Chapter 5
Effects of Nanoparticles on Germination, Growth, and Plant Crop Development

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Abstract The use of nanotechnologies in agricultural systems has been widely promoted. Nanomaterials have been proposed as a useful tool for the improvement of agricultural practices. Some plants have shown diverse effects in terms of morphological and physiological changes, with uptake and translocation into different parts. A relation has been demonstrated between the dose and the plant response in different crops, with variations from plant to plant. However, the use of nanoparticles for crop production still faces some challenges because of possible toxicity and hazardous effects, and especially because of the lack of experimental evidence that nanomaterials are harmless to plants and humans. Some studies have reported both positive and negative effects of nanoparticles on plant growth and development, depending on the nature of the nanomaterials, application, time of exposure, plant species, and soil characteristics. The objective of this chapter is to describe the effects of the application of nanoparticles on plant development, focusing on the physiological and biochemical mechanisms of plants in relation to nanoparticles. It also reviews the behavior of nanoparticles in the soil and water matrix and their effects on microbial communities interacting with plants.

Keywords Plant development · Uptake · Phytotoxicity · Crop yield

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1 Introduction

Nanotechnology is a fast-developing industry, and it has crucial impacts on the economy, society, and the environment, with implications for health, medicine, biomaterials, and treatment of solid, liquid, and gaseous residues (Fulekar 2010). The number of studies and researchers focused on the positive and negative effects of this sector have increased year after year around the world (Hullmann 2007). The multidisciplinary approach needed to understand this field has been integrated by policy makers, scientists, and social scientists, among others (Oberdörster 2010; Nikalje 2015; DeRosa et al. 2010; Ibrahim et al. 2016). The versatility of nanomaterials has reached a wide range of fields—e.g., agriculture, cosmetics, remediation technologies, robotics, chemistry, and optics (Vance et al. 2015)—leading to the release of nanomaterial residues into the air, water, and soil.

Balbus et al. (2007) classified nanomaterials into four groups: (1) carbon-based materials (CNMs), usually including fullerene, single-walled carbon nanotubes (SWCNTs), and multiwalled carbon nanotubes (MWCNTs); (2) metal-based materials such as quantum dots, nanogold (nano-Au), nanozinc (nano-Zn), nanoaluminum (nano-Al), and nanoscale metal oxides such as TiO_2, ZnO, and Al_2O_3; (3) dendrimers, which are nanosized polymers built from branched units capable of being tailored to perform specific chemical functions; and (4) composites, which combine nanoparticles with other nanoparticles or with more abundant, bulk-type materials. The first two types are common and are often studied.

Nanomaterials present physical and chemical characteristics that can modify their properties, such as conductivity, reactivity, and optical sensitivity. Therefore, these materials can generate adverse biological effects in living cells (plants and animals) (Wiesner et al. 2006; Vecchio et al. 2012; Shang et al. 2014). Some studies have demonstrated effects of nanoparticles and nanomaterials on human cells (Soenen et al. 2015; Suliman et al. 2015) and bacterial communities (Barnes et al. 2010; Ge et al. 2012; Yang et al. 2014); however, the number of studies describing the effects of nanomaterials on plants is limited relative to the vast numbers of plant species and nanomaterial types (Monica and Cremonini 2009). A significant number of nanoparticle and nanomaterial types have been tested on different types of plant (Lin and Xing 2007; Stampoulis et al. 2009; Ma et al. 2010; Lee et al. 2012; El-Temsah and Joner 2012; Liu and Lal 2015); these studies have contributed to the understanding of nanoparticles and their effects on biological systems.

Agriculture is one area that has been modified with the incorporation of nanomaterials, improving the yields of crop cultivars, increasing their nutritional values, and facilitating environmental monitoring of the cultivation conditions (Srilatha 2011; Razzaq et al. 2015). Nanomaterials have diverse uses in agriculture, such as micronutrient delivery systems, detection of pathogens, and crop and food system security. Since nanomaterials are in the same size range as viruses or bacteria, they can be used as materials for detection and eradication (Perlatti et al. 2013). In the agricultural sector, nanotechnology research and development are likely to aid and frame the next level of expansion of genetically modified crops, animal production inputs, chemical pesticides, and precision farming techniques (Scrinis and Lyons 2007).

Changes in agricultural technology have been a significant factor shaping modern agriculture. In the latest line of technological innovations, nanotechnology occupies a prominent position in transforming agriculture and food production. So far, the use of nanotechnology in agriculture has been mostly theoretical (Kumari and Yadav 2014), but it has begun to—and will continue to—have a significant impact in the main areas of the food industry, development of new functional materials, product development, and design of methods and instrumentation for food safety and biosecurity (Prasad et al. 2012).

2 Presence of Nanoparticles in the Environment and Their Interactions with Plants

In general, nanoparticles are structures that can be described as particulate matter in the nanoscale size range. Materials of this size also occur naturally in the environment. For the past 30 years, most of the works published in the literature regarding nanoparticles have mainly focused on synthetically customized nanoparticles, referred to as engineered nanoparticles. Because of their unique size, shape, and chemistry-related properties, engineered nanoparticles have been widely and successfully used in electronic, pharmaceutical, medical, cosmetic, and life science applications (Dionysiou 2004). Environmental cleanups such as improvement of environmental quality, water treatment processes, and remediation are among the activities in which engineered nanoparticles are also used (Crane and Scott 2012). Because of their commercial applications, concerns have been raised about their risks and fate in the natural environment when they are released accidentally or deliberately.

3 Sources of Engineered Nanoparticles in the Environment

In the last 20 years, the use of engineered nanoparticles in diverse applications (Nowack and Bucheli 2007) has been increasing. Although their presence in soil and water has been proved, the occurrence of nanoparticles in these environmental matrixes is complicated to estimate (Praetorius et al. 2013). The last estimation made by the Royal Society and Royal Academy of Engineering estimated delivery of around 60,000 tonnes of nanoparticles by 2020 (Maynard et al. 2006).

The chances of engineered nanoparticles being emitted into the environment are growing; therefore, their potential risks and toxicity could affect all living organisms on earth. There are several ways in which engineered nanoparticles can reach the natural environment by intentional and unintentional releases into solid and liquid waste streams from households, manufacturing sites, and waste treatment plants, and by emissions into the air. Uses of nanoparticles as additives in fabrics [e.g., silver nanoparticles (Ag-NP)], paints (TiO_2), personal health care products (sunscreens), and cosmetics are examples of their commercial applications. According to studies by Gottschalk et al. (2009), aquatic organisms could be those most affected by the release of Ag, TiO_2, and ZnO nanoparticles because of their presence in sewage effluent and wastewater sludge (Brar et al. 2010).

Anthropogenic nanoparticles are released into the environment from activities such as accidental spills, wearing of car tires, fuel exhaust, and urban air pollution (Sajid et al. 2015). Activities involving the use of engineered nanoparticles such as iron oxide and zero-valent iron nanoparticles (nZVI) in contaminated groundwater remediation and agriculture (use of fertilizers) are examples of the intentional release of engineered nanoparticles into the natural environment (Crane and Scott 2012). However, the current primary source of engineered nanoparticles deposited on land is the disposal of wastewater treatment plant sewage sludge, in which the nanoparticles released from commercial products into wastewater streams end up in the sewage sludge generated during municipal and industrial wastewater treatment processes (Stasinakis 2012; Xu et al. 2012). It has been observed that these engineered nanoparticles are unlikely to enter the environment in their original form. According to the literature, naturally occurring nanoparticles disappear from the environment by dissolution, and their change into bigger particles by aggregation is a widely studied and well-known mechanism. However, engineered nanoparticles are reported to potentially persist in the environment, especially in natural aquatic systems, because of the stabilizers used to coat these nanoparticles, which may contain toxic elements in their structures at specific concentrations (Handy et al. 2008, 2012). Therefore, concerns about the emission of engineered nanoparticles into the environment are growing in regulatory organizations worldwide.

