Chapter 3
Implications of Nanotechnology on Plant Productivity and Its Rhizospheric Environment

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Abstract Nanotechnology requires the ability to understand the materials and precisely manipulate it to nanoscale in a useful way. Nanotechnology emerged as a new broad science of diverse fields such as basic sciences, materials science, and engineering to assemble at the nanoscale. In contrast to conventional or other contaminants, nanoparticles are posing some new environmental challenges for scientists and environmentalists worldwide. Being a new area of science, nanotechnology will leave no field untouched including agriculture and allied sectors. So far, the use of nanotechnology in agriculture has been mostly theoretical, but it has begun to have a significant effect in the main areas of agrochemical industry. Nanoparticles finding great potential as delivery systems to specific targets in living organisms and is being used in medical sciences. In plants, the same principles can be applied for a broad range of uses, particularly to tackle phytopathological infections, nutrition supplement and as growth adjuvant. Nanoparticles can be tagged to agrochemicals or other substances as delivery agent to plant system and tissues for controlled release of chemicals. Doing so, the negative effects of nanomaterials on plant productivity and soil microbes and environment must not be overlooked, such as toxicity generated by free radicals leading to lipid peroxidation and DNA damage. Key focus of the chapter particularly relates the use of nanoparticles on agricultural crops and its toxic implications to plants and microbes naturally present in soil and generation of nanowaste in agroecosystem.

Keywords Nanoformulations · Phytotoxicity · Nanowaste · Agroecosystem

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3.1 Introduction

The developments in nanotechnology and nanotechnology-based industries and products are tremendously growing. Recent estimates till October 2013, the nanotechnology-based consumer products inventory grows to 1,628 products or product lines (Fig. 3.1). The use of nanomaterials (NMs) in biomedicine (Zhang et al. 2008) and in agriculture (Joseph and Morrison 2006) is one of the most intensely studied areas in nanotechnology. Nanoscale materials have shown to be taken up by bacteria (Liu et al. 2009b), and also have the ability to penetrate plant cells (Liu et al. 2009a) and induce phytotoxicity at high doses (Stampoulis et al. 2009). Nanotechnology-based agrochemical researches have motivated a number of scientists and environmentalists worldwide to consider the use of nanotechnology for agricultural crops.

Practically, nanotechnology permits broad advantages in agricultural research, such as disease prevention and treatment in plants using various nanocides (Carmen et al. 2003) and nutrient management of agriculture field using nanofertilizers (Priester et al. 2012). Various kinds of nanomaterials such as; metal, nonmetal, carbon nanotubes, quantum dots, magnetic particles, polymers, etc. have been studied for their use and possible effect in different areas. Each of these nanomaterials exerts its positive and negative effects mostly depending on its size and interaction with the plant tissues or microbes. However, the current level of knowledge does not convey any clear evidence of the benefits and/or risks (Kah et al. 2013).

The route of entry of these nanomaterials in food chain may be from direct application on land or biosolids treated in conventional wastewater treatment plants (WWTPs) (Brar et al. 2010). However, manufactured nanomaterials (MNMs) although measurable in WWTP systems (Kiser et al. 2009) are neither monitored nor regulated. Though there are scientific reports on measurement and detection of such material and contaminants using sophisticated instruments (Khodakovskaya et al. 2011), but the use of such high cost monitoring tools seems to be nonfeasible on routine basis. Despite the success of nanotechnology, the lack of scientific knowledge concerning the potential health and environmental risks needs to be addressed well in advance.

