TiO_2 nanoparticles and its ecotoxic effect on algae (EC50: 44 mg/L) and daphnids with maximum concentration of 50 mg/L and found that ecotoxicity of nanomaterials depend upon nature of particles. Toxicity found in algae is more than daphnids. Daohui and Xing (2007)) worked on phytotoxicity of nanomaterials. They used MWCNT, Al, Al_2O_3, Zn, and ZnO in their experiment on radish, rape, rye-grass, lettuce, corn, and cucumber and found that seed germination of corn and rye-grass are affected by nano scale ZnO and Zn, respectively. Al_2O_3 nanoparticles showed phytotoxicity only on corn, reduced the root elongation by 35 %. Al improved root growth of rape and radish and inhibited root elongation of rye-grass and lettuce but had no effect on cucumber. Some of the toxicological studies on the effect of nanomaterials are presented in Table 7.5.

The level of toxicity in plants due to nano-particles is in direct relation with size and nature of the particles. ZnO nanoparticles easily dissolve in soil and uptake by plant and TiO_2 nanoparticles accumulate in soil and retain for log time and stick with the cell wall of wheat plant. Both are reduced the biomass of wheat crop (Du et al. 2011). Phytotoxicity was studied by Mazumdar and Ahmed (2011) on rice crop. They found that silver nanoparticle accumulated inside the root cell and damage the cell wall during penetration of particles due to complex mechanism and small size of particles, it was damaged the external and internal portion of cell wall. The other factor for plant toxicity is the concentration of nanoparticle because a nanoparticle of same size in different concentration change its chemical properties. ZnO nanoparticle shows great toxicity in different concentration. Boonyanitipong et al. (2011) investigate that ZnO start showing adverse effect on rice plant from 100 mg/L and fully inhabit root growth and biomass at 500–1000 mg/L concentration.

Table 7.5 Toxicological effect of nanoparticles on plant

NPs	Size (nm)	Crop	Adverse effect	Reference
TiO_2, and ZnO	20–100 (TiO_2) and 40–50 (ZnO)	Wheat (*Triticumaestivum*)	Wheat biomass was reduced by 7.6 % due to TiO_2. No significant result due to ZnO	Du et al. (2011)
Zno and TiO_2	N.A.	Rice (*Oryzasativa L.*)	75 % reduction in root as concentration of ZnO increased from 10 to 1000 mg/L. No significant reduction with TiO_2	Boonyanitipong et al. (2011)
TiO_2	<100	Corn (*Zea mays*)	Aberration index increased from 0.5 % to 2.5 % with control and 4 % concentration respectively. Inhibit root elongation by 34 %	Castiglione et al. (2011)
Au	25	Rice (*Oryzasativa L.*)	Damage of internal and external cell wall of root due to deposition of Au through xylem	Mazumdar and Ahmed (2011)
Aluminium oxide (Al_2O_3)	N.A.	Tobacco (*Nicotianatabacum*)	As concentration of Al_2O_3 increased as 0–1 %, the average root length, biomass per seedling, and germination rate significantly decreased as 93 %, 83 % and 2 %, respectively	Burklew et al. (2012)
ZnO and Fe-ZnO	18.4 (ZnO) and 13.4 (Fe-ZnO)	Green pea (*Pisumsativum L.*)	Chlorophyll and ROS (Reactive oxygen species) production were reduced by 27 % and 50 % respectively	Mukherjee et al. (2014)

7.4.3 Water

The nanoparticles can easily be released in water body or air and uptake by living organisms, create toxic effect for human, animals and also for aquatic life. TiO_2 reduced the light to entrap the algal cell and thus reduce the growth (Sharma 2009). The toxicity effect of Ag, Cu, AL, Ni, TiO_2 and Co nanomaterials on algal species, zebrafish, and daphnids revealed that Ag and Cu nanoparticles cause toxicity to all organisms (Griffitt et al. 2008) and the metal form are less toxic than soluble form of nanoparticles. Table 7.6 describe the aquatic toxicity of use of nanomaterials release in surface water body. It has been proved from different studies that nanoparticles like Ag, Cu, Al, Ni, TiO_2 and Causes unrecoverable toxic effect on aquatic ecosystem. Silver, iron oxide and copper nanoparticle adversely affected health of Zebrafish. It enhance mortality, hatching and reduce heartbeat and survival rate affected normal development (Asharani et al. 2008; Griffitt et al. 2007; Zhu et al. 2012). Therefore, the level of nanotoxicity in soil, plant and water mainly depend on the composition, size (<20 nm) and concentration (>100 ppm) of the nanoparticle.

