Fernando López-Valdez
Fabián Fernández-Luqueño *Editors*

# Agricultural Nanobiotechnology

## Modern Agriculture for a Sustainable Future

Springer

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ISBN 978-3-319-96718-9 ISBN 978-3-319-96719-6 (eBook)
https://doi.org/10.1007/978-3-319-96719-6

Library of Congress Control Number: 2018959433



This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

# Preface

The purpose of this book is to describe the state of the art in research on nanoparticles (i.e., nanoproducts such as nanofertilizers) in the recently named discipline of agronanobiotechnology—modern agriculture for a sustainable future. This work on nanoparticles and nanotechnologies (herbicides, pesticides, sensors, and nanomaterials, among others), covers the main fields such as agriculture, modern agronomy, and technological improvements to increase crop yields, with special emphasis on sustainable management and the environmental impacts of nanofertilizers.

We are confident that this book provides cutting-edge knowledge on both theoretical and applied aspects of nanoparticle design, formulation, application, and management, as well as the effects of nanoparticles on soil properties and plant characteristics, and some biotic interactions. This book is aimed at undergraduate and postgraduate students, researchers, and other professionals in agricultural and related disciplines.

This work is divided into four parts. Part I—titled "Agronanobiotechnology: An Introduction to Nanoparticles"—includes two chapters. The first chapter discusses the newly introduced discipline of agronanobiotechnology and its innovative products. The second chapter discusses nanoparticle design (synthesis) and physicochemical properties, considering plant requirements. Part II—titled "Fertilizers and Plant Nutrients in Germination, Growth, and Development of Crops"—presents four chapters on nanoparticles, including nanofertilizers and their delivery of nutrients, nanoformulations, plant cell processes, entry of nutrients into plants, advantages and disadvantages of nanoparticles, effects of nanoparticles on plants, and their physiological and biochemical mechanisms, behavior of nanoparticles in the soil and water matrix, and effects of nanoparticles on the growth and development of crops in indoor agriculture applications. In Part III—titled "Improving Soil and Water Quality"—we present two interesting chapters. The first one, which focuses on engineered nanomaterials, reviews recent studies on their application in soils, assesses their advantages and disadvantages, and discusses challenges and perspectives of engineered nanomaterial applications for food production and improvement of soil quality. The second chapter discusses the availability of agronanobiotechnologies to improve water quality and watering efficiency in agricultural irrigation systems, and describes the design of inexpensive and eco-friendly filters, using natural or engineered nanomaterials, from organic waste. Finally, Part IV—titled "Environmental Topics"—presents two interesting chapters. The first one describes the effects of nanoparticles on plants, earthworms, and microorganisms, and discusses the advantages and disadvantages of engineered nanomaterials under laboratory and greenhouse conditions. In the second chapter we highlight the application of several nanoparticles in various fields (biology, medicine, and biomedical engineering) and discuss concerns regarding human and environmental health.

This book makes a very valuable contribution to agricultural and crop sciences. This work would not have been possible without the invaluable contribution, knowledge, and expertise of the authors.

Tlaxcala, Mexico Fernando López-Valdez
Coahuila de Zaragoza, Mexico Fabián Fernández-Luqueño

# Acknowledgements

We are so thankful to the contributors for their effort and interest in this project, in which we have sincerely found the collaboration of each of the participating authors to be priceless. It is our great pleasure to offer you our sincere congratulations in completing this important project for all of us. Thank you so deeply!

We are also very thankful to our Springer editors, João Pildervasser [Associate Editor, Life Sciences] and Rahul Sharma [Project Coordinator (Books) for Springer Nature] for their infinite patience in this project. Thank you so much for your fine support!

Finally, we would like to offer our sincere thanks to our institutes—the Instituto Politécnico Nacional, Cinvestav–IPN, and CONACYT—for providing financial support and facilities for our research.

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# Part I
# Agronanobiotechnology, an Introduction to Nanoparticles

# Chapter 1
# Use of Agronanobiotechnology in the Agro-Food Industry to Preserve Environmental Health and Improve the Welfare of Farmers

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**Abstract** Agronanobiotechnology is a term that refers to the intersection of agronomy, nanotechnology, and biotechnology. Agronanobiotechnology is a discipline in which tools from nanotechnology are developed and applied to the study of agronomic and biological phenomena. The objective of this chapter is to present cutting-edge knowledge regarding agronanobiotechnology, which is aimed at preserving environmental health and improving the welfare of farmers while also increasing crop yields and the production of innocuous feed. Producers of innovative products in agronanobiotechnology are experiencing difficulties in bringing these products to market, because of their high production costs, which regularly are required in high

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F. López-Valdez, F. Fernández-Luqueño (eds.), *Agricultural Nanobiotechnology*, https://doi.org/10.1007/978-3-319-96719-6_1

volumes in the agricultural sector, while unclear technical benefits, legislative uncertainties, and negative public opinion are hampering the development of agronanobiotechnology; notwithstanding these difficulties, the possibilities offered by agronanobiotechnology in several agricultural applications are moving forward. Meanwhile, progress in legislation, nanoremediation, environmental monitoring, international safety regulation, and drug delivery techniques could improve the agricultural and livestock sector indirectly. For research and development in agronanobiotechnology to move forward, long-term in situ field trials are required, while social welfare must also be guaranteed in order to shape sustainable development.

**Keywords** Agricultural nanotechnologies · Crop production · Packaging · Plant breeding · Plant genetic modification · Remediation · Water purification

## 1 Introduction

Agronanobiotechnology is a discipline in which tools from nanotechnology are developed and applied to the study of agronomic and biological phenomena. Agronanobiotechnology may enable us to cope with the global challenges of crop production, food security, sustainability, and climate change. However, despite the potential benefits of nanotechnology in agriculture, soil science, and plant production, the potential advantages for farm producers have not yet reached the field (Mishra et al. 2017). Potential uses of agronanobiotechnology and concerns regarding its use are shown in Fig. 1.1.

Agronanobiotechnology has multidisciplinary applications worldwide (Medina-Pérez et al. in press). The increased dependency on chemical pesticides and fertilizers has generated serious issues related to sustainability, environmental impact, and health hazards. As a result, the innovative approach of using environmentally friendly biofertilizers or biopesticides as alternatives to agrochemicals has come into existence to ensure biosafety. However, it has been accompanied by some major issues of poor shelf life, poor on-field stability, poor performance under fluctuating environmental conditions and, most importantly, the high doses required for maximum area coverage. Interestingly, nanoparticle-based formulations have shown superiority over bioformulations in terms of addressing all of these issues (Mishra et al. 2017). As a result, modern agriculture is embracing the innovative approach of nanotechnology to combat the global challenges of crop production, food security, sustainability, and climate change. In addition to agriculture, it is important to consider that agronanobiotechnological applications have also demonstrated their relevance in all areas of food science, including food processing, food safety through improved packaging, enhancement of food nutrition, and superior-quality food contact materials. However, the underexplored areas of this important aspect—leading to apparent impediments, negative perceptions, and hesitation in adoption of agronanobiotechnology—cannot be overlooked (Mishra et al. 2017).