4 Fate of Nanoparticles in Environmental Matrixes

4.1 Fate of Nanoparticles in Soil

Research publications on the behavior and fate of engineered nanoparticles in soil systems are very limited and are less numerous than work carried out in water systems. This is mainly due to the lack of methodologies and techniques for characterizing and investigating the interactions of nanoparticles with the different components in soil (i.e., organic matter, minerals, and microbial biomass) (Boxall et al. 2007). In fact, most of the research on the behavior of engineered nanoparticles in soils has been carried out on soil suspensions and not in soil systems as such. The interactions between natural colloids and other particles such as humic substances (HSs) and clay particles in soil have been shown to differ from those between these soil elements and engineered nanoparticles (Ben-Moshe et al. 2010). Once this interaction occurs, partitioning of these newly formed composites between the aqueous and solid phases within the soil takes place through desorbing mechanisms (Darlington et al. 2009). It has also been observed that in environmental conditions of low ionic strength and high concentration of organic matter, nanoparticles are less likely to interact with and sorb to soils, increasing the mobility in the case of metal nanoparticles (Tourinho et al. 2012).

Under environmental conditions, HSs are negatively charged, so these natural organic colloids can sorb to metal nanoparticle surfaces, improving their stability and reducing aggregation and sedimentation. However, this phenomenon does not occur with all metal nanoparticles. In the case of Al_2O_3 nanoparticles, different transformations have been observed (Ghosh et al. 2008). Environmental conditions and physicochemical features of nanoparticles dictate how these particles interact with the solid phase and hence their transport through soils; in porous media the mobility of nanoparticles is governed by Brownian diffusion (Lecoanet et al. 2004). However, gravitational forces become relevant as nanoparticles agglomerate and aggregate, making these larger particles interact more with the soil particle surfaces. There are also interactions such as electrostatic attraction and repulsion between nanoparticles and soil, which are controlled by the surface charges of the soil and the engineered nanoparticles. When the charge is similar in both systems, repulsion and therefore high mobility of nanoparticles are observed (Darlington et al. 2009). Repulsive forces are observed to decrease among nanoparticles in soil conditions of higher ionic strength, promoting more aggregation and sorption to the solid phase of the soil.

In some soil studies reported in the literature, smaller particles have been shown to be more mobile and to penetrate and reach groundwater. In the case of larger aggregates, more retention has been observed. These particles tend to remain in the top layers of soils, resulting in soil clogging, which is another factor to take into account in nanoparticle transport and mobility studies in the soil. In previous works carried out using copper oxide nanoparticles, it was observed that flow rate influences the deposition of these particles and also affects their aggregation in porous media (Darlington et al. 2009).

In the case of CNTs, the association of these nanomaterials with solid phases is one of the most relevant processes affecting the distribution of CNTs between water, soil, and sediments. Only one type of soil organic matter has been found to sorb acid-treated MWCNTs with sodium concentrations between 4 and 40 mM (Zhang et al. 2011). The sodium ions affect the surface charge of the soil organic matter and CNTs, facilitating interactions between these two components. Additionally, Zhang and coworkers showed that removal of dissolved organic matter–coated MWCNTs from the aqueous phase in the presence of peat was not affected by a change in pH from 4 to 8 (Zhang et al. 2011). Experimental results from the same work also suggested that in hard water or seawater, MWCNTs are more readily sorbed by sediments, whereas in aquatic systems with high concentrations of dissolved organic matter, MWCNTs tend to stay dispersed in the water.

4.2 Fate of Nanoparticles in Water

There are several mechanisms that engineered nanoparticles can undergo once they reach natural aquatic systems. Aggregation, dispersion, dissolution, sedimentation, photochemical reactions due to sunlight, transformation reactions, degradation by living organisms, and interactions with natural colloids and other water elements are some of the processes that need to be thoroughly understood to predict the fate, bioavailability, and ecotoxicity of engineered nanoparticles in water (Delay and Frimmel 2012).

As has been described, nanoparticles are known to repel each other when they are in close proximity, because of Brownian motion. This phenomenon is observed when their negatively charged surfaces overcome the weak bonding caused by van der Waals forces, which are also known as agglomeration attractive forces (Jiang et al. 2009). However, when nanoparticles are electrostatically functionalized, reduced stabilization can occur because of the counterions present in an aqueous solution.

Dissolution and chemical transformation are also possible processes that nanoparticles can undergo under environmental conditions. These processes are initially triggered by the speciation of the metal nanoparticles, which is facilitated by the redox and pH conditions of natural waters. The oxidation, dissolution, and speciation of zero-valent metal nanoparticles into the corresponding metal ions and the solubility of these ions are increased by acidic pH conditions (Levard et al. 2012). Once these metal ions are released from the nanoparticle surface, they can also undergo chemical transformation on the basis of their reactions with other inorganic species in natural waters, within thermodynamic constraints and possibilities.

Oxidation may occur not only for metal nanoparticles. In the case of CNTs, it is well known that the chemical oxidation of these CNMs requires strong oxidative forces, which are unlikely to occur spontaneously in the environment (Petersen et al. 2011). However, photo-oxidation reactions are possible. Several oxygen radicals [reactive oxygen species (ROS)] are produced when carboxylated SWCNT solutions are exposed to sunlight or to lamps that emit light within the solar spectrum (Chen and Jafvert 2010). These radicals can oxidize CNTs at the same time and modify their surfaces. Some oxidants such as ozone (which is commonly used in wastewater treatment) may potentially impact CNTs released into the environment through this pathway.

5 Incorporation of Nanoparticles into Plants

5.1 Fate of Nanoparticles in Soil

Most of the research performed on nanoparticles to analyze their distribution and behavior in ecosystems has focused on water systems; this is because of the limitations in the availability of methodologies for characterizing and investigating interactions with soil components (organic matter, minerals, microorganisms). Experiments to describe the behavior of nanoparticles in soil have been developed in soil suspensions (Nowack and Bucheli 2007), not in soil systems.

Among the organic compounds present in the soil, HSs are the most abundant; some colloids and clay are present in the soil matrix as well. Partitioning of the newly formed composites between the aqueous and solid phases take place, and sorption and desorption mechanisms are present; the presence of HSs and organic compounds could enhance the interaction of nanoparticles with soils, increasing the mobility of metallic nanoparticles, mainly.

The environmental conditions in the soil favor the negative charge of humic and fulvic acids, so the nanoparticles are attracted to them and form colloids to improve stability and reduce aggregation and sedimentation. This phenomenon does not occur with all metal nanoparticles; for instance, nanoparticles of aluminum show different transformations (Grillo et al. 2015). Some physicochemical features of nanoparticles—i.e., electrostatic repulsion, size, pH, organic matter content, ionic strength, solubility, surface charge, flow rate, van der Waals forces, and Brownian motion (Tourinho et al. 2012)—dictate their behavior and interactions with the solid phase in the soil, affecting transport and mobilization (Riding et al. 2015).

The surface coating of nanoparticles can affect their agglomeration/aggregation in soils; this is due to the presence of hydroxyl (–OH) groups, which can accept and release protons and can take up dissolved chemical species such as metal ions and ligands (Peijnenburg et al. 2015). Surface charging results in the formation of an electrical double layer, comprising the charged surface, in response to the charge; this potential (zeta potential) can be measured, and its variation is dependent on the pH value, tending to a zero value when the pH reaches the isoelectric point (Badawy et al. 2010).

The transformation of nanoparticles and nanomaterials is a phenomenon that affects the environment—for instance, dissolution, which has been widely studied for Ag and Zn nanoparticles (Xiu et al. 2012)—however, in realistic conditions (environmental conditions) this effect is present with simultaneous transformations such as deposition and aggregation with organic matter (Thio et al. 2011).

5.2 Microbial Role of Microorganisms in Plant Nutrition

Soil microbial communities, as a critical component of soil, favor a sustainable environment for plants and animals. The soil is a dynamic ecosystem and storage system for microorganisms, including bacteria, actinobacteria, cyanobacteria, fungi, archaea, microalgae, protozoa, and viruses (Lange et al. 2015). Microbes play an essential role in element cycling, affecting the composition and concentration of nutrients in the soil (Paul 2014). The carbon, nitrogen, sulfur, and iron cycles are driven and mediated by microorganisms in soils (Falkowski et al. 2008). The microorganisms generate nutrients such as vitamins, trace elements, and amino acids, which are fundamental for plant growth. The microbial communities coexist in the vicinity of plant roots and on the surfaces of the roots (rhizosphere and rhizoplane microbial communities) (Dennis et al. 2010).