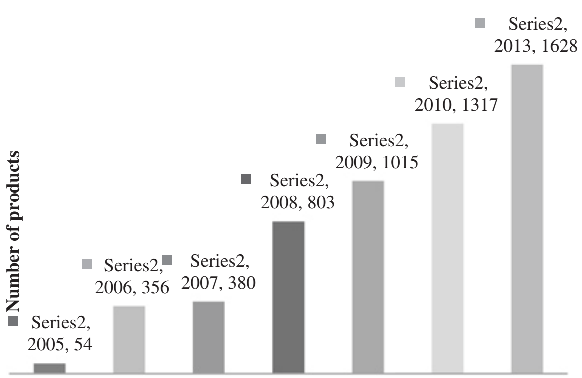

Fig. 3.1 Year wise inventory update for total nanotechnology-based products (*Source* Project on Emerging Nanotechnologies (2014))

3.2 Nanomaterial as Delivery Systems

Agrochemicals are in general applied to crops in the form of suspension/solution by spraying. Due to problems such as leaching of chemicals, degradation by photolysis, hydrolysis, and by microbial degradation, most of the chemicals is lost. Hence, repeated application is necessary to have an effective control which on the other hand results in deterioration of soil and water quality. In this context, nanoencapsulated agrochemicals need to be designed in such a way that they possess all necessary properties such as effective concentration (with high solubility, stability, and effectiveness), time controlled release in response to certain stimuli, enhanced targeted activity and less toxicity (Boehm et al. 2003; Green and Beestman 2007; Wang et al. 2007). Tsuji (2001) reported the control of parasitic weeds with properly designed functional nanocapsulated herbicides which have better penetration through cuticle to controlled release of active constituents and to reduce the phytotoxicity of herbicides on crops.

Likewise, use of surface modified hydrophobic nanosilica to control a range of agricultural insect pests (Rahman et al. 2009) and surface functionalized mesoporous silica nanoparticles (MSNs) to precisely manipulate gene expression at single cell level by delivering DNA and its regulators in a controlled fashion is reported (Torney et al. 2007). Magnetic nanoparticles have shown very specific localization to release their load, which is of great interest in the study of nanoparticulate delivery for plants with no toxicity (Zhu et al. 2008). Quantum dots (QDs) of CdSe/ZnS conjugated with glycine, mercaptosuccinic acid, cysteine, and amine were reported to be visibly transported to a limited extent in the vasculature of ryegrass, onion, and chrysanthemum plants when cut stems were placed in aqueous QD solutions. However, they were not seen to be taken up at all by rooted whole plants (Al-Salim et al. 2011).

Single-walled carbon nanotubes (SWCNTs) were reported to enhance root elongation in onion and cucumber (Canas et al. 2008). Similarly, Khodakovskaya et al. (2009) reported the effects of multiwalled carbon nanotube (MWCNT) on the seed germination and growth of tomato plants. Also, Lin and Xing (2007) reported positive effects of MWCNTs on radish, rape, rye grass, lettuce, corn, and cucumber. These results showed significant and encouraging effects on growth and development processes of plants.

The use of polymer matrix that is subject to swelling and dissolution was found to influence the diffusion pathways and thus alter the release behavior (Kaunisto et al. 2013). Examples of polymers used include nanospheres of polyethyleneglycol (Yang et al. 2009) or polyvinylpyrrolidone (Botts et al. 2006). Such materials are often used because they are well established from medical applications. The use and preparation of nanopolymer such as liposomes as delivery system for the slow release of insecticide was first described by Bang et al. (2009). Since then, two reports (Hwang et al. 2011; Kang et al. 2012) highlighted insecticidal efficacy of liposome based formulations. Kang et al. (2012) described that nanoformulation of pyrifluquinazon had its best lethal efficiency for 14 days after treatment compare to pure compound which lasts for 2 days. Similarly, Xiang et al. (2013) used cellulose based polymer and demonstrated that increasing the cellulose nanocrystal content in the fibers, increases the rate of fiber degradation and release of thiamethoxam herbicide.

3.3 Nanomaterial in Agro-system

3.3.1 Nanopesticide and Herbicides

Conventional methods to control the pathogens and pests have affected both the environment and economy of farmers, as 90 % of the applied pesticides are lost to the air during application and as runoff. Additionally, indiscriminate usage of pesticide increases pathogen and pest resistance, reduces soil biodiversity, diminishes nitrogen fixation; contributes to bioaccumulation of pesticides, pollinator decline and destroys habitat for birds (Ghormade et al. 2011). Nanoscaled delivery system with active compound (pesticide and or herbicide) can be applied only when necessary in the field (Gruere et al. 2011).

