10 Soil Ecological Pros and Cons of Nanomaterials: Impact on Microorganisms and Soil Health

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10.1 Introduction

Nanotechnology, a technology at a level of nano, has a positive implication over the scientific community. The term "nanotechnology" was coined by Professor Norio Taniguchi with a fineness of 1 nm (10^{-9} m) in either dimension (Rai and Ingle 2012; Aslani et al. 2014; Huang et al. 2015). Moreover, it could be considered as a promising field and has the potential to widen opportunities in various human scientific fields like agriculture and medicine. The application of nanotechnology to agriculture is also getting attention nowadays (Prasad et al. 2014). In developing countries like India where there is food shortage, food production can be doubled or achieved through introduction of nanotechnological innovation in agriculture as nanofertilizers, nanopesticides, nanoherbicides, and nanobiosensors (Panpatte et al. 2016). Different systems of agriculture such as conventional or conservation agriculture have different cultural practices like applications of weedicide, herbicide, and fertilizer, which could disturb soil health. The current scenario of intensive modern agriculture fully depends on higher levels of inputs such as chemicals, fertilizers, and pesticides to sustain the crop production. Moreover, nanoparticles and its behavior curb the attention in sustainable agriculture in emerging countries like India. Nanoparticle research in soil sciences, which is a blend of physics, biology, chemistry, and pedology (Adewopo et al. 2014), is not well established in relation to nutrient cycling, nutrient transport, and microbial proliferation because the high surface area of nanoparticles is more biologically and chemically active than bulk particles in soil (Sozer and Kokini 2009; Ma et al. 2010). Due to the interaction between nanoparticles and plants, many morphological and physiological characters of plants may be altered, and it is highly depending on the properties of these nanoparticles. (Siddiqui et al. 2015). Furthermore, the efficacy of these nanoparticles is determined by their chemical composition, size, shape, surface area,

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reactivity, and most importantly the dose at which they are effective in soil. Studies are not enough to find the positive effects on the nanoparticle interaction and biological inputs.

10.2 Soil Ecological Services/Microbial-Mediated Soil Health

Soil is the most important component in maintaining the ecosystem balance on Earth, and it is a crucial non-renewable resource and is formed by chemical and biological weathering of underlying rocks. In natural system, soil is the heart of abundant microflora (bacteria, fungi, actinomycetes, etc.) which constitute up to 75–90% of the soil-living biomass, comprising of beneficial as well as harmful microbes. Microorganisms are the primary decomposers of organic matter and play an important role in the improvement of soil structure as well as stabilization of soil aggregates and solubilization of mineral phosphates and other nutrients (Miller and Jastrow 2000), by secretion of phosphatase, a-gluconase, dehydrogenase, and antibiotics (Hass and Keel 2003). Soil microbial communities underpin the productivity of all agricultural enterprises and are primary drivers in ecological processes such as the nutrient and carbon cycling, degradation of contaminants, and suppression of soilborne diseases. These organisms live on soil, organic matter, or other soil organisms and perform many vital processes in the soil. Some of them perform critical functions in the nutrient and carbon cycles. The functions may vary between the microorganisms and processes driven by soil microorganisms. Microbial diversity of soil is governed by the presence of variety of substances like organic compounds (Tiedje et al. 2001). The presence of substances is responsible for the diverse microbial community in soil.