5.3 *Effects of Nanoparticles on Soil Microbial Communities*

The benefits of nanoparticles and nanomaterials in medicine, biotechnology, agriculture, etc., are well known; however, it is necessary to understand the environmental implications of nanoparticles for components of it, such as soil microbial communities. Shah and Belozerova (2009) reported the importance of the soil microbial communities for ecosystem sustainability and its relationship with microbial diversity and soil and plant quality. Diverse studies (Ge et al. 2011; He et al. 2011; Frenk et al. 2013) have been performed to describe the interaction of nanomaterials and microbial diversity by using methods based on molecular analysis, such as fluorescent in situ hybridization (FISH), denaturing gradient gel electrophoresis (DGGE), and next-generation sequencing (NGS). The beneficial and adverse effects of nanomaterials on microbial communities have been analyzed, especially those focused on the use on metal and metal oxide nanoparticles (Du et al. 2011), fullerenes and carbon nanotubes (Tong et al. 2007), and nZVI (Fajardo et al. 2012).

Soil microbial communities, known as plant growth–promoting rhizobacteria (PGPR), mediate nitrogen fixation and the exoenzymatic activity of microbial communities (Bhattacharyya and Jha 2012). Karunakaran et al. (2013) performed studies that demonstrated adverse effects of Al_2O_3, TiO_2, and SiO_2 nanoparticles on *Bacillus subtilis* and *Pseudomonas fluorescens*, and also the toxic effects of nanosilica and bulk silica and alumina particles on PGPR members. Since the relationships between microbial communities and plants are apparently known, it is a priority to elucidate the effects of these nanomaterials on soil microorganisms and their effects on plant nutrition.

6 Behavior of Nanoparticles in Hydroponic Conditions

This cultivation method is suitable for semiaquatic plants and terrestrial plants, with the root system being immersed in a water nutrient solution or an inert medium. Because it allows better control of biotic and abiotic factors, hydroponics allows us to understand the nutritional status of plants and their growth; also, in this system, control of pH, microorganisms, and microbial enzymatic machinery are easily monitored (Schwabe et al. 2013). Many studies have been performed to describe the effects of nanoparticle solutions on seed germination (Lin and Xing 2007; Stampoulis et al. 2009; El-Temsah and Joner 2012), biomass growth (i.e., root elongation), root morphology, and cell morphology (Juhel et al. 2011; Yin et al. 2012; Wang et al. 2012). The same nanoparticle characteristics (physical and chemical) are essential for interactions with plants and mobilization in plant tissue in both hydroponic and soil media.

7 Uptake of Nanoparticles into Plants: Root Uptake

Uptake of nanoparticles by plant roots occurs via two routes: the apoplastic and symplastic routes. Plant cell walls are a complex matrix where pores permit passage into the plant cell (Deng et al. 2014). In uptake via the apoplastic route, nanoparticles that pass through these pores are diffused between the cell walls and the plasma membrane, and are subjected to osmotic pressure (Navarro et al. 2008). These nanoparticles can reach the endodermis. The symplastic pathway allows entrance of nanoparticles through the inner side of the plasma membrane; this route is more important than the apoplastic route. The processes involved in the passage of nanoparticles through the plant are represented in Fig. 5.1. Nanoparticles can use the carrier proteins in cells through aquaporin proteins, which regulate water passage in cells, ion channels, and endocytosis (Qian et al. 2013).

The interactions of nanomaterials with cells and with the environment occur mostly through van der Waals, electrostatic, and steric forces. The nanoparticles and endosome or protein complexes can translocate to another cell through plasmodesmata (measuring approximately 50 nm) (Zhai et al. 2014). Not all nanoparticles can enter plant cells, and reports have confirmed the passage through the plant cell of

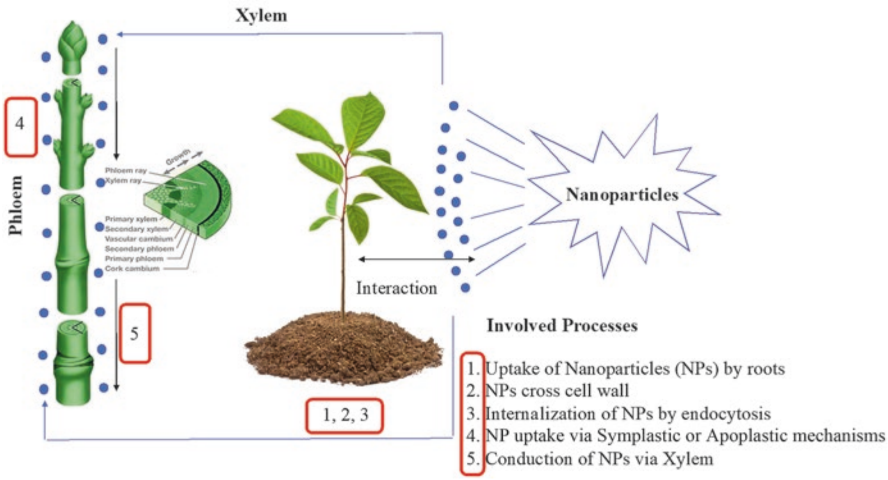

Fig. 5.1 Mechanisms involved in nanoparticle transport through a plant. After plant exposure to nanoparticles, these nanostructures pass vegetal barriers; some specific mechanisms are triggered, and some critical effects can be observed

ZnO nanoparticles (Lin and Xing 2008) and TiO_2 (Du et al. 2011); however, the question remains as to why other nanoparticles do not present the same behavior.

7.1 Uptake of Nanoparticles into Plants: Foliar Uptake

Depending on the exposure route, foliar entrance of nanoparticles also occurs in some cases and under specific conditions; the reported mechanism occurs via the stomatal pores (Hong et al. 2014). In recent years, some studies have reported foliar incorporation of metallic nanoparticles (i.e., CeO_2, TiO_2, Fe_2O_3, Mg and Zn oxides, and Ag) (Chichiriccò and Poma 2015); foliar uptake of nanoparticles has been demonstrated in *Vicia faba* L., *Lactuca sativa* L., and *Cucumis sativus* L. Since foliar internalization of nanomaterials in edible plants is possible and this may affect the food chain, more research in this area is necessary.

8 Physiological and Morphological Responses of Plants to Nanomaterials

Considering the global conditions related to the urgent need to feed the growing world population, in this century it has become imperative to increase crop production in a sustainable manner while protecting the environment, especially in developing countries (Pikaar et al. 2017; Srivastava et al. 2016; Tomberlin et al. 2015). To meet this increasing demand, researchers are trying to develop efficient and eco-friendly production technology based on innovative and emerging techniques to increase seed germination, seedling vigor, plant growth, and yield, through sustainable physical seed and plants treatments (Snapp and Pound 2017). Validation of emerging technologies such as nanotechnology (NT), for helping to improve food productivity without any adverse impact on the ecosystem, has been also one of the most important issues in the experimentation field under laboratory and field conditions (Baker et al. 2017). From this perspective, development of controlled delivery systems for slow and sustained release of agrochemicals based on nanotechnology is essential for modern and sustainable agriculture (Quiñones et al. 2017; Volova et al. 2016).

In recent decades, nanomaterials in the form of nanoparticles have been synthesized and studied for incorporation into many industrial, medical, and agricultural applications (Prasad et al. 2017). Because their physical and chemical properties differ from those of bulk materials, research is focused on understanding their interactions with their surroundings and ecosystems, as well on the physiological, morphological, and biochemical responses of crop plants (Du et al. 2017). Many recent studies have shown the potential of nanoparticles in improving seed germination and growth, plant protection, pathogen detection, and pesticide/herbicide residue detection (Anderson et al. 2017; Saharan and Pal 2016).

Plants respond differently, depending on the specific nanoparticles applied, the growth conditions, the exposure dose and time, and the target plant (Cox et al. 2016), as well as the physiological and biochemical functions the nanoparticles perform in the plant, and also depending on whether they act as an essential micronutrient, such as copper, zinc, or iron (Wang et al. 2015). It is well known that optimal crop production requires recommended doses of nutrients, which are presumably in agreement with the physiological needs of the crop or the soil nutrient levels (Dimkpa et al. 2017). In addition to the concepts appeared with the green revolution, there are many ways to increase the productivity of crops, one of which is use of biological or natural agrochemicals in the necessary quantity at the time when they are necessary or during the appropriate phenological stage (Shiva 2016).