Avermectin, a pesticide which is known to block neurotransmission in insects by inhibiting chloride channel. It is inactivated by ultraviolet on the fields with half-life of 6 h only, whereas, slow release of encapsulated avermectin by the nanoparticles (NPs) carrier was reported for about 30 days (Ghormade et al. 2011). Similarly, a commercial product 'Karate® ZEON' is a quick release microencapsulated formulation containing lambda-cyhalothrin which breaks open upon contact with leaves. In contrast, the gutbuster microencapsules containing pesticide that breaks open to release its contents upon coming in contact with alkaline environments, including the stomach of certain insects (Lyons et al. 2011).

A series of polyethylene glycol (PEG) based insecticide formulations found to release active compounds at slower rate compare to commercial formulations comprising imidacloprid (Adak et al. 2012), carbofuran (Pankaj et al. 2012), and thiram (Kaushik et al. 2013). The release of insecticide was noted to be dependent on PEG molecular weight. The release of β-cyfluthrin from the nanoformulation was recorded over a period that ranged from 1 to 20 days (Loha et al. 2011), whereas release from a commercial formulation was found within 4–5 days (Loha et al. 2012). In another report, a nanofiber network composed of poly (lactic acid) and cellulose nanocrystals loaded with thiamethoxam were efficient against whitefly over a 9 day period in a glass house experiment, at 50 % of the recommended dosage of thiamethoxam (Xiang et al. 2013). Active compounds conjugated in nanoformulations for agricultural use found to be more effective compared to their conventional counterparts (Table 3.1).

Nanoformulations containing glyphosate was found to increase the bioavailability of the herbicide while avoiding a number of the adjuvant present in current glyphosate formulations, which have been associated with toxicity to non-target organisms (Piola et al. 2013). Kanimozhi and Chinnamuthu (2012) used

Table 3.1 Nanomaterial based formulations for agricultural use

Nanoformulations	Materials used	Active compounds	References
Herbicide	Zn–Al	2-4-dichlorophenoxyacetate	Hussein et al. (2005)
Pesticide	SiO_2	Validamycin	Liu et al. (2006)
Pesticide	Polymer	Bifenthrin	Liu et al. (2008)
Insecticide	TiO_2/Ag	Dimethomorph	Guan et al. (2010)
Pesticide	PEG	Carbofuran	Shakil et al. (2010)
Insecticide	TiO(2)	Avermectins	Guan et al. (2011)
Insecticide	Chitosan	Etofenprox	Hwang et al. (2011)
Insecticide	Polymer	Thiamethoxam	Sarkar et al. (2012)
Insecticide	Polymer	β-cyfluthrln	Loha et al. (2012)
Insecticide	A1	Nanoalumina	Stadler et al. (2012)
Insecticide	SiO_2	Chlorfenapyr	Song et al. (2012)
Pesticide	SiO_2	1-naphthylacetic acid	Ao et al. (2013)
Insecticide	Sodium alginate	Pyridalyl	Saini et al. (2014)
Herbicide	Polymer	Atrazine	Pereira et al. (2014)

manganese carbonate as core material coated with water soluble polymers such as sodium Poly Styrene Sulfonate and Poly Allylamine Hydrochloride. Further, Manganese carbonate core materials were etched out to form hollow-shell particles which were loaded with herbicide pendimethalin for field application.

3.3.2 Nanofertilizers

Soil fertility mainly depends upon its organic and inorganic components such as salts of sodium, potassium, and phosphorous; oxides of nitrogen and sulfur, etc. The soil organic matter provides the energy and nutrients for soil microbes which ensure high yields of healthy crops due to their enzymatic action. Thus, it is mandatory to conserve it for efficient physical, chemical, and biological soil functioning (Six et al. 2002).