The rhizosphere, that is, the narrow zone surrounding and influenced by plant roots, is a hot spot for numerous organisms and is considered as one of the most complex ecosystems on Earth (Hinsinger and Marschner 2006). Soil enzymes (originated from soil microbes) are constantly playing vital roles for the maintenance of soil ecology and soil health. These enzymatic activities in the soil are mainly being derived from intracellular, cell-associated, or free enzymes. Therefore, microorganisms are acting as the indicators of soil health, as they have active effects on nutritional cycling, also affecting the physical and chemical properties of soil. Microorganisms respond quickly even to minute changes by changing their population and activities, and thus, can be used for soil health assessment. They are the better indicators of soil health as changes of enzymes are much sooner than other parameters, thus providing early indications of changes in soil health. In addition, their activities can be used as the measures of microbial activity, soil productivity, and inhibiting effects of pollutants. The potential enzymes that play major roles in maintaining soil health are amylase, arylsulphatase, β-glucosidase, cellulase, chitinase, dehydrogenase, phosphatase, protease, and urease. Soil microbial activity consists of a vast range of activities in soil, for example, the evolution of CO_2 from degradation of organic substances under aerobic conditions, rate of ammonia oxidation to nitrate, DNA synthesis in bacteria, and dehydrogenase activity and the activity of several intracellular enzymes catalyzing the substances to smaller compounds. Extracellular enzyme activities are mainly induced by soil particles such as soil colloids, hold the enzymes for longer period, and persist even in harsh environment (Nannipieri et al. 2002).

10.3 Nanoparticles in Soil Environment

Generally nanoparticles entered into natural environment through different phenomena like application of nano products, spill during use of nano-containing materials, disposal of nano wastes, and urban sewage sludge containing nanoparticles (Tolaymat et al. 2017; Zuin et al. 2013). The annual release of manufactured nanoparticles into the soil environment is not clearly documented across the world and cannot be accurately estimated also. Meanwhile, Tran et al. (2015) classified exposure into different categories as occupational exposure, environmental exposure, and exposure from consumer products. Concerning agricultural soil, accumulation of nanomaterials occurs through various sources like a direct release into the soil (nanofertilizer), air (nanopesticides spray), and water (through leaching) in agriculture perspective and exposed nanoparticles can affect the soil environment. There are many possible ways for exposure of nanoparticles to the environemnt which can pose a serious threat to human and environmental health. Further sources of nanomaterials may be elaborated and classified into point (source of origin) and non-point (unknown sources). Point sources are desribed as the sites where naomaterial containing waste are directly dumped in to soil and water. Incorporation of nanomaterial in agriculktural practices also considered as point source (Prasad et al. 2012) (Fig. 10.1). Generally, water treatment plants generate sludge at the end of the processes and act as a major contributor to the accumulation of nanoparticles and heavy metal in the environment. They consist of heavy metal nanoparticles such as TiO2 and Ag nanoparticles that enter the soil environment and retained for many years (Tourinho et al. 2012; McGillicuddy et al. 2017).