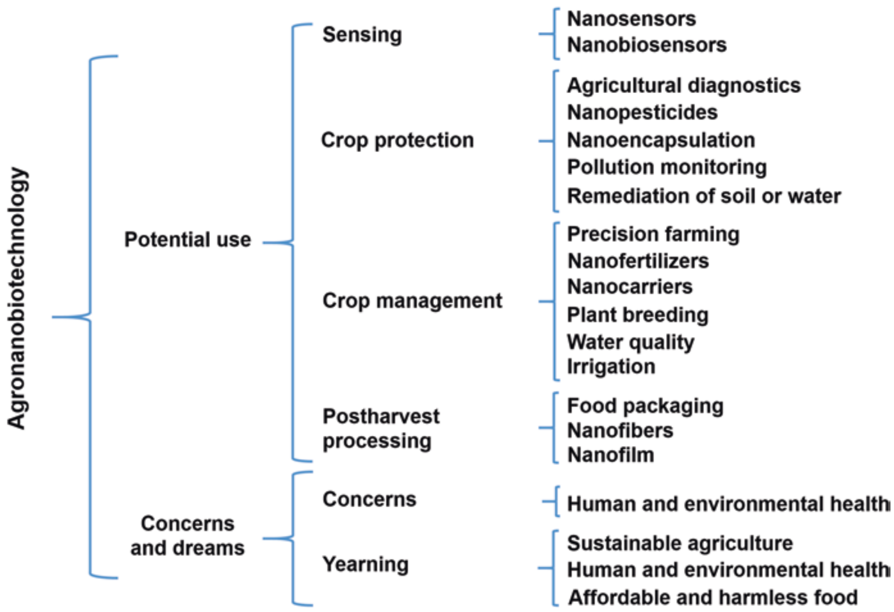


**Fig. 1.1** Potential uses of—and concerns regarding—some agronanobiotechnologies worldwide. For agronanobiotechnologies to move forward, long-term in situ field trials are required

Research on agricultural nanotechnology applications has now been ongoing for a decade, searching for solutions to several agricultural and environmental challenges such as sustainability, improvement in varieties, and increases in productivity. Several authors have discussed the growth trend in both scientific publications and patent applications in agricultural nanotechnology, especially for disease management and crop protection (Parisi et al. 2015). Prasad et al. (2017) stated that the ambitions of nanomaterial use in agriculture are to reduce the amount of spread chemicals, minimize nutrient losses in fertilization, and increase yield through pest and nutrient management.

The objective of this chapter is to present cutting-edge knowledge regarding agronanobiotechnology, which is aimed at preserving environmental health and improving the welfare of farmers while also increasing crop yields and the production of innocuous feed.

## 2 Relevant Applications of Agronanobiotechnology

Crop production (plant protection products or fertilizers), soil improvement (water/liquid retention), water purification (pollutant remediation), diagnostics (nanosensors and diagnostic devices), plant breeding (plant genetic modification), soil remediation (nanoremediation), and packaging are several knowledge areas in which outstanding developments have occurred recently. Society has to build a road of high technology

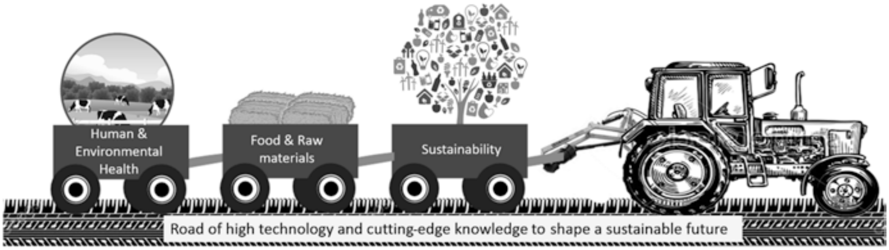


**Fig. 1.2** Some elements of the farm (world) involved in providing innocuous and affordable feed for the population

and cutting-edge knowledge to provide innocuous and affordable feed, and to shape a sustainable future (Fig. 1.2).

### *2.1 Crop Production*

It is estimated that nearly one third of global crop production is destroyed annually. The loss is due to various stresses such as pest infestation, microbial pathogens, weeds, natural calamities, lack of soil fertility, and other causes. To overcome these limitations, various technological strategies are implemented, but a majority of these have their own repercussions (Baker et al. 2017). A wide range of materials are used to make nanoparticles, such as metal oxides, ceramics, magnetic materials, semiconductors, quantum dots, lipids, polymers, dendrimers, and emulsions. Chitosan nanoparticles are being used in agriculture in seed treatment and as a biopesticide, which helps plants to fight off fungal infections (Duhan et al. 2017). The uptake efficiency and the effects of nanoparticles on growth and metabolic functions vary among plants (Fernández-Luqueño et al. 2014). The concentration of nanoparticles affects processes such as germination, photosynthetic activity, and plant growth (Medina-Pérez et al. 2018) (Table 1.1).

The worldwide consumption of pesticides is about two million tonnes per year, of which 45% is used in Europe alone, 25% in the USA, and 25% in the rest of the world (Duhan et al. 2017). Careless and haphazard pesticide use increases pathogen and pest resistance, reduces soil biodiversity, kills useful soil microbes, causes biomagnification of pesticides, causes pollinator decline, and destroys the natural habitats of farmers’ friends such as birds. Nanotechnology can address the adverse effects posed by the abundant use of chemical agrochemicals that are reported to cause biomagnification in an ecosystem, so the potential applications and benefits of nanotechnology are enormous (Baker et al. 2017). These include insect pest management via formulations of nanomaterial-based pesticides and insecticides, and increases in agricultural productivity using nanoparticle-encapsulated fertilizers for slow and sustained release of nutrients and water, which plays a vital role in the