Millan et al. (2008) reported the use of urea-fertilized zeolite chips, for slow release of nitrogen fertilizers. Ammonium-charged zeolite has shown its capacity to raise the solubilisation of phosphate minerals and thus goes to improved phosphorus uptake and yield of crop plants. In this line, Jinghua (2004) showed that application of a nanocomposite consists of N, P, K, micronutrients, mannose, and amino acids enhance the uptake and use of nutrients by grain crops. In an interesting strategy, Kottegoda et al. (2011) reported sustained release of nitrogen into the soil using urea-modified hydroxyapatite nanoparticle which were encapsulated under pressure into cavities of the soft wood of *Gliricidia sepium*. In this study, nanofertilizer showed an initial burst and a subsequent slow release up to day 60 compared to the commercial fertilizer, which released heavily at beginning followed by low and nonuniform quantities until around 30 day.

3.4 Phytotoxicity of Nanomaterials

To date research on interaction of nanoparticles that results into phytotoxicity is negligible. Apart from detrimental effect upon direct contact of NPs, these can also diffuse into the intercellular space, the apoplast, and be adsorbed or incorporated into the membranes (Nowack and Bucheli 2007). Plant cells carry a negative surface charge, which allows the transport of negatively charged compounds into the apoplast. The casparian strip poses a barrier to the apoplastic flow and transport, and only symplastic transport is possible into the xylem. However, this barrier is not perfect and compounds can enter the xylem through holes or damaged cells without ever crossing a cell membrane and be further transported to the shoots. This process is found to be a dominant process for the uptake of metal complexes with chelators such as EDTA and their translocation to the shoots (Tandy et al. 2006). This indicates that negatively charged NP could enter the apoplasm of the root cortex and eventually also the xylem, but are not taken up by the cells.

In one of the study, Lee et al. (2008) demonstrated the effects of copper nanoparticles (CuNPs) on the seedling growth of mung bean and wheat wherein mung bean was found to be more sensitive to CuNPs than wheat. Transmission electron microscopy (TEM) images confirmed the entry of CuNPs across the cell membrane. Bioaccumulation of NPs increased with its concentration in growth media and their bioavailability to the test plants was estimated by calculating the bioaccumulation factor. Also, studies on the effects of CuNPs on the growth of zucchini plants showed reduced length of emerging roots (Stampoulis et al. 2009) and modulation of ascorbate-glutathione cycle, membrane damage, in vivo ROS detection, foliar H_2O_2 and proline accumulation and reduced seed germination percentage in rice (Shaw and Hossain 2013).

It is also important to mention that the phytotoxicity due to bioaccumulation, biomagnification, and biotransformation of engineered nanoparticles in food crops are still not well understood. Few studies have been reported on the accumulation of engineered nanomaterials in crop plants such as rape, radish, lettuce, corn, and cucumber (Rico et al. 2011). The carbon-based fullerenes (C_{70} and fullerols $C_{60}(OH)_{20}$) and most of the metal-based nanomaterials (titanium dioxide, cerium oxide, magnetite, zinc oxide, gold, silver, copper, and iron) were reported to be accumulated in the plants (Rico et al. 2011). Moreover, accumulated nanomaterials in the plants can be the part of biological food chain. As a part, positive effects of metal-based nanomaterial on plant encouraged for some crops, on the other hand, significant negative effects were also observed, such as reduced germination, root growth, and shoot length (Thul et al. 2013).

The seed germination of rye grass and corn was reported to be inhibited by nanoscale Zn (35 nm) and ZnO (15–25 nm), respectively. Root growth was found to be significantly inhibited, however, such an inhibition for seed was not detected when soaked in nano-ZnO suspension due to the selective permeability of seed coat (Lin and Xing 2007). Not only the size of NPs, but reduced length of shoot and root of wheat was observed in a dose-dependent manner (Dimkpa et al. 2013).