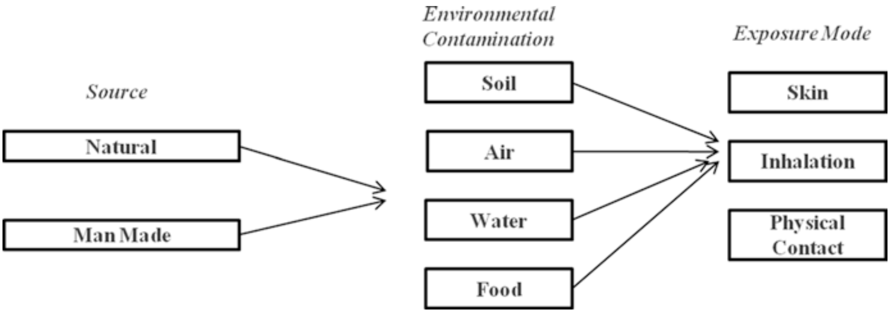

Fig. 10.1 Sources of nanoparticles in the environment

Nanoparticles in soil environment are in situ and man-made (engineered); generally, in situ consists of fractions of soil such as colloids, fine, and ultrafine particles which are in the range of nano and also actively involved in soil reactions through cation exchange capacity and particle orientation. Moreover, soil nanoparticles were developed by weathering; erosion process induces the formation of nano clays, amorphous minerals like Fe and Mn oxides. The man-made source of the nanoparticle is categorized into broad categories viz., metal oxides (ZnO, CuO, SiO2), metal (Zn, Fe, Al, Ag, Ni, Si), and carbon-based nanomaterials (fullerene). Among these, metal nanoparticles were widely used and studied by various researchers concerning the microbial diversity and its functions in soil (Yadav et al. 2014; Singh and Kumar 2016; Priester et al. 2017; You et al. 2017). Their small size (less than 100 nm) and the very high surface to volume ratio enabled them to display a superior reactivity potential over the bulk material. Further, nanoparticles have a place between transitional range of molecules and bulk material. After their release in the environment through many pathways and sources, nanoparticles undergo transformations such as dissolution, fixation, and toxicity development and accumulate in various environmental matrices such as air, water, soil, and sediments including wastewater sludge. It is inevitable that engineered nanoparticle will be released into the soil and waters during their use and increase the load of nanoparticles in different environmental matrixes, as reflected by an increasing concern over the potential impact on environment, aquatic, and terrestrial organisms. Once released in the soil environment, microorganisms may absorb the nanoparticles by active or passive mechanism of uptake (Fig. 10.2). Absorbed nanoparticles may enter into the microorganisms and cause serious damage to the microbial population. Because of its highly reactive nature and large surface areas, they have the potential to carry the toxic content to a wide range of microbial species. The intensity of hazards imposing on environment implies on size distribution, agglomeration, crystallinity nature, elemental composition, volume to surface ratio, and surface area of nanoparticles (Colvin 2003). However, understanding of nanoparticle behavior in soil was not well studied and still under an infant stage and unopened (Table 10.1).

Nanoparticles differ in size, shape, chemical composition, and many physicochemical properties. It is therefore crucially important to know which properties may cause adverse health effects. The accumulation of engineered NPs (ENPs) has been shown in various organisms and environmental compartments, such as blue and green algae, fish and other aquatic organisms, as well as soil and sediments.

10.4 Mechanisms Involved in Toxicity of Nanomaterials

Soil microorganisms quickly respond to the added nanomaterials by absorbing the nanoparticles within their bodies through their gut (Lin et al. 2007), translocation within the body, diffusing through cell membranes, endocytosis (Kim et al. 2006), and adhesion to the microbe’s cell. However, unknown interactions