7.4.4 Human Health

The rising field of nanotechnology has created an interest on health risk associated to nanoparticles. These particles create new challenge for researchers to understand and find risk associated with human health. Exposure of these materials occurs

Table 7.6 Adverse effects of nanoparticles on aquatic species

NPs	Size (nm)	Aquatic species	Effect	References
Fullerene (nC60)	10–200	Daphnia	Mortality was increased by 40 % and offspring production was reduced by 50 %	Oberdorster et al. (2006)
Cu	80	Zebrafish	NKA (Na/K atpase) activity was reduced by 88 %	Griffitt et al. (2007)
Ag	5–10	Zebrafish	Heartbeat (150–50 beat/min) was decreased from 150 to 50 beat/min and mortality rate was10 %	Asharani et al. (2008)
TiO_2	21	Rainbow trout	Glutathione level was reduced by 65 %	Federici et al. (2007)
	10–100	Marine phytoplankton	Toxic to the aquatic life in sunlight	Miller et al. (2012)
Ag	18	Freshwater fish Cyprinuscarpio	Mortality was 100 % at 1 ppm NP's concentration	Hedayati et al. (2012)
FeO	30	Zebrafish	About 75 % of fishes were killed at high concentration (50 mg L^{-1}) of NP	Zhu et al. (2012)

Table 7.7 Adverse effects of nanoparticles on human health

NPs	Size (nm)	Body part	Effect	Reference
MWCN and Carbon nano fibres (CNFs)	20 (MWCN) and 150 (CNFs)	In-vitro on lung tumour cells	MWCN and CNFs reduced the living cells by 33 % and 58 %, respectively	Magrez et al. (2006)
TiO_2, Ag, Al, Zn, and Nickel (Ni)	N.A.	Alveolar epithelial cells and apoptotic damage	Cell damage was observed in all cases	Park et al. (2007)
ZnO	30	Epidermal cells	Glutathione (51–59 %), catalase (55–64 %) and superoxide dismutase (72–75 %) were reduced	Sharma et al. (2009)
Ag	<10	Hepatoma cells	Cytotoxicity (oxidative stress) was noted	Kim et al. (2009)
CuO	<50	Lung epithelial cells A549	Cell viability was decreased by 40 %	Moschini et al. (2010)
TiO_2	1–200	Mammalian cell	Reactive oxygen species production, cytokines level, apoptosis and genotoxicity were increased and cell viability and proliferation were reduced	Iavicoli et al. (2011)
Cadmium Sulphide (CdS)	~3	Escherichia coli and HeLa cells	Oxidative stress in both Escherichia coli and HeLa cells. Reduced growth of E. Coli by 50 %	Hossain and Mukherjee (2013)
Ag	10–80	–	Cell viability was decreased by 20–40 %, Oxidative stress in cells	Nguyen et al. (2013)
Ag	10–50	Lung cell (via inhalation)	The Ag particles of size 10 nm were found more Cytotoxic than other size	Gliga et al. (2014)
Cu	23.5	Nerve cells and astrocyte cell	Central nervous system was damaged	Bai et al. (2014)

through inhalation, ingestion and dermal exposure during synthesis, manufacturing and application of these nanomaterials. Table 7.7 shows the adverse effects of nanomaterials on human health.