In another study, uptake of ZnONPs causes damage of epidermal and cortical cells and transport from one cell to other through plasmodesmata (Lin and Xing 2008). Similarly, the evidence for the entrapment of AgNPs by the cuticle, and penetration into the leaf tissue through stomata, and oxidation of AgNPs and complexation of Ag^{+} by thiol-containing molecules was reported by Larue et al. (2014). Furthermore, the cytotoxic and genotoxic impacts of AgNPs were reported in root tips of onion (Kumari et al. 2009). Similar effects of chromosomal aberrations and DNA damage were also observed with TiO_2 (Pakrashi et al. 2014). Recently, TiO_2NPs were reported to affect the molecular expression profiles of microRNAs (Frazier et al. 2014).

3.4.1 Metal Nanoparticle Induced Predictive Physiological and Biochemical Changes in Plant

The manifestation of the metal and their nanoparticles interaction and accumulation in plant systems could be responsible for changes in vegetative growth, development and differentiation, onset of senescence, dormancy, abscission, flowering and fruit setting, and other ecological productivity (Gardea-Torresdey et al. 2004; Vernay et al. 2008). It has also been reported that nanomaterials can generate ROS, affect lipid peroxidation (Cabiscol et al. 2000). This has significant biochemical and molecular effect on the membrane permeability and fluidity, making cells more susceptible to osmotic stress and failure to nutrient uptake. It is known that the stress is perceived through the growth matrix, i.e., soil and water and a series of metabolic activities (Viswanathan et al. 2004; Sarangi et al. 2009) are triggered to alleviate the metal stressors (Verbruggen et al. 2009). In order to deal with the situation; in the first step plants modulate their action actively to prevent metal entry through the expense of energy. In the second step, further entry of the metal into the cytosol is prevented by modulation of transporters in the plasma membrane so that intracellular buildup of metal ions does not exceed the threshold concentration. In order to prevent metal ion buildup, the plant system have developed several well synchronized system to efflux the ions from the cellular milieu (Lin et al. 2006). In case of failure in these strategies, plants actively chelate the metal particles through specific low and moderately large sized molecules such as; phytochelatins (Cobbett and Goldsbrough 2002), metallothionins (Maitani et al. 1996; Guo et al. 2008), and other thiol rich compounds which act as chaperons to maintain the cellular homeostasis (Nelson 1999). In the extreme case of failure of the above mentioned strategies, plants try to compartmentalize the metal particles into vacuoles. All such metabolic processes are active processes in the expense of energy from metabolites (Bertrand and Poirier 2005). Expense of the metabolites is a penalty on the plant; which are otherwise required for growth and development to complete its annual or perennial lifecycle. Although, the concentration of nanoparticles affecting the biochemical and physiological processes of biological organisms is a matter of debate, it needs to be worked out through systematic investigation. However, it is predicted that the reactivity of a particular metal nanoparticles would depend on the niche; biochemical and physiological alterations in crops and plant systems that impact on crop yield and ecological productivity.

3.5 Influence of Nanomaterials on Rhizospheric Environment

The effect of specific metal nanoparticles on soil microflora could be conspicuous. The germicidal properties of Ag and Cu nanoparticles are well documented. Uptake of manufactured nano-CeO_2 nanomaterials into roots and root nodules found to eliminate N_2 fixation potentials and impaired soybean growth (Priester et al. 2012). Also, Fan et al. (2014) observed the impact of nano TiO_2 on *Rhizobium*–legume symbiosis using garden peas and *Rhizobium leguminosarum* bv. *viciae* 3,841, and found that nano TiO_2 exert morphological changes in bacterial cells. Further, it was noticed that the interaction between these two organisms was disrupted in the form of root nodule development and the subsequent delay in onset of nitrogen fixation. The alteration of bacterial communities was reported to be in a dose-dependent manner, with some taxa increasing as a proportion of the community, whereas more taxa decreasing that resulted in reduced diversity (Ge et al. 2012).