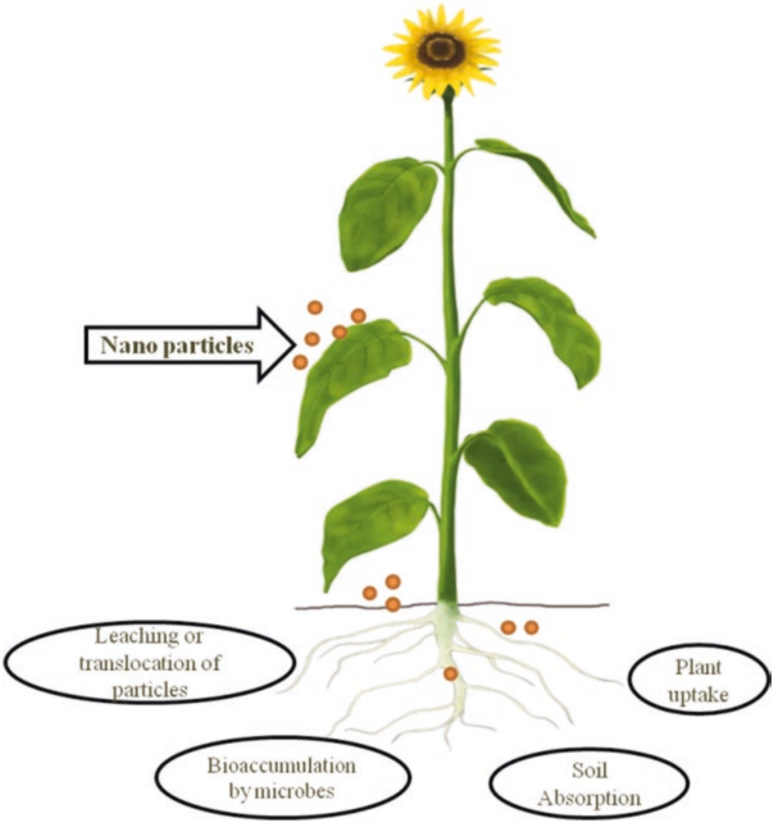

Fig. 10.2 Fate of nanoparticles in soil environment

are more relevant to environmental impacts, which may cause toxicity and adversely impact the soil biota. The possible mechanisms include disruption of membranes, oxidation of proteins, genotoxicity, interruption of energy transduction and formation of reactive oxygen species, and release of toxic constituents (Medintz et al. 2005). Bacterial cell membrane acts as an important part for cellular functions, such as regulation of material transport, energy transduction, and intercellular communication. Whereas nanomaterials between 5–80 nm have been reported to enter bacterial cells (Kloepfer et al. 2005) and as well living cells of bacteria would accumulate the aggregated materials. Attached and adsorbed nanoparticles may disrupt the cell integrity and functions of the cell substances, which makes the cell membrane conducive for translocation. Puncturing of the bacterial cell membrane in a gram-positive bacteria strain by added nanoparticles like Si, fullerene, and cyclo-fullerene (Tsao et al. 1999), in a similar way as gold nanoparticles, has been reported to weaken the cell membranes in *E. coli* (Hwang et al. 2007). Nanomaterials can also indirectly cause membrane damage through the generation of reactive oxygen species (ROS),

Table 10.1 Effect of nanoparticles application on different soils

Type of soil	Nanoparticle	Concentration in soil	Major impact	Reference
Sandy	Ag	0.14 mg kg^{-1}	Modification of bacterial communities	
		1.25 μg kg^{-1}	Decreased enzyme activities	Colman et al. (2013)
		1–1000 mg kg^{-1}	Effect on enzymes	
	Au	0.1–100 mg kg^{-1}	Significant effects on soil enzyme activities, microbial communities and nutrient cycling	Asadishad et al. (2017)
	Al_2O_3, SiO_2	50 mg kg^{-1}	Dehydrogenase and urease activity reduced	McGee et al. (2017)
Acidic soil	Fe, Ni, Ag	550 mg pot^{-1}	Pyrosequence analysis showed no significant effect on soil microbial richness	Shah et al. (2014)
Red sandy loam soil	CuO, Fe_3O_4	10 g kg^{-1}	Affected soil microbial community and also affected by Fe_3O_4 and changes humic substances	Ben-Moshe et al. (2013)
Sandy clay loam	TiO_2	20 g kg^{-1}	Decreased bacterial diversity and modified diversity	Ge et al. (2012)

which cause a series of actions that trigger radical formation by Fenton reaction, lipid peroxidation, and DNA cleavage. This results in membrane disruption and makes cells more susceptible to osmotic stress or hinders nutrient uptake (Cabiscol et al. 2000). Development of toxicity in applied nanoparticles is generally governed by the concentration of organic matter in soil, which enhances the formation of aggregates and interaction of bio-materials with the nanoparticles. Soil pH influences ionic solution and effective cation exchange capacity. Toxicity of nanoparticles was assumed to be caused by higher surface compared to bulk materials which increases their potential to dissolve into a solution.

10.5 Types of Nanoparticles and Their Interaction with Soil Health

The behavior of nanoparticles varies soil to soil, transportability of nanoparticles, retention capacity of the soil, mobility nature of nanoparticles (Wang et al. 2012), and properties such as pH, soil organic matter, ionic strength of the medium, buffering capacity, and colloids of soil. For instance, the presence of high organic matter content may adsorb the metal nanoparticles especially Cu and Zn easily and may release the adsorbed metals to the soil solution that increases the mobility of those involved in the reactions. Application and accumulation of nanoparticles in soil alter the chemical and biological properties of the soil but not its physical properties. For example, added Fe nanoparticles and carbon nanotubes did not affect the soil porosity and clogging (Elliott and Zhang 2001).