7.4.4.1 Inhalation

The most common way of exposure is inhalation of airborne nanoparticles. Greatest emission risk occurs in the manufacturing process with poor filtering and ventilation system (AFSSET 2006). Factors affecting inhaled dose are particle geometry and physiochemical properties, lung morphology, respiration physiology, and environmental condition (Shade and Georgopoulos 2007). Nanoparticles deposit in respiratory traces after inhalation and increase the total deposition fraction (TDF) in the lungs with decreasing in particle sizes. Nanoparticles can also be uptaken in the brain through the olfactory epithelium (Borm et al. 2006; Jaques and Kim 2000). Ultrafine airborne particles may increase respiratory and cardiovascular morbidity and mortality (Shade and Georgopoulos 2007).

7.4.4.2 Ingestion

Ingestion is another source of entry of nanoparticles into human body. The nano particles entered through gastrointestinal tract directly through intentional ingestion or indirectly via water, food, animal food and fish (Bergin and Witzmann 2013). Mucociliary escalator can be excreted inhaled particles and ingested into the gastrointestinal tract, ingestion also depends upon physicochemical characteristics and size of particles (Hagens et al. 2007). Jani et al. (1990) found that particle size less or equal to 50 nm is more uptake or absorbed across gastrointestinal tract and can be passed to the liver, spleen, blood and bone marrow by the momentary lymph supply and nodes. Plants have more resistance to prevent translocation of nanoparticles than mammalian barriers (Birbaum et al. 2010).

7.4.4.3 Dermal Exposure

Dermal exposure is an import route to absorb nanoparticles via the skin. Skin contents approximately 10 % weight of body and plays an important role as barrier against environmental impurities with the protection, homeostasis maintaining, metabolism, synthesis, and deposition function (Crosera et al. 2009). Penetration of nanoparticles depends upon physicochemical characteristics of nanoparticles and medical condition of skin such as eczema, dermatitis, and skin irritation. Absorption between epidermis and dermis or permeability increase in damage skin (Nielsen et al. 2007). Dermal exposure of small size nanoparticles lower than 10 nm is more dangerous. This size of particles may cause erythema, oedema and eschar formation. Further larger size particles cannot penetrate into the skin from transappendageal routes (Gautam et al. 2011).

Nanoparticles adversely affect human health and the potential routing could be through inhalation, ingestion and dermal exposure. It is understood that the nanoparticles show significant health complications in human when exposed to the size of particles less than 50 nm.

7.5 Conclusion

Nanotechnology is in its beginning face and it provides enormous possibility to transform the way of agriculture and lure the microbiologists and other researchers to contribute to food safety with innovative green chemistry approaches. Nanotechnology can facilitate additional advantage in food processing, distribution and packaging and functional food, but it couldn't make its presence in large scale agricultural production. Academics and industrial patents are rapidly increasing in agro-chemical sector but the end products from this technology have not hit the market so far (Gogos et al. 2012; Parisi et al. 2014). After reviewing many articles related to nanotechnology, it is understand that the governments of the USA, Germany and Japan are more supportive in nanoresearch and the research publications and patents are largest for China and USA, respectively. The carbon walled, metal and metal oxide based nanofertilizers successfully helped in increasing germination, photosynthesis, nutrient use efficiency and plant growth. The metal oxide nanomaterials like ZnO, TiO_2, Cu and SiO_2 are increasing their presence in pesticide and fungicide to protect plant from bacterial disease and control microbial activity. Silver, copper and gold nanoparticles are being used as bio-nanosensors and electrical-nanosensors to detect a potential pathogen problems in plant and postharvest foods. The level of nanotoxicity in soil, plant and water mainly depend on the composition, size (< 20 nm) and concentration (>100 ppm) of the nanoparticles. Nanoparticles adversely affect human health and the potential routing could be through inhalation, ingestion and dermal exposure. It is understood that the nanoparticles show significant health complications in human when exposed to the size of particles less than 50 nm.

It is clear that nanotechnology has potential to increase production of agriculture, but there is very limited knowledge about its long term adverse effect on soil, plants and ultimately on human. It is required to study about the non-toxic limit of nanoparticles related to its size and concentration. The positive benefit of nanoparticles should be selected on the basis of their risk related to environment and human. An intelligent use of nanotechnology may help to achieve food security with the qualitative and sustainable environment.

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