Nanotechnology can be employed as a tool to modify nanoparticles in fertilizer formulations to increase their uptake in plant cells in such a way that nutrient loss is minimized, and to increase the crop use efficiency of fertilizer micronutrients (Monreal et al. 2016). According to research results, nanomaterials can improve crop productivity by increasing the seed germination rate, seedling growth and vigor, plant photosynthetic activity, nitrogen metabolism, carbohydrate synthesis, and protein synthesis. In this section we review the current literature on the use of nanoscale essential micronutrients such as metals (Cu, Fe, Mn, Zn, etc.), metal oxides (CeO_2, Fe_2O_3, TiO_2, ZnO, etc.), and CNMs to suppress crop disease and subsequently enhance germination, vigor, plant growth, and yield (Servin et al. 2015).

9 Carbon Nanomaterials

Several research groups have evaluated the positive effects of carbon nanomaterials (CNMs) and their derivatives—SWCNTs and MWCNTs—in plant growth and development. The most common effects of CNMs are summarized in Table 5.1. Jakubus et al. (2017) pointed out that carbon nanotubes (CNTs) are currently one of the most promising groups of materials for agriculture and industrial applications because of their interesting properties such as lightness, rigidity, high surface area, high mechanical strength in tension, good thermal conductivity, and resistance to mechanical damage. Some earlier reports by Khodakovskaya et al. (2012) demonstrated that introduction of CNTs into the soil mix through watering could affect the phenotype of tomato plants. They also showed that Solanaceae plants grown in soil supplemented with CNTs produced the same number of leaves but twice as many flowers and fruit as plants grown in nontreated soil. This work provided new perspectives on technological applications for the introduction of CNTs as growth regulators in modern agricultural practice.

It has also been reported that CNMs have the capacity to increase leaf and root growth, as well as seedling development of crop plants (Zhang et al. 2017; Cañas et al. 2008). Similarly, it has been revealed that MWCNTs can activate the growth of tomato plants by affecting the expression of genes that are essential for cell divi-

Table 5.1 Physiological effects of carbon nanomaterials (CNMs) cited in the literature

CNMs	Concentrations	Plant species	Physiological effects	Reference
MWCNTs	10, 20, 40, 60 mg L^{-1}	Broccoli	Positive effect on growth, increased water uptake, enhanced assimilation of CO_2	Martínez-Ballesta et al. (2016)
SWCNHs	0.025, 0.05, 0.10 mg L^{-1}	Barley, corn, rice, soybean, switchgrass, tomato, tobacco cell culture	Activated seed germination and enhanced seedling growth; increased growth of tobacco cells	Lahiani et al. (2015)
CNTs	10–40 mg L^{-1}	Tomato, onion, turnip, radish	Toxic effects on onion and radish seed germination	Haghighi and da Silva (2014)
MWCNTs	0–100 mg L^{-1}	Rice	Promotion of seed germination and root growth at lower concentrations; may have had toxic effects at high concentrations	Jiang et al. (2014)
MWCNTs	20–50 mg L^{-1}	Wheat, maize, peanut, garlic	Positive influence on root and shoot elongation observed for all seeds	Rao and Srivastava (2014)
MWCNTs	5, 10, 20, 40, 60 mg L^{-1}	Sweet corn	Germination and seedling growth enhanced at a low concentration but depressed at a higher concentration	Tiwari et al. (2014)
Graphene oxide	100, 200, 1600 mg L^{-1}	Faba bean	Both positive and negative effects such as a reduction in peroxidase enzyme activity and stress on plant development and growth	Anjum et al. (2013)
MWCNTs	0, 50, 1000, 5000 mg kg^{-1}	Zucchini, tomato, corn, soybean	No effects on zucchini and tomato; reduced biomass of corn and soybean	De La Torre-Roche et al. (2013)
SWCNTs, MWCNTs,few-layer graphene	50, 100, 200 mg L^{-1}	Tomato	CNTs resulted in production of twice as many flowers and fruit; MWCNTs upregulated stress-related genes	Khodakovskaya et al. (2013)
Fullerol [$C_{60}(OH)_{20}$]	0.943, 4.72, 9.43, 10.88, 47.2 nM	Bitter melon	Fullerol was found in the root, stem, petiole, leaf, flower, and fruit; it promoted plant development and enhanced fruit yield and growth	Kole et al. (2013)
MWCNTs	50, 100, 200 mg L^{-1}	Barley, soybean, corn	Activated expression of seed-located water channel genes that belong to different gene families of aquaporins; positive effect on seed germination	Lahiani et al. (2013)

CNMs	Concentrations	Plant species	Physiological effects	Reference
MWCNTs	0, 25, 50, 100 mg kg^{-1}	Alfalfa	No significant effects on soil microbial activities, composition, respiration, and enzymatic activities at a lower concentration	Shrestha et al. (2015)
MWCNTs	0, 20, 200, 1000, 2000 mg L^{-1}	Red spinach, lettuce, rice, cucumber, chili, lady's finger, soybean	Growth retardation; root and shoot length of spinach and lettuce significantly affected at 1000 and 2000 mg L^{-1}	Begum et al. (2012)
CNTs	0, 125, 250, 500, 1000 mg L^{-1}	Red spinach	Growth inhibition, changes in tissue structure	Begum and Fugetsu (2012)
MWCNTs	100 mg L^{-1}	Wheat, rapeseed seeds	Less than 0.005% of the applied MWCNTs was taken up by plant roots and translocated to the leaves	Larue et al. (2012)
MWCNTs	40–2560 mg L^{-1}	Alfalfa, wheat	Germination of both species was tolerant up to 2560 mg L^{-1}; increased elongation in alfalfa and wheat seedlings; increased root elongation in alfalfa seedlings; increased wheat germination	Miralles et al. (2012)
Graphene	500–2000 mg L^{-1}	Cabbage, tomato, red spinach, lettuce	Inhibition of plant growth and reduction of biomass; increases in ROS and cell death; no significant toxic effect was observed in lettuce	Begum et al. (2011)
MWCNTs	10, 20, 50 mg L^{-1}	Onion	Genotoxic responses caused by MWCNTs could cause chromosomal aberrations, DNA fragmentation, and apoptosis in root cells	Ghosh et al. (2011)
Oxidized MWCNTs	0.0023, 0.0069, 0.023, 0.046 μg L^{-1}	Mustard	Short germination time; improvements in root growth and development of stem seedlings	Mondal et al. (2011)
SWCNTs	10, 20, 30, 40 mg L^{-1}	Salvia, pepper, tall fescue	Increased seed germination	Pourkhaloee et al. (2011)

CNT carbon nanotube, *MWCNT* multiwalled carbon nanotube, *ROS* reactive oxygen species, *SWCNH* single-walled carbon nanohorn, *SWCNT* single-walled carbon nanotube sion and plant development (Villagarcia et al. 2012; Khodakovskaya et al. 2011). Current research has shown that the positive effects induced by MWCTs in plant development are associated with changes in lipid composition, stiffness and permeability of plasma membranes in roots, and increases in gibberellin content (Zhang et al. 2017; Martínez-Ballesta et al. 2016).

It has been reported that MWCNTs can increase the number of nodules and nitrogen activity at the roots of the rhizobium–legume association (Yuan et al. 2017). In a similar way, Liu et al. (2009) confirmed that SWCNTs are of a suitable size to penetrate cell walls and membranes of tobacco cells; this ability of nanoparticles to penetrate plant cells has generated considerable interest because, like aquaporins, CNTs can help transport water and nutrients within plants (Joseph and Aluru 2008). Khodakovskaya et al. (2011) demonstrated that *Lycopersicon esculentum* Mill. plants stressed by MWCTs showed upregulation of aquaporins. A separate study involving tobacco in cell culture found that MWCNTs enhanced tobacco cell growth at a low concentration (5 μg mL^{-1}) but were toxic at higher concentrations (Khodakovskaya et al. 2012). Consequently, the enhanced plant growth reported so far has been linked to increased water penetration in seeds and increased activity of crucial water channel proteins in developing seedlings. The similarity of these results across studies and research groups does suggest that MWCNT-stimulated growth may occur across some crop species (Servin et al. 2015).