**Table 1.1** Highlighted reviews where the benefits or disadvantages of nanoparticle use in crops are discussed (only reviews published during the last 3 years are included)

| Main arguments and findings | Reference |
|---|---|
| Little is known about the transgenerational effects of nano-$TiO_2$ exposure and the changes at agronomical and physiological levels. The effects of such nanoparticles in proteins and other metabolites are also not well understood | Tan et al. (2018) |
| CuO nanoparticles have toxic effects on cultivated crop plants through inhibition of seed germination, decreases in shoot and root lengths, reductions in photosynthesis and respiration rates, and morphological as well as enzymatic changes | Rajput et al. (2018) |
| Metal and metal oxide nanoparticles have both positive and negative effects on the growth, yield, and quality of important agricultural crops | Rizwan et al. (2017) |
| The toxicity of ag nanoparticles is translocated from plants to other communities through the food chain and leads to disruption of balanced ecosystems | Tripathi et al. (2017) |
| Nanoparticle toxicity promotes generation of oxidative stress, cytotoxicity, and genotoxicity | Cox et al. (2017) |
| Given the lack of experimental standardization and the divergent responses, even within similar plant species, it is challenging to conclude what the effects of nanomaterials are in plants | Zuverza-Mena et al. (2017) |
| Metal nanoparticles may damage DNA and promote the cell cycle, reactive oxygen species, and lipid peroxidation | Sadeghi et al. (2017) |
| Once nanoparticles are in contact with plants, their physical and chemical properties dictate the mechanisms of adsorption, uptake, transport, biotransformation and, in turn, phytotoxicity | De la Rosa et al. (2017) |
| The somewhat limited literature that exists regarding use of nanoparticles in specific crops is mixed for most species, with both positive and negative effects being observed. The reasons for these mixed effects are numerous (different exposure scenarios, growth conditions, particle types/concentrations, and species, among others) | Mukherjee et al. (2016) |
| Phytonanotechnology has the potential to generate (1) new tools for smart delivery of agrochemicals, (2) new ways to deliver particular bioactive molecules to manipulate plant breeding and genetic transformation, and (3) new approaches for intracellular labeling and imaging | Wang et al. (2016) |

protection of the environment by reducing leaching and evaporation of harmful substances.

Currently there is a slow progress in the evaluation of nanoparticles in the agriculture sector, which could reform the modern agricultural system. Applications of these nanomaterials can add tremendous value in the current scenario of global food scarcity.

Nanoparticle-mediated gene or DNA transfer in plants for development of insect pest–resistant varieties and use of nanomaterials for preparation of different kinds of biosensors that are useful in the remote-sensing devices required for precision farming are some of the boons of this modern nanotechnology.

Use of enormous amounts of fertilizer in the form of ammonium salts, urea, and nitrate or phosphate compounds has increased food production considerably, but they have many harmful effects on beneficial soil microflora. Most of the fertilizer is not available to plants because of runoff, and so it causes pollution (Poulsen et al. 2018).

Nitrate is heavily used as an agricultural fertilizer and is now a ubiquitous environmental pollutant. Environmental endocrine effects caused by nitrate have received increasing attention over the last 15 years. Nitrate is hypothesized to interfere with thyroid and steroid hormone homeostasis and developmental and reproductive end points. The current review focuses on aquatic ecotoxicology with emphasis on field and laboratory controlled in vitro and in vivo studies. Furthermore, nitrate is just one of several forms of nitrogen that are present in the environment, and many of them are quickly interconvertible. Therefore, our focus is additionally confined to the oxidized nitrogen species (nitrate, nitrite, and nitric oxide (Poulsen et al. 2018)).

Fertilizers coated in nanomaterials can solve these problems. Nanomaterials can potentially make contributions in slow release of fertilizers, as nanoparticles more strongly limit release of the material to the plant as they have higher surface tension than conventional surfaces. Moreover, nanocoatings can provide surface protection for larger particles.

A major contribution of nanotechnology predicted to emerge from the promising results of nanopesticide use is the use of nanoparticle encapsulation and stabilization of crop protection agents, which will increase agricultural sustainability (Kim et al. 2018).

## *2.2 Soil Improvement*

It is well known that nanoparticles exist in the soil environment, including smectite, imogolite, halloysite, palygorskite, sepiolite, allophane, hematite, and goethite (Ghasabkolaei et al. 2017). As Ghasabkolaei et al. (2017) noted, soil mechanics research has defined a new category of soil particles called "nanosol"—particles measuring 1–100 nm—as distinct from clay particles.

Engineered nanoparticles have novel properties because of their extremely small size, resulting in extremely high specific surface areas (SSAs) and surface charges. As a result, these particles react very actively with other particles in the soil matrix (Ghasabkolaei et al. 2017). Iranpour and Haddad (2016) noted that the addition of more than the optimum value of nanomaterials causes agglomeration of particles, leading to negative side effects on the mechanical properties of the soil; thus, it is better to combine nanoparticles with soil in the form of colloidal solutions to reduce this negative effect.

Ghasabkolaei et al. (2017) stated that the presence of even very small amounts of nanomaterial can have significant effects on the engineering properties of soil, while the use of nanoparticles in a soil mixture increases strength, the swelling index, and compressibility, as well as decreasing permeability, the liquefaction potential, settlement, and volumetric strains. It should be noted that the behaviors of nanomaterials vary depending on the type of particles and the soil they are mixed with.

According to Huang and Wang (2016), there are four typical nanomaterials that have been applied for soil improvement: carbon nanotubes, colloidal silica, bentonite, and laponite. These nanomaterials have been used over the last 10 years in preliminary experimental explorations of their potential for soil strength improvement.

### *2.3 Water Purification*

Because of their unique physicochemical characteristics and small size, nanoparticles have utmost importance in the agri-food sector, particularly in preservation and packaging. Future applications may focus on shelf life, food quality, safety, fortification, and biosensors for contaminated or spoiled food, irrigation water, and drinking water. Dasgupta et al. (2017) published an outstanding review in which several points regarding some applications of nanotechnology in agriculture and water quality management were discussed, such as (1) nanomaterials for agriculture and water quality management; (2) research interests such as nanoscale carriers, fabricated xylem vessels, nanolignocellulosic materials, clay nanotubes, photocatalysis, bioremediation of resistant pesticides, disinfectants, agricultural wastewater treatment, nanobarcode technology, and quantum dots for staining of bacteria and nanobiosensors; and (3) nanotechnological applications in agriculture, which include nanolignodynamic metallic particles, photocatalysis, desalination, removal of heavy metals, and wireless nanosensors.

Nanoscience and nanotechnologies have vast applications in water quality management through heavy metal removal, nanobioremediation through use of nanolignodynamic metals, desalination, disinfection processes, and sensors to check for quality (Medina-Pérez et al. in press). Nevertheless, many of their applications are at an early stage and require high-quality research and development for safe application.

Although the research regarding the application of nanotechnology is growing every day, there is still insufficient scientific evidence available regarding its harmlessness. Also, testing of nanomodified agricultural products and treated water should be mandatory before they are allowed to be introduced into the market or spread in the environment, while standardized test procedures are required to study the impacts of nanoparticles on living cells for risk assessment of human or environmental exposure to nanoparticles. Currently, the toxicology of nanoparticles is poorly understood. Hence, regulatory bodies and policy makers should provide guidance documents and validated protocols for safe use and safe disposal of nanoparticles (Dasgupta et al. 2017). Understanding of safe application of nanoscience and nanotechnology in agri-food and water quality management will aid sustainable growth of agronanobiotechnology.