The direct application of NPs on land or treated biosolids containing mobile NPs may come in contacts with the soil microbes (Fig. 3.2). These microbes are also efficient to adsorb and accumulate one or other form of nanomaterials, which in turn initiates the mobilization of nanomaterials through food chains and can alter communities comprising multiple populations (e.g., plant, fish, bacteria) within food webs (Holden et al. 2013). Plants generally depend on soil bacteria and fungi to help mine nutrients from the soil. A study finds that the popular microbicidal AgNPs negatively impacts on the growth of plants and kills the soil microbes that sustain them (Zeliadt 2010). Not only microbes, but activity

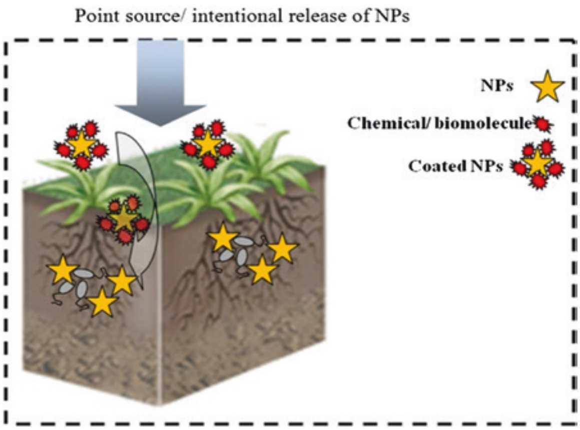

Fig. 3.2 Fate and sink of NPs in agricultural ecosystem (Thul et al. 2013)

of several soil enzymes such as soil protease, and catalase, and peroxidase were found to be significantly reduced by ZnO and TiO_2NPs (Du et al. 2011).

Moreover, inorganic TiO_2, SiO_2, and ZnO were found to exert toxic effect on bacteria. The toxicity of these elements further significantly enhanced in presence of light (Adams et al. 2006). A range of studies has been reviewed and focused on nanoparticles—microbial interactions to correlate the physicochemical properties of engineered metal and metal oxide NPs and their biological response. Further, it has been concluded that the species specific toxicity can be attributed to nanoparticles' size and shape. However, the surface coating of the material, which can be altered significantly by environmental conditions, can ameliorate or promote microbial toxicity (Suresh et al. 2013). Studies on ecologically relevant bacterial species such as *E. coli, Bacillus subtilis, Pseudomonas putida*, and other have clearly indicated that NPs can be taken up by microbes (Table 3.2).

Table 3.2 Nanotoxicity on diverse microbes

Microbes	Toxicity	Nanomaterials	References
E. coli	Inhibition of bacterial growth, bactericidal action	Ag	Pal et al. (2007)
Pseudomonas putida	Inhibition of bacterial growth	ZnO	Li et al. (2011)
B. subtilis, E. coli	Mild toxicity due to ROS production	TiO_2, SiO_2, ZnO	Adams et al. (2006), Sapkota et al. (2011), Li et al. (2011)
E. coli, P. aeruginosa, Staphylococcus aureus, and *Salmonella typhimurium*	Antibacterial activity	Ag	Sahu et al. (2012)
Nitrogen fixing root nodules	Decrease of N_2 fixation potentials	CeO_2	Priester et al. (2012)
Rhizobiales, Bradyrhizobiaceae, Bradyrhizobium, Methylobacteriaceae	Decline in bacterial communities and reduced diversity	TiO_2, ZnO	Ge et al. (2012)
AMF (*Trifolium repens*)	Reduced mycorrhizal clover biomass	FeO, Ag	Feng et al. (2013)
Proteobacteria and *Verrucomicorbia*	Decrease in community abundance	MWCNTs	Khodakovskaya et al. (2013)
B. cereus, *P. stutzeri*	Decreased microbial transcriptional response	Ag, Al_2O_3	Fajardo et al. (2014)
P. stutzeri	Increased oxidative stress	nZVI	Sacca et al. (2014)
Gram-positive and Gram-negative bacteria, and fungi	Reduced biomass	SWCNT	Jin et al. (2014)
Rhizobium leguminosarum	Morphological changes to the bacterial cells	TiO_2	Fan et al. (2014)