Information from several sources (Vithanage et al. 2017; Zhang et al. 2017; De La Torre-Roche et al. 2013; Lin and Xing 2007) is presented in Table 5.1. Here we point out that CNMs induce many morphological effects on several horticultural and grain plants such as zucchini (*Cucurbita pepo* L.), garlic bulb (*Allium sativum* L.); tomato (*Solanum lycopersicum L.*), lettuce (*Lactuca sativa* L.), cucumber (*Cucumis sativus* L.), rape radish (*Raphanus sativus* L.), oilseed rape (*Brassica napus* L.), ryegrass (*Lolium perenne* L.), corn (*Zea mays* L.), rice (*Oryza sativa* L.) soybean [*Glycine max* (L.) Merr], and wheat (*Triticum aestivum* L.).

It is well known that stimulation of plant growth by CNMs is dependent on the morphology of the material, with a better biological performance structure with small diameters (Tripathi et al. 2016). Although CNMs can be considered plant growth promoters, this occurs only at a low concentration, because these materials become toxic with increased concentrations and time of exposure (Vithanage et al. 2017). The concentration of CNMs has to be optimized to obtain the best germination performance of various crop seeds (Vithanage et al. 2017; Haghighi and da Silva 2014; Rao and Srivastava 2014).

The extent and mechanisms by which terrestrial plant species accumulate MWCNTs is currently unknown (Zhao et al. 2017). However, it is well known that CNMs can penetrate the plant cell wall, in addition to the cell membrane, by creating more pores, thus allowing greater water uptake into the seeds (Khodakovskaya et al. 2009). Development of CNTs as nanotransporters for intact plant cells is of practical and fundamental importance for plant intracellular labeling and imaging, for genetic transformation, and for advancing our knowledge of plant cell biology and crop production (Liu et al. 2009). Servin et al. (2015) have pointed out that although some published work on carbon-based nanoparticles appears promising regarding enhanced growth and pathogen suppression, the mechanisms of the interaction between plants and microbes with different CNMs is not well understood, and the reported instances of phytotoxicity demonstrate the need for caution.

10 Metallic Engineered Nanomaterials

Recent investigations have shown that carbon-based nanomaterials and metal-based engineered nanomaterials (ENMs), which are used as components of consumer goods and agricultural products, have the potential to build up in sediments and biosolid-amended agricultural soils. Moreover, reports indicate that both carbon-based and metal-based nanomaterials affect plants differently at the physiological, biochemical, nutritional, and genetic levels (Zuverza-Mena et al. 2017). The toxicity threshold for each nanoparticle formulation is species dependent, and responses to ENMs are driven by a series of factors including the characteristics of the nanomaterial and the environmental conditions. The dynamics of interactions between plants and ENMs are not yet completely understood, and our ability to forecast the effects of ENM formulations in different soils and on diverse crop plants awaits the acquisition of information bases coordinating multiple physical, chemical, and biological factors (Anderson et al. 2017).

In recent times, abundant research has demonstrated that metallic nanoparticles have a dual effect, since they can both stimulate and inhibit seed germination and plant development. Nanoparticles containing essential metals such as Fe, Mg, Zn, Cu, and Mn are proposed to be used as fertilizers at low doses and as pesticides at higher doses (Liu and Lal 2015; Servin et al. 2015) because these metals are vital for cellular function but toxic above certain thresholds (Marschner 2011; Welch and Shuman 1995).

ENMs such as Fe, Zn, Cu, and their oxides are the focus of this section because these metals are essential micronutrients in crop plants (Jeyasubramanian et al. 2016) and are nontoxic in a wide concentration range; at the same time, they can be used as antagonists of bacteria and fungi, with huge potential for use in pesticide formulations (Le Van et al. 2016; Giannousi et al. 2013). Metallic ENMs such as Au, Ag, Cu, Cr, Fe, and Zn have demonstrated their potential to be used as antimicrobial/pesticidal agents for plant protection; however, precautions should be taken to avoid higher concentrations not only in plant systems but also for the sake of other constituents in society, the environment, and the economy (Tolaymat et al. 2017).

Therefore, further research is necessary to explore the stimulatory and inhibitory effects of engineered metallic nanoparticles in soil media to broaden the horizon of sustainable agricultural production of higher and safer yields to meet the food requirements of the human population (Auvinen et al. 2017). Additionally, as ENMs of CuO, ZnO, TiO_2, and Ag are increasingly used in consumer products, they will most probably enter the natural environment via wastewater, atmospheric deposition, and other routes (Markus et al. 2016); consequently, it is predictable that nanoparticles are capable of being transported over long distances, in much the same way as suspended particulate matter. For that reason, it is critical to keep in mind that the life cycle of ENMs should be well studied, and large-scale synthesis of them must be executed with consideration of their fate in ecosystems, since in the quest for innovation and advancement of science, environmental problems are becoming more severe and uncontrolled (Khan et al. 2016).

11 Zinc-Based Nanoparticles

Zinc oxide (ZnO) nanoparticles in agricultural production are studied for their antimicrobial activity (Sabir et al. 2014; Fang et al. 2013) and for their potential as nanofertilizers, improving zinc deficiencies and promoting seed germination and plant growth (Dimkpa et al. 2015; Raskar and Laware 2014; Naderi and Danesh-Shahraki 2013). Recent studies have pointed out that high concentrations (1000 mg L^{-1}) of ZnO nanoparticles stimulate phytotoxicity and inhibit germination (Rizwan et al. 2017; Zhang et al. 2015; Ko and Kong 2014). Although low doses (<50 mg L^{-1}) have shown significant positive effects on plant growth and development (Jyothi and Hebsur 2017; Zuverza-Mena et al. 2017; Prasad et al. 2012), usually the effect on crop plants implies greater dry biomass and a greater total leaf area. These helpful effects have been attributed to zinc because this metal is an essential micronutrient needed for cell division and is very important as a component of several enzymes (Pandey et al. 2010); moreover, it is involved in the synthesis of proteins, carbohydrates, lipids, and nucleic acids in plants (Tarafdar et al. 2014). Likewise, Priester et al. (2012) observed high Zn accumulation (344.07 mg kg^{-1}) in soybean leaves after 50 days of exposure to ZnO nanoparticles.

Some reports have shown that ZnO nanoparticles promote seed germination and seedling vigor (Siddiqui et al. 2015; Ko and Kong 2014). Analogous results reported by Adhikari et al. (2016a) indicated that germination percentages were improved in coated seeds of *Z. mays* L., *G. max* L., *Cajanus cajan* L., *Druce*, and *Abelmoschus esculentus* Moench treated with ZnO nanoparticles. Foliar application of ZnO nanoparticles doped with silver at 1.25% and 2.5% increased plant growth and dry biomass production of *Capsicum annuum* L. (Méndez-Argüello et al. 2016). Recently Raliya et al. (2015) studied the effects of biosynthesized ZnO nanoparticles on mung bean plants. They found that Zn acts as a cofactor for P-solubilizing enzymes such as phosphatase and phytase, and nano-ZnO increased their activity. Biosynthesized ZnO also improved plant phenology such as the stem height and root volume, and biochemical indicators such as the leaf protein content and chlorophyll content. Similarly, Tarafdar et al. (2014) reported that pearl millet (*Pennisetum americanum* L.) exposed to ZnO nanoparticles showed significant enhancements in shoot and root length, chlorophyll content, plant dry biomass, and enzyme activity involved with the assimilation of phosphorus.

Zhao et al. (2013) amended soil with either CeO_2 or ZnO nanoparticles at concentrations of 0, 400, or 800 mg kg^{-1}. The results showed that at the concentrations tested, neither CeO_2 nor ZnO nanoparticles impacted cucumber plant growth, gas exchange, or chlorophyll content. However, at a concentration of 800 mg kg^{-1}, CeO_2 nanoparticles reduced the yield. In soil amended with either ZnO nanoparticles or Zn^{2+}, cowpea [*Vigna unguiculata* (L.) Walp.] plants showed no differences in growth, accumulation, or speciation between the ion treatment and the ZnO nanoparticle treatment (Wang et al. 2013). The authors explained that these outcomes emphasized the importance of the growth matrix when studying nanoparticle–plant interactions. ZnO nanoparticles are considered an emerging contaminant when applied at high concentrations, and their effects on crops and soil microorganisms present new concerns and challenges. It has been stated by Wang et al. (2016) that beneficial microorganisms such as fungi (which form mutualistic symbioses with most vascular plants) and arbuscular mycorrhizae may contribute to alleviation of adverse effects of ZnO nanoparticles and zinc accumulation in maize. Soil pH plays a vital role in the solubility and availability of plant nutrients. For instance, Watson et al. (2015) grew wheat (*T. aestivum* L.) in acidic and alkaline soils that had been amended with ZnO nanoparticles; the authors reported 200-fold higher soluble Zn content in the acidic soil and a ten-fold higher concentration in wheat shoots, in comparison with the alkaline soil. However, plants grown in the ZnO nanoparticle (500 mg kg^{-1})–amended alkaline soil had increased lateral root production, whereas wheat grown in the acidic soil had decreased root growth. Independently of the exposure route, nanoparticles can trigger positive and negative responses in exposed plants, which are grouped into physiological and biochemical responses; these are schematized in Fig. 5.2.