Recently, the application of nanomaterials for removing selenium from wastewater has received increasing interest from the power generation and industrial mining sectors. Several classes of nanomaterials such as nanoscale adsorbents, catalysts, and reactants show promising potential in removing selenium in a wide range of oxidation states (Holmes and Gu 2016). Additionally, recently published literature has focused on the modification of different nanomaterials to achieve high surface adsorbing activity, high reactivity, high selectivity, and sustainable treatment capability in efforts to remove several heavy metals (Fernández-Luqueño et al. 2013). Physical, chemical, or biological technologies could be used to remediate water pollution (He et al. 2018; Wen et al. 2018; Shakoor et al. 2017), while engineered nanomaterials also have the potential to decontaminate water (Bishoge et al. 2018; Ge et al. 2018). Several biological strategies to degrade pollutants in water have been described by Fernández-Luqueño et al. (2017a, b).

## *2.4 Diagnostics*

Nanomaterials could act as sensors for monitoring soil quality in agricultural fields and thus maintain the health of agricultural plants. The development of sensors for monitoring of toxic metals or other pollutants in different matrices, especially in water or soil, is very important. Nanomaterials such as metal (gold, silver, cobalt, etc.) nanoparticles, carbon nanotubes, magnetic nanoparticles, and quantum dots have been actively investigated for their applications in biosensors, which have become a new interdisciplinary frontier between biological detection and material science. A biosensor is a device that combines a biological recognition element with physical or chemical principles (Prasad et al. 2017).

As a powerful analytical tool, nanomaterial-based chemical sensors have been extensively employed in detection of heavy metals and other pollutants. These nanosensors offer several advantages, including high sensitivity, high selectivity, portability, on-site detection ability, and improved performance of devices (Ullah et al. 2018). Moreover, deployment of molecular recognition probes on nanostructures for selective binding has enhanced the selectivity and detection ability.

Although enormous advances and innovations have been witnessed, the detection of heavy metal ions by these nanosensors still faces great developmental challenges associated with their applicability in real-world samples, including river water and biological samples. Novel nanosensors have been reported for primary applications in improving crop practices, food quality, and packaging methods; thus, they could change the agricultural sector to produce potentially better and healthier food products (Kim et al. 2018).

Biosensors are widely employed as cost-effective, fast, in situ, and real-time analytical techniques. The need for portable, rapid, and smart biosensing devices has prompted the recent development of biosensors with new transduction materials, obtained from nanotechnology, for multiplexed pollutant detection (Justino et al.

2017). As Rapini and Marrazza (2017) noted, the growing number of contaminants requires the development of new analytical tools to meet the increasing demand for legislative action on food safety and environmental pollution control. In this context, electrochemical aptamer-based sensors, such as those based on nanotubes, appear particularly promising among all biosensors because they permit multiplexed analysis and provide fast responses with high sensitivity, high specificity, and low cost.

### 2.5 Plant Breeding

The development of nanotechnology provides a new method for genetic engineering, as the development of modern agriculture and biotechnology is closely connected with the use of novel and effective genetic engineering methods. Torney et al. (2007) described the delivery of DNA and chemicals into plants through a honeycomb mesoporous silica nanoparticle (MSN) system with 3-nm pores that can transport DNA and chemicals into isolated plant cells and intact leaves.

So far, use of nanoparticles as gene carriers has mainly been applied in mammalian cells. Fu et al. (2012) observed that zinc sulfide (ZnS) nanoparticles modified with positively charged poly-L-lysine (PLL) successfully delivered beta-glucuronidase (GUS)–encoding plasmid DNA into tobacco cells by means of an ultrasound-assisted method. They obtained stable genetically modified plants mediated by ZnS nanoparticles. The great potential of nanoparticles as gene carriers in plant transformation has been demonstrated and represents a novel approach for plant genetic decoration (Fu et al. 2012).

Plant genetic modification in which nanoparticles carrying DNA or RNA are delivered to plant cells for their genetic transformation or to trigger defense responses, activated by pathogens, has been also reported (Sadhu et al. 2018; Zhao et al. 2017; Wang et al. 2011).

### 2.6 Soil Remediation

Soils are contaminated by toxic pollutants from either natural or anthropogenic sources at concentrations capable of posing great risks to human and environmental health (Thome et al. 2015). The problems of contaminated soils have raised serious concern among environmental agencies because of the existence of a large number of polluted sites, mainly in urban and industrialized areas (Medina-Pérez et al. in press).

The concept of deliberately injecting nanoparticles into soils and groundwater for remediation purposes has raised questions and concerns about their toxicity and negative impacts on the environment, despite their beneficial effects of destruction and transformation of toxic contaminants (Thome et al. 2015).

Overall, the remediation technique using nanoparticles is complex and is influenced by several biophysicochemical processes that occur depending on the site-specific geological, hydrogeological, and contaminant conditions. But nanotechnology has great promise to remediate different contaminants effectively, efficiently, and economically (Thome et al. 2015). Several countries need to take advantage of the knowledge already acquired from previous studies and adapt these techniques to their own specific soil and climate conditions so it will be possible to apply this technology to remediate contaminated sites in the near future. Specific topics related to use of nanoparticles for soil remediation have been discussed in several reviews such as those by Thomas and Natarajan (2018), Mahfoudhi and Boufi (2017), and Lefevre et al. (2016).

Zou et al. (2016) reviewed the excellent capacity of nanoscale zero-valent iron (NZVI)–based materials for removal of various heavy metal ions and environmental remediation. They took a new look at NZVI-based materials (e.g., modified or matrix-supported NZVI materials), their possible interaction mechanisms (e.g., adsorption, reduction, and oxidation), and their latest environmental applications. Zou et al. (2016) showed that NZVI-based materials have satisfactory capacities for removal of heavy metal ions and play an important role in cleanup of environmental pollution, while possible improvement of NZVI-based materials and potential areas for future applications in environment remediation are also proposed.

## 2.7 Packaging

Application of nanotechnology has enhanced the delivery of fertilizers, pesticides, herbicides, and plant growth regulators with the help of nanoscale carriers. In addition, nanomaterials are being further researched to keep products fresher with an increased shelf life. The development of nanocomposites is a new strategy to improve the physical properties of polymers, including mechanical strength, thermal stability, and gas barrier properties. The most promising nanoscale-sized fillers are montmorillonite and kaolinite clays (Arora and Padua 2010). Nanocomposites represent a new alternative to conventional technologies for improving polymer properties. Nanocomposites exhibit greater barrier properties than their neat polymers and conventional composites. According to Arora and Padua (2010), biopolymers have attracted considerable attention as potential replacements for conventional plastic packaging materials because of increased interest in sustainable development. Biopolymers include plant-derived materials (starch, cellulose, other polysaccharides, and proteins), animal products (proteins and polysaccharides), microbial products (polyhydroxybutyrate), and polymers synthesized chemically from naturally derived monomers (polylactic acid).