Most of the microbes have developed effective molecular mechanisms and operated specific biochemical pathways to efflux, detoxify, and accumulate the metals ions much before it was learnt by the plants. Further, microbes are also capable to volatilize some of the metal ions to get rid of its acute toxicity (De Souza et al. 1999). Although microbes have developed resistance and avoidance mechanism, but more targeted studies are needed in regards to beneficial soil microbes such as N_2 fixing, phosphate solubilizers, AM fungi to establish the uptake mechanisms and consequences in soil and microbes.

3.6 Fate of Nanomaterials and Generation of Nanowaste

3.6.1 Accumulation in Plants

So far, very few nanoparticles and plant species have been studied with respect to the accumulation and subsequent availability of nanoparticles in food crops (Yin et al. 2011). The transfer of NPs into the food chain through edible plants is of great concern. The fruits of one such food plant *Cucumis sativus* L. which is a freshly consumed as garden vegetable analyzed using synchrotron μ-XRF and μ-XANES, showed root-to-fruit translocation of TiO_2 without biotransformation (Servin et al. 2013). Similarly, bioaccumulation of Ce and Zn was confirmed by μ-XRF images, suggesting that Ce moves between tissues with water flow during transpiration (Zhao et al. 2013b). Likewise, modified ultra-small TiO_2 (anatase) surface with Alizarin red S, and sucrose is found to accumulate in *Arabidopsis thaliana*. This study demonstrated that nanoconjugates traversed cell walls, entered into plant cells, and accumulated in specific subcellular locations (Kurepa et al. 2010). Microscopic observation reported by Ma et al. (2013) for plant seedlings of cattail (*Typha latifolia*) and hybrid poplars (*Populous deltoids* × *Populous nigra*) indicated that large amount of nZVI coated on plant root surface as irregular aggregates and some penetrated into several layers of epidermal cells of poplar root cells. Shi et al. (2014) investigated the phytotoxicity and accumulation of CuO NPs to *Elsholtzia splendens* (a Cu-tolerant plant) under hydroponic conditions is dose-dependent. Cu K-edge X-ray absorption near-edge structure analysis revealed CuO NPs-like deposits in the root and leaf cells. Similarly, Hu et al. (2014) have reported that aggregation and dissolution of ZnONPs are responsible for zinc accumulation in leaves and roots of *Salvinia natans* after 7 days of exposure. In another study, Zhai et al. (2014) observed that uptake and presence of AuNPs in cytoplasm and various organelles of root and leaf cells of poplar plant by transmission electron microscopy and measured by inductively coupled plasma mass spectrometry (ICP-MS).

3.6.2 Aggregation in Soil and Water Bodies as Nanowaste

Quantitative data related to concentrations of nanoparticles in natural water have not been reported so far. However, a recent report using a simplified box model and their known uses (Boxall et al. 2007), Klaine et al. (2008) has suggested environmental concentrations of approximately 1–100 μg L^{-1} as compared to typical dissolved and colloidal organic matter in freshwaters which may be found at 1–10 mg L^{-1} concentrations.

Soils and water are likely to be increasingly at receiving end of NPs due to growing consumer products that contains NPs. The level of NPs in soil and water is increasing due to the growing consumer products that contained NPs. Investigation on waste streams revealed the occurrence of NPs (Biswas and Wu 2005; Bystrzejewska-Piotrowska et al. 2009), indicating the necessity of further systematic investigation into the fate and bioavailability of nanoparticles in soils. Retention of NPs in soils was studied by Cornelis et al. (2012), wherein the dominant properties that determine the retention of AgNP in natural soil was correlated to negatively charged AgNP which was found to be adsorbed preferentially at positively charged surface sites of clay-sized minerals. The high organic carbon content in the agricultural soil likely contributed to an organic surface coating and resulted in NPs mobility through the soil. Further, Cornelis et al. (2014) have thoroughly reviewed the fate and bioavailability of engineered nanomaterials in soils, wherein author concluded that salinity, texture, pH, concentration and nature of mobile organic compounds, and degree of saturation determine ENM bioavailability.