Though treatments with relatively low ZnO nanoparticle concentrations (10 and 20 μg mL^{-1}) have been reported to improve germination of onion seeds and enhance root and shoot lengths, application of higher concentrations of ZnO nanoparticles had detrimental effects on these characteristics (Raskar and Laware 2014). However, Prasad et al. (2012) reported that application of a ZnO nanoparticle dose of 1000 mg L^{-1} to peanut plants (*Arachis hypogaea* L.) increased seed germination and root and stem length; moreover, the plants exhibited early flowering and a higher chlorophyll content—effects similar to those of plant growth regulators or chemical messengers for intercellular communication.

The effects of ZnO nanoparticles on plant growth could be related to the activity of zinc as a precursor in the production of growth-regulating auxins such as indole-3-acetic acid (IAA), which also promotes cell elongation and division (Shyla and Natarajan 2014; Rehman et al. 2012). In addition, it has been reported that zinc is an essential nutrient and a very important component of several enzymes responsible for many metabolic reactions (Shyla and Natarajan 2014). It also plays an essential role in the production of chlorophyll, seed germination, pollen production, and biomass production (Pandey et al. 2010).

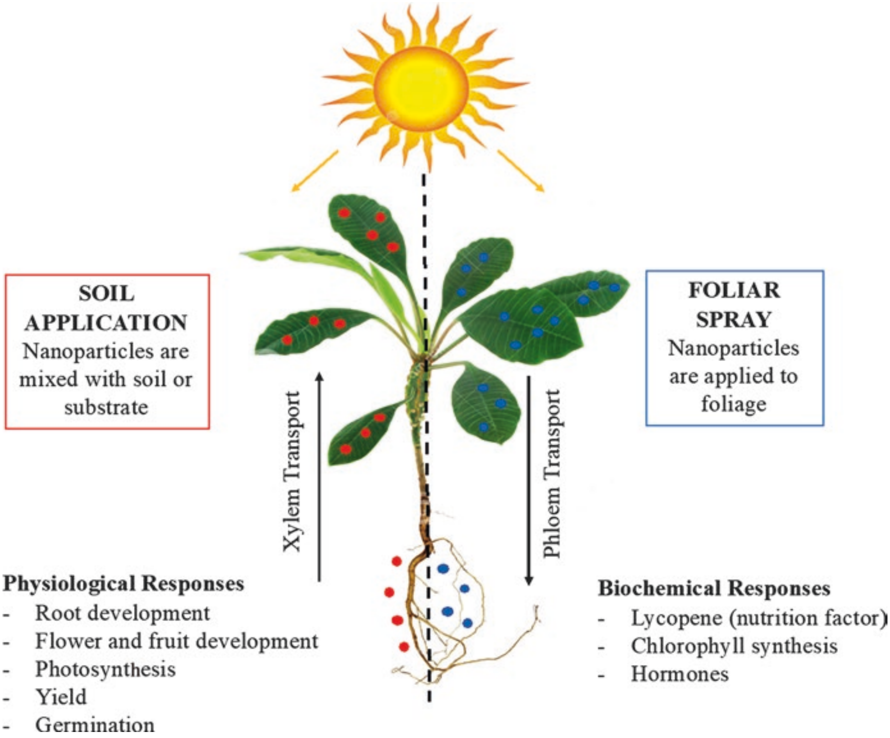

Fig. 5.2 Positive and negative responses in plants after exposure to zinc oxide nanoparticles. Plants can show physiological and biochemical responses observed in the flowering time, yield, expression of genes involved in the biosynthesis of chlorophyll, etc. The interpretation of these responses is crucial for decisions regarding field trials

12 Iron-Based Nanoparticles

Iron (Fe) is an essential micronutrient, which is highly unavailable for plants in calcareous soils, such as in those in most areas of the north of Mexico and in other countries. Iron is an essential element for both plant and animal nutrition; it is required for critical cell functions such as respiration, photosynthesis, DNA synthesis, nitrogen fixation, and hormone production (Jalali et al. 2017). Regardless of its absolute requirement, Fe reacts in cells with oxygen and generates noxious ROS, which have deleterious effects on plant growth and development (Thomine and Vert 2013). Regardless of the abundant presence of iron on our planet and in agricultural soils, the low solubility of Fe compounds in many calcareous soils prevents plant iron uptake and induces the development of Fe deficiency symptoms (Lucena and Hernandez-Apaolaza 2017).

Agricultural plant iron deficiency has economic significance, as crop quality and yields can be severely compromised; therefore, the use of expensive corrective methods such as application of iron chelates is often required (Fernández and Ebert 2005). Lately, uses of Fe in the form of magnetic nanoparticles (Fe-NP) for agronomic purposes have been experimentally explored (Corredor et al. 2010). Iron oxide (Fe_2O_3) nanoparticles have emerged as an innovative and promising method of Fe application in agricultural systems. However, the possible toxicity of Fe_2O_3 nanoparticles and their uptake and translocation require further study prior to large-scale field application (Li et al. 2016).

Iron oxides exhibit great potential in fields of life science such as biomedicine, agriculture, and environmental science. Fe nanoparticles are considered to be biologically and chemically inert (Ren et al. 2011) and are useful for imaging and separation techniques because of their magnetic properties and environmental remediation. In plants, Fe participates in chlorophyll biosynthesis, respiration, redox reactions, and biosynthesis of phytohormones. However, Fe deficiency is a widespread agronomic issue caused by poor Fe solubility in the vast majority of soils and consequential insufficient Fe availability to plants (Lucena and Hernandez-Apaolaza 2017). A report by Hao et al. (2016) regarding the effects of different nanoparticles on seed germination and seedling growth pointed out that Fe_2O_3 nanocubes, Fe_2O_3 short nanorods, and Fe_2O_3 long nanorods all significantly promoted root length and stimulated shoot growth at most concentrations but had no apparent effect on the fresh weight of rice (*O. sativa* L.) plants.

Askary et al. (2017) investigated the impact of iron oxide nanoparticles—applied at 0, 10, 20, or 30 μM concentrations—on physiological parameters of peppermint (*Mentha piperita* L.) under salt stress. Fe_2O_3 nanoparticles caused increases in fresh leaf weight and dry weight, and in P, K, Fe, Zn, and Ca content of the peppermint under salinity stress, but did not affect sodium content. Lipid peroxidation and the proline content of the peppermint under salinity decreased significantly with application of Fe_2O_3 nanoparticles. Maximum activities of the antioxidant enzymes catalase (CAT), superoxide dismutase (SOD), and guaiacol peroxidase (GPOD) were observed in plants treated with 150 mM of NaCl, but application of Fe_2O_3 nanoparticles decreased these antioxidant activities. The results suggested that application of an appropriate concentration of Fe_2O_3 nanoparticles could be used to increase the stress resistance of peppermint.

Furthermore, Shankramma et al. (2016) investigated the effect of Fe_2O_3 nanoparticles on *Solanum lycopersicum* plants. Exposure of tomato seeds to iron nanoparticles increased the shoot and root length, and it was noted that the nanoparticles were deposited preferentially in root hairs and in root tips, followed by the nodal and middle zones of the plant. Likewise, Iannone et al. (2016) reported that Fe_3O_4 nanoparticles had positive effects on growth of wheat (*T. aestivum* L.). When Rui et al. (2016) applied Fe_2O_3 nanoparticles to *A. hypogaea* L. as a fertilizer, the plants showed increases in the root length, plant height, biomass, and chlorophyll index [Soil Plant Analysis Development (SPAD) value], which were due to regulation of phytohormone content and antioxidant enzyme activity. Increased chlorophyll levels have also been reported in soybean seedlings treated with Fe_3O_4 nanoparticles; translocation into soybean stems was reported by Ghafariyan et al. (2013). Analogous results were achieved by Zhu et al. (2008), who reported that *Curcubita* *maxima* exposed to magnetite (Fe_3O_4) nanoparticles showed translocation and accumulation of the nanoparticles in plant tissues. Crop species such as barley (*Hordeum vulgare* L.) and flax (*Linum usitatissimum* L.) were evaluated for toxicity of nZVI, using seed germination tests. The nanoparticles did not affect germination, but shoot growth was more sensitive. Complete inhibition of germination was observed at 1000–2000 mg L^{-1} of this kind of nanoparticle (El-Temsah and Joner 2012).