Numerous cutting-edge studies on the advantages of nanotechnology have been conducted in the field of food packaging, while the market for this area of research has grown steadily and is expected to continue to do so (Azeredo et al. 2011). Mihindukulasuriya and Lim (2014) published a paper discussing nanotechnology developments targeting active packaging applications, including antimicrobial applications, oxygen scavenging, and shelf life extension of food. Nanotechnologies that are currently being exploited for development of intelligent packaging with enhanced communication functions were presented, focusing mainly on oxygen, humidity, and freshness indicators.

Use of nanoparticles in food packaging is a novel technology, so there are gaps in our knowledge that raise questions for the scientific community, especially regarding toxicity and ecotoxicity. Theoretically, nanoparticles have potential to migrate into the foodstuffs that are packaged, but migration assays and risk assessment are still not conclusive (Souza and Fernando 2016). However, Kumar et al. (2017) have suggested that natural biopolymer–based nanocomposite packaging materials may have a promising future for a broad range of applications in the food industry, including advanced active food packaging with biofunctional attributes.

Research and development in agronanobiotechnology have continued to progress, but the importance of several questions should not be underestimated—in particular, those regarding human and environmental health, and affordable and harmless food.

## 3 Conclusion

Producers of innovative products in agronanobiotechnology are experiencing difficulties in bringing these products to market, because of their high production costs, which regularly are required in high volumes in the agricultural sector, while unclear technical benefits, legislative uncertainties, and negative public opinion are hampering the development of agronanobiotechnology; notwithstanding these difficulties, the possibilities offered by agronanobiotechnology in several agricultural applications are moving forward. Nanotechnology is progressing at a rapid pace in other fields such as energy or medicine, but over time the knowledge gained in those sectors may be transferred or may spill over into the agricultural sector. Fuel, additives, and lubricants could improve the performance and decrease the carbon footprint of agricultural machinery, while improvements in packaging technologies could benefit farmers by reducing spoilage of products before purchase or consumption. Meanwhile, progress in legislation, nanoremediation, environmental monitoring, international safety regulation, and drug delivery techniques could improve the agricultural and livestock sectors indirectly. For research and development in agronanobiotechnology to move forward, long-term in situ field trials are required, while social welfare must also be guaranteed to shape sustainable development.

**Acknowledgements** This research was funded by Ciencia Básica SEP-CONACYT project numbers 151881 and 287225, the Sustainability of Natural Resources and Energy Programs (Cinvestav-Saltillo), and Cinvestav-Zacatenco. G.M.-P. and R.G.-R. received grant-aided support from Becas CONACYT. F.F.-L., F.L.-V., R.G.C.-M., E.V.-N., S.L.-S., I.A.-B., O.E.R.-R., and A.M.-N. received grant-aided support from Sistema Nacional de Investigadores (SNI), Mexico.

**Competing interests** The authors declare that they have no competing interests.

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# Chapter 2
# Design and Production of Nanofertilizers

**Sein León-Silva, Ricardo Arrieta-Cortes, Fabián Fernández-Luqueño, and Fernando López-Valdez**

**Abstract** The use and application of nanotechnology in the agricultural field is marked by utilization of fertilizers, herbicides, pesticides, sensors, emulsions, and growth formulations with nanomaterials. These revolutionary products offer a wide range of promising options for improving the quantities and quality of plants and seeds grown for consumption, reducing the costs of production as well as negative impacts on the environment, to achieve sustainable food development. Because of their small size and physicochemical characteristics such as shape, surface chemistry, electrical charge, and agglomeration, nanofertilizers can be synthesized depending on the requirements and needs of each crop, using several kinds of material such as silver, titanium, zeolite, copper, silica, aluminum, carbon, zinc, and nitrogen. Different applications in this sector include desalination and removal of heavy metals from wastewater, reduction of soil erosion, tracking devices, targeted delivery of nutrients, and food safety. Nevertheless, before nanofertilizers are industrialized and commercialized, more studies should be carried out to evaluate their impact once they come into contact with human beings and the environment, to guarantee social safety while avoiding—as much as possible—toxic effects.

**Keywords** Agriculture · Nanotechnology · Nanofertilizer · Nanosensors · Risk · Toxicity

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F. López-Valdez, F. Fernández-Luqueño (eds.), *Agricultural Nanobiotechnology*, https://doi.org/10.1007/978-3-319-96719-6_2

# 1 Introduction

One of the greatest challenges for sustainable development is the necessity to provide enough food for the growing world population without compromising the limited resources of future generations (World Commission on Environment and Development 1987). To achieve this goal with continuous population growth and rapid urbanization, with the world population being expected to reach 9.6 billion by 2050 (Melorose et al. 2015), it has been necessary to search for different solutions in agriculture that ensure reliable supply. Therefore, the use of fertilizers, herbicides, and pesticides, among other substances, has played a pivotal role in modern agriculture all over the world. Nevertheless, the excessive use of these substances has caused various environmental problems such as erosion, land infertility, eutrophication, and destabilization of soil microbial flora (Zamir 2001; Chinnamuthu and Boopathi 2009; Conley et al. 2009; Sekhon 2014; Chhipa 2017). In addition, low efficiency coupled with toxicity to humans, animals, plants, water sources, and air sources have given rise to a search for new solutions capable of satisfying the population's needs while reducing—as much as possible—negative impacts.

Organic or chemical fertilizers, and also microbial inoculants, have been developed during recent decades to produce affordable and harmless food. In this context, new alternative technologies that are less toxic and more efficient have been developed, such as the use of genetically modified varieties of plants and seeds and, more recently, the use of nanofertilizers (NFs). Actually, nanotechnology (NT) has caused a revolution in the design and production of materials, not only by modifying their properties and characteristics according to different needs, but also because of its wide range of applications in several areas such as medicine, electronics, biotechnology, material science, physics, chemistry, and definitely agriculture (Ramsurn and Gupta 2013; León-Silva et al. 2016; Prasad et al. 2017). In this sector, nanotechnology can provide various potential benefits such as enhancing crop quality, diagnosing plant diseases, improving the absorption of soil nutrients, controlling pests, monitoring water treatment, and reducing use of agrochemicals (DeRosa et al. 2010; Mukhopadhyay 2014; Prasad 2014).

# 2 Challenges in Agricultural Practice

The use of fertilizers in agriculture requires a high concentration of chemical and toxic substances to deal with plagues, diseases, and other difficulties; despite this, fertilizers cannot always ensure an optimal crop yield (Shilatha 2011). Besides, constant use of agrochemicals, contributes to the acceleration of soil degradation, underground water pollution, and bacterial resistance (Ali et al. 2014; Chhipa 2017).