10.6 Nanofertilizers

Plant nutrition through nanomaterial is getting more attention and making a provision of nutrient application for the commercial/field crops. Nano-nutrients, which are generally prepared from inorganic sources, may cause impact over soil microorganisms. However, nanoparticles prepared through organic or biotic method are definitely environmentally friendly and easy to use (Ditta et al. 2015). Enhanced plant growth and productivity were observed with the use of different nano-nutrients such as formulation of nanofertilizers and nano-porous zeolites (Scrinis and Lyons 2007). It is also reported that nanomaterials have great implications in sustainable agricultural crop production and productivity (Ditta et al. 2015). The evaluation of these materials as a nutrient source and their critical concentration may cause positive/negative impact to the soil biota. List of materials using nanofertilizers is given below (adapted from Tarafdar and Adhikari 2015):

- Nitrogen nanofertilizers
- Phosphate nanofertilizers
- Potassium nanofertilizers
- Sulfur nanofertilizers
- Iron oxide nanoparticle
- Magnesium nanofertilizers
- Copper oxide nanoparticles
- Manganese nanoparticles
- Zinc oxide nanoparticles
- Silicon nanoparticles

10.7 Oxide Nanoparticles

Metal oxide nanoparticles are highly reactive against soil microbial communities. The responses had been varied with the nanoparticle properties, especially ZnO nanoparticles that highly vary with the system properties and amount of Zinc applied to the soil. This caused major alteration in the soil microbial diversity, growth inhibition, and species-specific toxicity (Ge et al. 2011 and Rousk et al. 2012).

10.8 Carbon Nanoparticles

Toxicity developed by nanoparticles in soil matrix depends on various species and properties of nanoparticles itself (surface area, size, and shape), and the mean time interaction with soil colloids also varies with pH, organic matter content, and concentration of nanoparticles (Musee 2010). Generally, nanoparticle impact on microbial species is described with inhibition and toxicity. With respect to the nanoparticles, Zn was highly studied among the nanoparticles. However, single species was tested with Zn nanoparticles to testify the sensitivity (Dimkpa et al. 2012). Various single species and nanoparticle interaction studies provided an insight into the mechanisms involved in nanoparticle interaction and microbes. Moreover, literature indicated that the oxidative damage which leads to the oxidation of protein is the main cause of toxicity produced by applied nanoparticles to the microbes

Table 10.2 Toxic effects of nanomaterials on bacteria

Nanomaterial	Toxic effects	References
C60 water suspension (nC60)	Antibacterial to a broad range of bacteria	Sayes et al. (2004)
C60 encapsulated in polyvinylpyrrolidone	Antibacterial to a broad range of bacteria	Kai et al. (2003)
Hydroxylated fullerene	Bactericidal for Gram-positive bacteria	Rozhkov et al. (2003)
Carboxyfullerene (malonic acid derivatives)	Bactericidal for Gram-positive bacteria due to fullerene insertion into the cell wall; inhibitory or ineffective against Gram-negative bacteria	Mashino et al. (1999)
Carbon nanotubes	Single-walled antibacterial to *E. coli*, cell membrane damage	Wei et al. (2007)
Multi-walled carbon	Cytotoxic to microbes	Biswas and Wu (2005)
Metallic quantum dots	Penetrate cells by oxidative damage to membrane; uncoated quantum dots toxic to *E. coli* and *Bacillus subtilis*	Hardman (2006)
Silver	Bactericidal; viricidal	Sondi and Salopek-Sondi (2004)
Gold	Low toxicity to *E. coli* and *Staphylococcus aureus*	Goodman et al. (2004)
Metal oxides	Low toxicity to *Shewanella oneidensis*	De Windt et al. (2006)
Magnetite		
TiO_2	Accelerates solar disinfection of *E. coli* through photocatalytic activity and reactive oxygen species (ROS); surface coatings photocatalytically oxidize *E. coli, Micrococcus luteus, B. subtilis*, and *Aspergillus niger*	Rincon and Pulgarin (2004)
MgO	Antibacterial activity against *B. subtilis* and *S. aureus*	Huang et al. (2005)
CeO_2	Antimicrobial effect on *E. coli*	Sawai et al. (1995)
ZnO	Antibacterial activity against *E. coli* and *B. subtilis*	Thill et al. (2006)
Others	Mild toxicity due to ROS production	Adams et al. (2006)
SiO_2		