13 Copper-Based Nanoparticles

Copper (Cu) is an essential micronutrient for plants, which acts as a structural element in regulatory proteins and participates in photosynthetic electron transport, mitochondrial respiration, oxidative stress responses, cell wall metabolism, and hormone signaling (Marschner 2011). Nevertheless, when Cu is either deficient or present in excess, it can cause disorders in plant growth and development by adversely affecting crucial physiological processes in plants, with negative impacts on crop growth and quality (Yruela 2009). The behavior of Cu nanoparticles in plants is similar to that of other nanomaterials, with their effects being dependent on the exposure time, nanoparticle characteristics, and plant species. Application of CuO nanoparticles to wheat grown in sand caused morphological changes such as root hair proliferation and shortening of the zones of division and elongation; these changes were associated with accumulation of nitric oxide (NO), which promoted root hair proliferation (Adams et al. 2017). However, there have also been reports of inhibitory effects of CuO nanoparticles. Le Van et al. (2016) found that CuO nanoparticle concentrations greater than 10 mg L^{-1} inhibited the growth and development of cotton in terms of its height, root length, root number, and biomass production. Also, concentrations of the hormones IAA and abscisic acid (ABA) were affected. Moreover, the treatments reduced the uptake of nutrients such as B, Mo, Mn, Mg, Zn, and Fe, and inhibited the transport of Na and Mn in cotton plants. Da Costa and Sharma (2016) reported that exposure of *O. sativa*, var. Jyoti to CuO nanoparticles decreased its germination rate, root and shoot length, and biomass.

Perreault et al. (2014) observed that inhibition of the photosynthetic activity of duckweed exposed to CuO nanoparticles was due to release of Cu^{2+} ions from the nanoparticles. A study performed in *Phaseolus radiatus* L. and *T. aestivum* L. revealed a differential effect between species, with *P. radiatus* L. being more sensitive; this outcome also suggested that Cu nanoparticles can cross the cell membrane, because Cu aggregates in root cell vacuoles of both species (Lee et al. 2008). Although the mechanism through which CuO nanoparticles get into the plant vascular system is still not well understood, they can be assimilated by plants and enhance their growth by regulating different enzyme activities.

Recently, exposure to Cu-based nanoparticles was shown to increase P and S in *Medicago sativa* L. shoots while reducing Fe and P in shoots of other crops such as *L. sativa* and *Coriandrum sativum* L. (Hong et al. 2015; Zuverza-Mena et al. 2015).

Application of Cu nanoparticles in chitosan–PVA hydrogels affected the growth, development, and quality of *S. lycopersicum* L. and *C. annuum* L. plants (Pinedo-Guerrero et al. 2017; Juarez-Maldonado et al. 2016). Similarly, it was reported by Adhikari et al. (2016b) that CuO nanoparticles applied through a solution culture, as well as a spray, enhanced the growth of *Z. mays*. The nanoparticles could get into the plant cells and improve growth by activation of enzymes from the pentose phosphate pathway and enzymes involved in oxidative stress. Peng et al. (2015) also demonstrated that CuO nanoparticles could enter the xylem through lateral roots in *O. sativa* and translocate to the leaves; moreover, these nanoparticles were transformed and reduced in the rice plant. Previously, Wang et al. (2012) had reported the same behavior in *Z. mays* L. plants, where CuO nanoparticles were translocated from the roots to the shoots via the xylem and retranslocated from the shoots to the roots via the phloem; during this translocation, Cu could be reduced from Cu (II) to Cu (I). Using a split-root exposure system, Ma et al. (2017) illustrated uptake and translocation of manufactured nanoparticles by the xylem and phloem in hydroponic cucumber plants; this was the first report of root-to-shoot-to-root redistribution after transformation of metallic nanoparticles in plants.

14 Reactive Oxygen Species and Biochemical Responses

Reactive oxygen species (ROS) are produced in plants as by-products of aerobic metabolism, and ROS levels increase during abiotic or biotic stress conditions. Plants generate ROS as signaling molecules to control various processes, including pathogen defense, programmed cell death, and stomatal behavior (Apel and Hirt 2004). Nanomaterials can produce ROS in plants; the amounts of ROS formed by nanoparticles correlate with the particle size, shape, surface area, and chemistry. ROS possess multiple functions in cellular biology. ROS are a crucial factor in nanomaterial-induced toxicity, as well as in modulation of cellular signaling involved in cell death, proliferation, and differentiation (Abdal Dayem et al. 2017).

The recent literature indicates that nanomaterials cause oxidative stress in treated plants through increased lipid peroxidation, oxidized glutathione (GSSG), and antioxidant enzyme activities, or through decreased chlorophyll content and photosynthesis (Da Costa and Sharma 2016; Wang et al. 2016). Metallic nanoparticles from heavy metals such as Cu and Zn are essential for healthy plant growth, although elevated concentrations of both essential metals can result in growth inhibition and toxicity symptoms (Ruttkay-Nedecky et al. 2017). According to Hossain et al. (2012), metals can induce an increase in GSSG, so plants have decreased levels of reduced glutathione (GSH), with GSH being a vital antioxidant in plant defense against ROS (Apel and Hirt 2004). As a result, plants activate enzymatic antioxidant defense [peroxidase (POD), CAT, ascorbate peroxidase (APX), SOD] and nonenzymatic antioxidant defense (glutathione, ascorbic acid, phenolic compounds, vitamin A, vitamin E, etc.) to scavenge excess ROS and maintain general homeostasis (Marslin et al. 2017). Disruption of ROS homeostasis impairs plant growth and

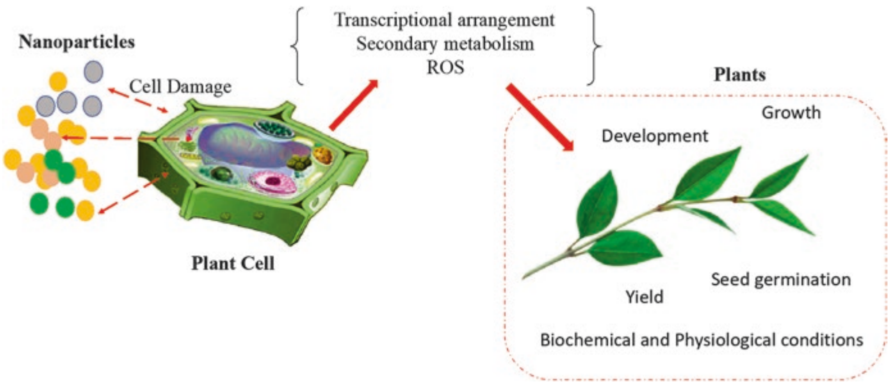

Fig. 5.3 Effects of nanoparticles on plant cells. Most of the mechanisms involved in the responses to nanoparticle exposure are related to oxidative stress. *ROS* reactive oxygen species

development, whereas maintenance of ROS levels within appropriate parameters stimulates plant health (Mittler 2017). It is generally expected that alterations in enzyme activities in exposed plants are responses to modulations in ROS concentrations. The role of nanoparticle chemical attributes in the modulation of the antioxidant defense system in plants is still unclear. As can be observed in Fig. 5.3, when nanoparticles come into contact with plant cells, a continuous response is observed after the first effect of the nanomaterials on the living organism (cell damage) occurs; the end point of this event is observed at a macroscopic level.

15 Nanoparticle Impacts on Crop Yields

The early information regarding the effects of nanoparticles on plant growth and yield suggests a significant potential of metallic nanoparticles to act as nanofertilizers or nanoinsecticides, with either foliar or root application, to suppress disease and increase crop yields. Future research should be targeted at uncovering the precise nature of these enhancements, including efforts to optimize treatment success and maximize yields (Servin et al. 2015).