The surface properties of the nanoparticles are known to be one of the most important factors that govern their stability and mobility as colloidal suspensions, or their adsorption or aggregation and deposition. Zhao et al. (2013a) observed coexistence of ZnONPs with Zn dissolved species were continuously released into the soil solution to replenish the Zn ions or ZnONPs scavenged by roots as compared to soil treated with alginate which promotes the bioaccumulation of Zn in corn plant tissues. In another interesting study, the fate of Cu and ZnONPs was monitored over 162 days and it was observed that both NPs traveled through the soil matrix at differential rates. CuNPs reported to be retained in the soil matrix at a higher rate compared to ZnONPs. Leaching of Cu and Zn ions from the parent NPs was also observed as a function of time (Collins et al. 2012). Physicochemical characteristics of NPs (e.g., shape, size, and surface charge) and soil (e.g., pH, ionic strength, organic matter, and clay content) affect physical and chemical processes, resulting in NPs dissolution, agglomeration, and aggregation. The combined results reported in the literature, suggests that metallic CuNPs can be considered the least mobile as compared to Fe_3O_4, CuO, TiO_2 and ZnONPs (Ben-Moshe et al. 2010). The behavior of NPs in soil controls their mobility and their bioavailability to soil organisms which may interact with beneficial soil microbes (Fig. 3.2) and extend the impact on their survival.

Failure to address the concerns of leftover of leachates from excess and after use NPs ultimately finds the way and accumulates over a time period in the form of aggregates and colloids in soil and water bodies. These aggregates and colloids containing NPs will generate an additional anthropogenic waste (nanowaste) in the agroecosystem (Fig. 3.3). This needs continuous monitoring of the fate of nanoproducts vis-a-vis the left over nanowaste and soil composition.

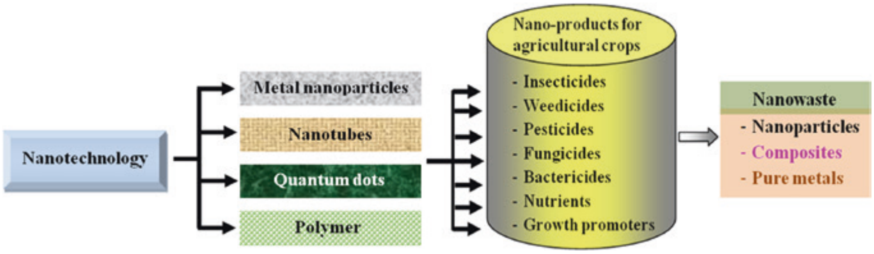

Fig. 3.3 A schematic pathway of nanotechnology to nanowaste in agroecosystem (Thul et al. 2013)

3.7 Conclusions

Recent rapid advances in understanding, synthesis, and manipulation of nanoparticles undoubtedly will continue with phenomenal growth of nanomaterial encompassed products. Use and its application in the field of agriculture, for improved crop growth, have shown significant promising potency and active uptake of necessary ingredients and absorbents. However, due to the very small size, reactivity, and efficient penetration ability, metal nanoparticles could reach many intracellular and extracellular sites of plants. This may trigger a set of physiological processes such as senescence affecting plant growth, crop yield, and ecological productivity. Moreover, there are major concerns on the use of NMs due to the toxicity to microbial systems present in the soil environment. The nanoparticle interactions with bacteria can vary. Scientific reports suggest that metal and metal oxide NPs of small size are more toxic. The long-term deposition of nanomaterials in the form of aggregates and colloids, not only threaten the security of soil and water resources, but, may prove to be impossible to remediate. In view of the foreseeable use of NPs based products, there is a need for systematic study to evaluate the effects of nanoparticles on crop plants and their environmental consequences.

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