(Kumari et al. 2011). But such kind of single species studies lacks in complexity behavior (Table 10.2).

10.9 Studies on Bacteria

Microorganisms are of great environmental importance because they are the foundation of soil ecosystems and provide key environmental services ranging from primary productivity to nutrient cycling to waste decomposition. Consequently, an understanding of nanomaterial toxicity to microbes is important to evaluate the potential impacts of NMs in the environment. When nanoparticle attached to microorganisms, their fate and behavior get damaged (Lyon et al. 2007). The literature on toxicity of various nanomaterials on soil microorganisms is documented but very limited. However, the toxic effects of nanomaterials in prokaryotic systems are increasingly being characterized. Silver nanoparticles and titanium dioxide are among the best studied with respect to microbial toxicity. The bactericidal effect of silver compound and silver ions is well known and has been applied as pesticide against important pathogen. Release of silver ions from nanoparticle induced is one of the particle effect toxic mechanisms of silver nanoparticle (Morones et al. 2005).

Accumulation of nanoparticles into the soil might have a significant impact because of resistant nature of nanoparticles against native degradation. Soil properties, especially soil microbial biomass and diversity, are directly and indirectly affected when exposed to nanoparticles (Torsvik and Ovreas 2002). Toxicity level on soil microbial population varies with concentration level. It was observed that the high concentration level induced reduction in dehydrogenase activity (Josko et al. 2014). Considering the presence of nanoparticles in soil, it is significant to study their influence on soil biodiversity (Bondarenko et al. 2013). Soil properties such as pH, texture, structure, and organic matter content influence the soil microbial community and particle size of nanoparticle. The composition of the organic matter altered microbial populations in some soils. Thus, there is a need to compare the toxicity of the nanoparticles in various types of soils (Calvarro et al. 2014).

10.10 Nano on Enzymes

Microorganisms are involved in the cycling of carbon, nitrogen, sulfur, and phosphorus in geochemical cycles of Earth. Because microorganisms are especially sensitive to environmental changes (Sadowsky and Schortemeyer 1997), the structure and abundance of the microorganism community may shift in response to foreign nanomaterials (Ge et al. 2011; Kumar et al. 2011; Tong et al. 2007). Because microorganisms help regulate and maintain overall ecosystem health and function (Kaye et al. 2005; Janvier et al. 2007), changes in the microbial community will have a great effect on the entire ecosystem (Kanerva et al. 2008). Therefore, a better understanding of how microorganisms respond to nanomaterials can help to address environmental and health concerns brought about by the manufacture and use of nanomaterials. Due to the existence of multiple factors in complicated environments such as soil, investigations of the effects of nanoparticles on bacteria in situ are more meaningful than those under pure culture. However, there are limited and inconsistent data regarding the effect of nanoparticles on the soil microbial community. For instance, fullerenes have little impact on the structure and function of the soil microbial community (Tong et al. 2007), whereas nano-TiO_2 and ZnO have negative effects on soil bacterial communities (Ge et al. 2011).