To analyze the impact of cerium oxide nanoparticles on wheat (*T. aestivum* L.), Rico et al. (2014) cultivated grain in soil amended with 0, 125, 250, or 500 mg kg^{-1} of $nCeO_2$. The results showed that relative to the control, $nCeO_2$-H improved plant growth, shoot biomass, and grain yield by 9.0%, 12.7%, and 36.6%, respectively. Ce accumulation in roots increased with increased $nCeO_2$ concentrations, but did not differ across treatments in leaves, hulls, and grains, indicating a lack of Ce transport to the aboveground tissues. The findings suggest the potential of cerium oxide nanoparticles to modify crop physiology and food quality, with unknown consequences for living organisms.

Reviewing the effects of nanofertilizers on the growth and yield of selected cereals, Jyothi and Hebsur (2017) reported that nanofertilizer application increased the plant height, chlorophyll content, and numbers of reproductive tillers, panicles, and spikelets in rice; the magnitudes of these increases in comparison with the control were 3.6%, 2.72%, 9.10%, 9.10%, and 15.42%, respectively. Exposure to Zn nanoparticles (at 0, 25, 50, 75, 100, or 150 mg L^{-1}) caused significant changes in root and shoot lengths, and in biomass. ZnO nanoparticles increased the shoot dry matter and leaf area indexes by 63.8% and 69.7%, respectively. The effects of TiO_2 nanoparticles were significant in terms of the numbers of corns cobs on the plant, dry maize weight, and corn yield. Application of silver nanoparticles at a concentration of 25 parts per million (ppm) resulted in significant improvements in the maximum leaf area and grain yield, while a 75 mg L^{-1} concentration resulted in a decrease in the grain yield in wheat.

Yasmeen et al. (2017) studied the proteomic and physiological changes of wheat seeds exposed to Cu and Fe nanoparticles. The outcomes indicated that the spike length, number of grains per spike, and 1000-grain weight were increased in wheat varieties treated with 25 mg L^{-1} of Cu and Fe nanoparticles; these improvements implied an increase in grain yield. The exposure to Cu nanoparticles increased proteins involved in starch degradation and glycolysis. The authors suggested that Cu nanoparticles improved stress tolerance in wheat varieties by mediating starch degradation, glycolysis, and the tricarboxylic acid cycle through nanoparticle uptake.

Experiments were carried out by Arora et al. (2012) to determine the effect of gold nanoparticles (Au-NP) on the growth profile and yield of *Brassica juncea* (L.) Coss. under field conditions. Five different concentrations (0, 10, 25, 50, and 100 mg L^{-1}) of Au nanoparticles were applied through a foliar spray. Various growth and yield-related parameters—including the plant height, stem diameter, number of branches, number of pods, and seed yield—were positively affected by the nanoparticle treatments. An optimal increase in seed yield was recorded with an Au nanoparticle treatment of 10 mg L^{-1}. These results, for the first time, demonstrated successful use of Au nanoparticles in enhancing the growth and yield of *B. juncea* (L.) Coss. under actual field conditions and presented a viable alternative to genetic modification of crops to ensure food security.

Findings by Bradfield et al. (2017)—who studied sweet potato (*Ipomoea batatas* var. Georgia Jet) subjected to treatments of ZnO, CuO, and CeO_2 nanoparticles—demonstrated that adverse effects on yield were observed only at higher exposure concentrations (1000 mg kg^{-1} of dry weight). The effects of ZnO nanoparticles on growth, productivity, and zinc biofortification in maize were studied by Subbaiah et al. (2016). The highest germination percentage and seedling vigor index were observed with 1500 mg L^{-1} of ZnO nanoparticles. The yield was 42% greater than that of the control plants and 15% greater than that observed with 2000 mg L^{-1} of $ZnSO_4$. These results indicated that ZnO nanoparticles have significant effects on the growth, yield, and zinc content of maize grains, which is an important feature for human health.

16 Pros and Cons of Nanoparticles in Agriculture and Food Supply

There is not doubt that nanotechnology offers some benefits to modern agriculture around the world. The relative attractiveness of this novel technology depends on many circumstances, but it is clear that it could be beneficial to promote sustainable agricultural practices and to help make food production more efficient, because use of nanoparticles is predicted to allow less use of agrochemicals such as pesticides (fungicides, bactericides, insecticides, herbicides), antibiotics, and veterinary medicines; this implies less harm to ecosystems by lessening environmental pollution and diminishing chemical runoff, as well as resulting in less carry-over of harmful chemical residues in food. Since nanoparticles can promote longer shelf life of fresh and packed food products, it is possible for their use to contribute to a reduction in food waste and a more dependable food supply.

Also, application of nanotechnology to crop plants has the capacity to allow controlled release of agrochemicals and site-targeted delivery of several compounds required to improve plant growth and yield, with enhanced plant disease resistance and efficient macro- and micronutrient delivery to, and utilization by, crop plants. Nanotechnology can be used to enrich foods such as fruit and vegetables to deliver high nutrient density in such foods and to dissolve additives such as antioxidants, phenolic compounds, vitamins, and minerals. Furthermore, through nanoencapsulation technologies, additional nutrients can be added to food and beverage products without altering their flavor or quality.

According to the United Nations Food and Agriculture Organization (FAO), about 20–45% of plant, meat, and fish products are lost or wasted, amounting to 286 million tonnes of cereal products in industrialized countries. Therefore, at all stages of food production, there is a need to use sensors to monitor the quality of products to ensure food safety and commercial viability (Srivastava et al. 2017). Such sensors include electrochemical nanosensors, optical nanosensors, the electronic nose and electronic tongue, nanobarcode technology, and wireless nanosensors. They can detect food contaminants such as preservatives, antibiotics, heavy metal ions, toxins, microbial load, and pathogens. They can also monitor temperature, traceability, humidity, gas, and the aromas of foodstuffs. Additionally, the use of nanosensors in food packaging for detection of food spoilage is important for combating pathogenic microorganisms and consequently reducing foodborne illnesses in consumers.

With regard to the potential risks of using nanoparticles in agricultural practices, they are no different from those in any other business. Through the fast supply of nanoparticles to food products, whether they are in the food itself or part of the packaging, nanoparticles will practically come into direct or indirect contact with everyone. Since there is no regulation of the use and testing of nanotechnology, products incorporating nanomaterials are being produced without checks. The ability for these materials to infiltrate the human body is well known, but there is no information on the effects they may have. While there is no evidence of harm to people or the environment at this stage, use of nanotechnology in modern agriculture is a novel and evolving phenomenon that could cause a great deal of harm because the chemical properties of nanomaterials are not yet fully undestood (Prasad et al. 2014).

In the field of agriculture, there are still many possibilities to explore and a great deal of potential in upcoming products and techniques. Therefore, extensive studies are required to understand the mechanisms of nanomaterial toxicity and its impacts on the natural environment. Recently, Servin and White (2016) stated that robust literature assessing the toxicity of ENMs to terrestrial/agricultural plant species has begun to develop. However, much of this literature has focused on short-term, high-dose exposure scenarios, often conducted in model media. The literature generally confirms the existence of low to moderate toxicity to terrestrial plant species and phytotoxicity from nanoparticles generated in studies, but such studies are inadequate for assessing the actual risks posed to agricultural systems, including sensitive receptors such as humans.

17 Conclusion

It is clear that excessive use of fertilizers and pesticides has caused soil deterioration and contaminated water sources; consequently, there is an urgent need to develop more efficient agrochemicals. Nanotechnology is therefore becoming necessary to formulate nanoagrochemicals to help promote modern agriculture with a low environmental impact. The use of nanozeolite in agriculture represents a good option for slow release of water and fertilizers for efficient use of irrigation water and as a substrate for the growth of plants in biospaces such as greenhouses and tunnels. Nanotechnology is the emerging knowledge of the twenty-first century in all fields of science. In agriculture, its benefits include improving agricultural productivity by using nanoparticles as plant growth promoters, nanoencapsulated production for slow release of fertilizers, and formulation of nanopesticides and nanoherbicides. With the use of nanotechnology, very efficient nanosensors can also be manufactured for early detection of diseases. Nanotechnology can also be a useful tool for the transfer of DNA in plants, intended for the development of new plant varieties that are resistant to pests and diseases, as well as biotic and abiotic factors.

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