In this sense, sustainable agriculture should improve traditional methods to convert conventional techniques into precise and monitored procedures, capable of controlling—as much as possible—environmental variables depending on each situation and providing the maximum yield and quality of products (Chen and Yada 2011; Solanki et al. 2015). Currently, nanotechnology represents a promising tool for development of materials with new properties that are able to encapsulate and control delivery of active ingredients such as fertilizers and herbicides (Fig. 2.1) (Durán and Marcato 2013; Nuruzzaman et al. 2016).

## 3 Nanotechnology in Agriculture

Nanotechnology is defined as the design, characterization, production, and application of structures, devices, and systems at the nanoscale (Ali et al. 2014; Diallo et al. 2014). At this level, chemical and physical properties such as size, shape, structure, charge, surface composition, or agglomeration can be modified. Additionally, because of the scale reduction, the surface area is larger than that of bulk materials, allowing more contact with and reactive responses from target surfaces (Abou El-Nour et al. 2010; Favi et al. 2015). This technology represents a new revolutionary paradigm in agriculture, which can also include livestock and fishing; among the multiple benefits of its use, several properties stand out, such as controlled release of nutrients, efficiency of pest monitoring, and less chemical leakage (Iavicoli et al.

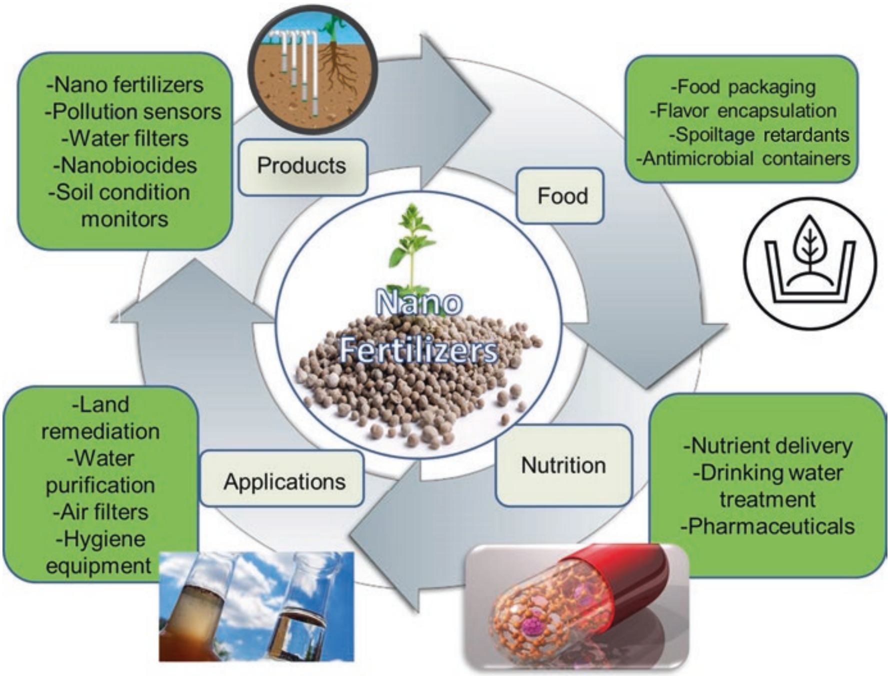


**Fig. 2.1** Nanofertilizer application areas

2017). Taking into consideration these multivariable characteristics, nanotechnology can serve as a key factor in sustainable development of agriculture, with custom-designed nanomaterials capable of increasing chemical reactions, improving productivity, reducing water consumption, and enhancing environmentally beneficial efforts (Liu and Lal 2015).

The application of nanomaterials in agriculture incorporates the development of nanofertilizers, nanoherbicides, nanopesticides, nanosensors, and nanotracers, which can contain different types of particle such as silica, carbon, iron, zinc, titanium, silver, gold, or magnesium (Naderi and Danesh-Shahraki 2013; Fernández-Luqueño et al. 2014; Dimkpa and Bindraban 2017). Actually, there are a wide variety of agricultural applications such as controlled release of herbicides or pesticides, and encapsulation of nutrients inside a nanoporous material for subsequent release, avoiding interaction and losses via soil, water, air, or microorganisms (Rai et al. 2012).

Furthermore, in the specific case of nanofertilizers, their release of nitrogen to crops can be synchronized with the demand (Malekian et al. 2011). Researchers such as DeRosa et al. (2010) have reported that use of nanofertilizers improved crop efficiency in comparison with conventional composts. Also, strategies have recently been developed to enhance the reaction of nanofertilizers to the environment in order to detect pH changes, temperature, moisture, humidity, etc. (Durán and Marcato 2013; Sekhon 2014).

Nanomaterials can also be exploited for their photocatalytic characteristics; for example, silver nanoparticles (Ag-NP) have been incorporated into agricultural activities for their antibacterial properties (Dubey and Mailapalli 2016), and silica nanoparticles (Si-NP) form films at cell walls, improving the stress resistance of plants (Shilatha 2011). Conley et al. (2009) have described the use of phosphorus in a nanoscale form to prevent soil fixation.

Nowadays, nanosensors are commonly used for environmental monitoring because of their quick, reliable, and sensitive responses (Thakkar et al. 2010; Servin et al. 2015). Dubey and Mailapalli (2016) studied several nanobased sensors, observing a significance range difference in detection of heavy metal traces in comparison with conventional instruments. For such applications, nanomaterials show numerous advantages over traditional methods in agriculture (Fig. 2.2).

## 4 Nanofertilizers

Nanofertilizers are modified fertilizers synthesized by chemical, physical, or biological methods using nanotechnology to improve their attributes and composition, which can enhance the productivity of crops (Singh et al. 2017) (Fig. 2.3). They exhibit several advantages over conventional fertilizers, as they increase the quality parameters of farming (Table 2.1); Narendhran et al. (2016) demonstrated that the use of zinc oxide nanoparticles (ZnO-NP) expanded the germination of the *Sesamum indicum* plant. Moreover, Kottegoda et al. (2017) synthesized urea–hydroxyapatite