The release of nanoparticles to the soil is inevitable due to increased development of the nanomaterials industry, disposal of nano-containing consumer goods, utilization of nano-containing materials, etc. Identifying bacterial responses provides valuable information on the influence of nanoparticles on soil health. Application of γ-Fe_2O_3 with varying concentrations may favor the bacterial growth in some soil. This impact of iron nanoparticles on the bacterial community could possibly be attributed to both the characteristics of nanoparticles (Ju-Nam and Lead 2008; Nowack 2009) and their contribution to the microorganisms metabolism. Due to their tiny size and stabilization, iron nanoparticles can be easily transported into soil. Nano-metal oxides have enhanced surface-to-volume ratio (Waychunas et al. 2005); therefore, partial decomposition and release of ions are more likely for nanoparticles compared to the bulk material. Furthermore, nanoparticles have the most active surface sites (mainly Fe-OH site on iron nanoparticles) that are able to bind to natural organic compound. For example, with the assistance of organic compounds in the soil, such as humic acids (HA) and fulvic acid (Illes and Tombacz 2006), addition could enhance the bioavailability of iron to the soil bacteria. Humic acid is formed during the physico-chemical and microbial degradation of plant and animal residues and is abundant in natural systems. It has a skeleton of alkyl and aromatic units that attach with carboxylic acid, phenolic hydroxyl and quinone functional groups, which could have strong affinity to the surface of IOMNPs. Therefore, the bio available iron ions in soil are increased and would subsequently stimulate the growth of some microbes in soil. Iron is an essential nutrient for almost all microorganisms because it plays an important role in optimum cell growth. Iron acts as a cofactor for a large number of enzymes, forms part of cytochromes and is required for many biochemical reaction, including respiration, photosynthetic transport, nitrate synthesis, nitrogen fixation and DNA synthesis. Microorganisms employ various iron uptake systems to secure sufficient supplies from their surroundings (Hantke 2001). It has been suggested that iron-based nanoparticles are toxic due to the generation of reactive oxygen species (ROS). Previous studies have shown that chemically stable nanoparticles (γ-Fe_2O_3) have no apparent cytotoxicity, whereas nanoparticles containing either Fe^{2+} or Fe^0 result in a dose-dependent decrease in the survival of *E. coli*, mainly due to oxidative stress. γ-Fe_2O_3 nanoparticles are composed of fully oxidized crystals and, consequently, are highly stable in the environment, indicating a lower capacity to generate oxidative stress. In contrast, Fe_3O_4 nanoparticles are unstable because of the high mobility of electrons within the structure and the diffusion of Fe^{2+}. Reduced iron oxides are known to be efficient ROS producers (Auffan et al. 2008).

Changes in the soil bacterial community could result in variation in soil enzyme activities. Soil enzymes play an essential role in matter and energy cycling in soil. Soil dehydrogenase, invertase, urease and phosphatase were significantly stimulated by iron nanoparticles, which could be caused by nanoparticles induced changes in the bacterial community. Actinomycetes facilitate the decomposition of organic matter; soil invertase and urease could be enhanced by the addition of iron nanoparticles.

10.11 Conclusions

Nanotechnology is a fascinating field of science that is widely exploited in various disciplines, and this chapter highlights the impact of nanoparticles on soil microbial diversity and soil environment. To enhance the research efforts in nanotechnology, agricultural scientists should take a cue from medical sciences as a guiding force that can be exploited in agricultural production systems. In this chapter, the literature review has clearly suggested that there is an abundance of scope to exploit the smart delivery of agricultural inputs which facilitate enhanced use efficiency and ensure environmental protection. Nanotechnology can be used as an enabling technology to revolutionize the world. Moreover, there is no doubt that nanomaterials have numerous positive and negative implications in various sectors including agriculture. Apart from positive effects on plant growth, more focus should be given on the negative impact and toxicity of various nanoparticles toward the soil microorganisms. On the one hand, nanoparticles promote the growth of the plants; on the other hand, they exert a negative impact on the agroecosystem, such as soil constituents and microflora. The toxicity of nanomaterials to the agroecosystem has become a great challenge; the development of effective strategies for the control of size, shape, and surface area, capping of nanoproducts using different non-toxic materials, and prevention of aggregation will help in the reduction of adverse consequences.

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