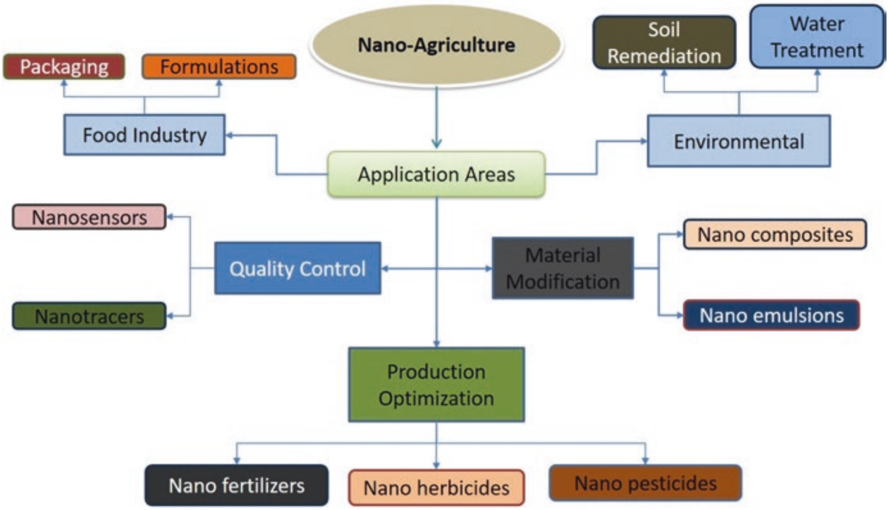


**Fig. 2.2** Nanotechnology developments in agricultural fields

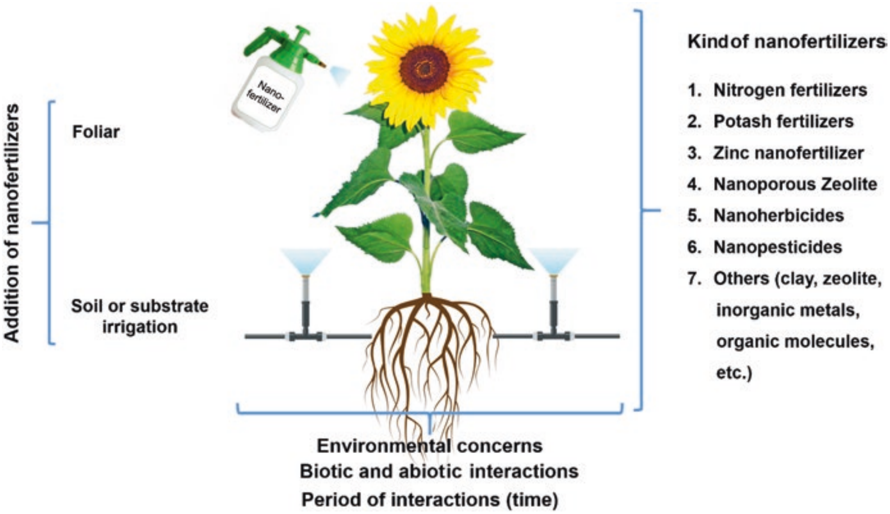


**Fig. 2.3** Different means of addition and different kinds of nanofertilizer, and associated environmental concerns

nanohybrids to achieve slow release of nitrogen, concluding that the use of nanourea can increase yields and reduce the use of conventional fertilizers. Additionally, Diallo et al. (2014), Liu and Lal (2015), Dimkpa and Bindraban (2017), and Singh et al. (2017) suggested that nanofertilizers have less toxic consequences for humans than traditional products, as well as minimizing costs by increasing the quantity and quality of products, and thereby maximizing profits.

**Table 2.1** Property comparison between nanofertilizers and conventional products

| Property | Nanofertilizer | Challenges |
|---|---|---|
| Controlled release | Nanofertilizers can control the speed and doses of nutrient solution release (Duhan et al. 2017) | Reactivity and composition variations due to environment factors |
| Nutrient loss | Leakage and waste caused by application of fertilizers can be reduced (Chinnamuthu and Boopathi 2009) | Environmental effects after conclusion of the nanofertilizer life cycle |
| Duration of release | Nanofertilizers can extend the duration of nutrient release in comparison with regular fertilizers (Servin and White 2016) | Phytotoxicity effects due to the dose and time of exposure |
| Efficiency | The uptake ratio is increased and the release time of nanostructures is reduced (Ditta and Arshad 2016) | Long-term environmental effects, as well as chronic effects on final consumers |
| Solubility and dispersion | Absorption and fixation of nutrients by the soil are improved, increasing their bioavailability (Prasad et al. 2017) | Complete ecotoxicological profiles, taking into account the consequences for health and the environment |

Specifically, among the various benefits of using nanofertilizers, the most representative are:

- Higher product quality with minimum remnants.
- Eco-friendly synthesis.
- Custom-made products.
- Lower-cost production, reducing the amount of fertilizers used.
- Less negative impacts and toxicity.
- Controlled release of plant nutrients.

## 5 Properties

One of the main characteristics of nanofertilizers is their ability to be synthesized using chemical, physical, and biological methods. The biological technique is also known as “green synthesis” because it involves use of plants, fungi, bacteria, algae, and yeasts as reducing and stabilization agents. It is a more energy efficient, safer, and less wasteful method than the other processes (Prasad et al. 2016). Table 2.2 lists some of the microorganism species used to synthesize several types of nanoparticle.

**Table 2.2** Microorganisms used in nanoparticle synthesis

| Microorganism | Types of nanoparticle | Reference |
|---|---|---|
| *Plants* | | |
| *Pelargonium graveolens* | Ag-NP | Iravani et al. (2014) |
| *Citrus sinensis* | Ag-NP | Solgi (2014) |
| *Cinnamomum camphora* | Au-NP, Ag-NP | Syed et al. (2013) |
| *Fungi* | | |
| *Aspergillus flavus* | Ag-NP | Marambio-Jones and Hoek (2010) |
| *Fusarium oxysporum* | $Bi_2O_3$ | Sharma et al. (2013) |
| *Colletotrichum* sp. | Au-NP | Mandal et al. (2006) |
| *Bacteria* | | |
| *Escherichia coli* | Au-NP | Krzyzewska et al. (2016) |
| *Pseudomonas aeruginosa* | Se-NP, Ag-NP | Grillo et al. (2015) |
| *Lactobacillus* sp. | Au-NP, Ag-NP | Tran et al. (2013) |
| *Yeasts* | | |
| *MKY3* | Ag-NP | Thakkar et al. (2010) |
| *Candida glabrata* | PbS-NP | Murphy et al. (2015) |
| *Saccharomyces cerevisiae* | $Sb_2O_3$ | Yu et al. (2013) |

*Ag-NP* silver nanoparticles, *Au-NP* gold nanoparticles, $Bi_2O_3$ bismuth oxide, *PbS-NP* lead sulfide nanoparticles, $Sb_2O_3$ antimony oxide, *Se-NP* selenium nanoparticles

## 6 Production

Recent applications of nanotechnology in agriculture have successfully demonstrated the utility of nanomaterials as a potential plant growth regulator, but practical application of nanomaterial-based fertilizers on agricultural lands requires a suitable substrate to effectively disperse the nanomaterials (Kumar et al. 2018).

The types of nanofertilizer include:

1. Nitrogen fertilizers.
2. Potash fertilizers.
3. Zinc nanofertilizer.
4. Nanoporous zeolite.
5. Nanoherbicides.
6. Nanopesticides.

## 7 Effects and Critical Considerations

The use of nanofertilizers in agriculture significantly influences seed germination and growth. They can easily penetrate soil and roots, increasing the release of nutrients, chlorophyll formation and dry matter production, which consequently improve plant growth (Suriyaprabha et al. 2012; Dhoke et al. 2013). However, Abdelmonem et al. (2015) concluded that most nanomaterials possess a natural tendency to agglomerate, and this property considerably reduces their efficacy and promotes the formation of reactive oxygen species (Kumari and Yadav 2014). To avoid such effects, different chemicals such as chitosan, oleylamine, surfactants such as gluconic acid, cellulose, or polymers such as polyethylene glycol (PEG), poly N-vinyl-2pyrrolidone (PVP), poly(methyl methacrylate) (PMMA), and poly(methacrylic acid) (PMAA) are used to stabilize and prevent agglomeration (Sintubin et al. 2009; Mwilu et al. 2013; Grillo et al. 2015).

Nevertheless, continuous use and consequent release of these substances can have major impacts on health and the environment (Navarro et al. 2008; Gottschalk et al. 2013; Kookana et al. 2014). Given their sizes and applications, they can come into contact with the human body through the skin and via the respiratory, gastrointestinal, and genital routes. Moreover, several physical and chemical factors—including size, shape, surface chemistry, agglomeration, surface charge, stability, and storage time (León-Silva et al. 2016)—influence the toxicity of nanoparticles in the final media.

For example, the relationship between the size and toxic effects of Ag-NP was studied by Larese-Filon et al. (2015), who observed that nanoparticles smaller than 40 nm present the potential for hazardous skin penetrations, and they concluded that the critical size should not be less than 70 nm. Also, Carlson et al. (2008) found a size-dependent toxicity mechanism in Ag-NP, causing formation of reactive oxygen species and thus oxidative stress. Another relevant factor is the shape of nanoparticles; Gorka et al. (2015) studied its influence on toxicity, finding that nanorod and nanocube shapes are less toxic than spherical particles. Moreover, the surface chemistry plays an important role in the behavioral effects of nanoparticles. Caballero-Díaz et al. (2013) analyzed the effects of different Ag-NP surface coatings, finding that different surface chemistries allow formation of agglomerates, and it is precisely this characteristic that is one of the principal toxic factors. In this context, Braydich-Stolle et al. (2005) investigated the in vitro mouse spermatogonial cell line and concluded that membrane leakage and mitochondrial cytotoxicity increase as agglomeration increases. This factor directly influences the superficial charge and stability of the nanoparticles. Huk et al. (2015) studied different charges of Ag-NP, finding that positive nanoparticles had a greater impact, in terms of cytotoxicity and genotoxicity, than neutral or negatively charged particles. On the other hand, El Badawy et al. (2010) found that the stability of nanoparticles was a function of diverse environmental conditions such as ionic strength, pH, storage time, and background surface composition.

In view of the above factors, and because use of nanofertilizers involves direct contact with plants, soil, and water systems, appropriate research, evaluation schemes, and regulation scenarios should include the natural uptake mechanisms, the influences of environmental factors, and the exposure conditions, in order to reduce their impact and toxicity.

Additionally, several areas should be explored while the growth of these nanomaterials occurs. Because of the current difficulty of measuring and tracking the impact of nanomaterials on human health and the environment, it is important to take into consideration that each substance will behave differently, so it is necessary to do individual studies and research on the effects of each material and to create models and evaluation methodologies capable of properly measuring the impact and fate of the nanomaterial after its use (Navarro et al. 2008; Kah et al. 2013; Fernández-Luqueño et al. 2014; Servin and White 2016). Furthermore, confirmation of suitable doses and concentrations of each material will require an exceptional number of studies in vitro, in situ, and in vivo to begin the standardization process of products and materials.

## 8 Health Risks

In general terms, a health “hazard” is an agent able to cause a disease under certain circumstances, while a health “risk” is the probability of a disease occurring, taking into account the level of exposure to the agent. Therefore, these directives are a means of evaluating the “hazard” of a substance and identifying disease hazards even when the risks are very low at current exposure levels, because new uses or unexpected exposures could promote risks that are significantly higher (Arrieta-Cortes et al. 2017).

The available literature suggests that many uncertainties remain about nanomaterials, including the potential for bioaccumulation and potential human health risks. While the proposed applications of nanotechnologies are wide and varied, developments are met with some caution, while progress may be stifled by lack of governance and potential risks (Cushen et al. 2012).

As with many new technologies, enthusiasm in the rush to market nanotechnologies may detract from the importance of investigation of possible health and environmental implications (Morgan 2005). The scientific community must learn from previous introductions of new technologies, being particularly sensitive in the food area. For example, genetically modified foods were not well received by consumers because there was a perceived risk associated with them. Thorough risk assessment of nanotechnologies in the food sector should provide a sound foundation on which commercial products can be launched with confidence or withdrawn to protect consumers and the environment from potential hazards (O’Brien and Cummins 2010a, 2011).

For nanotechnologies to be used to their full potential, they must be accepted by consumers. Clear communication of the benefits of using nanotechnologies for various purposes, instead of existing technologies, must be conveyed to the public. Both benefits and risks should be acknowledged; however, for acceptance it must be clear to the public that not only do the benefits outweigh the risks, but also the risks are acceptable (Cushen et al. 2012).

In modern agriculture, sustainable production and efficiency are unthinkable without the use of agrochemicals such as pesticides and fertilizers. However, every agrochemical has some potential issues, including contamination of water or residues on food products that threaten human and environmental health; thus, precise management and control of inputs could allow these risks to be reduced (Kah 2015).

Nanotechnology can play an important part in productivity through control of nutrients (Gruère 2012; Mukhopadhyay 2014), as well as participating in the monitoring of water quality and pesticides for sustainable development of agriculture (Prasad 2014). Nanomaterials have such diverse assets and activities that it is impossible to deliver a general assessment of their health and environmental risks (Prasad 2014). Nanoparticle properties (other than size) that influence toxicity—including their chemical composition, shape, surface structure, surface charge, behavior, and extent of particle aggregation (clumping) or disaggregation—may be associated with engineered nanoparticles (Ion et al. 2010).

For this reason, even nanomaterials that have the same chemical composition but are of different sizes or shapes can exhibit different toxicity. The implication of this is that nanotechnology research in the agricultural sector is necessary and even a key factor for sustainable development. In the agri-food area, pertinent applications of nanotubes, fullerenes, biosensors, controlled delivery systems, nanofiltration, etc. have been observed (Ion et al. 2010; Sabir et al. 2014).

This technology has proved to be useful in resource management in the agricultural field and for drug delivery mechanisms in plants, and it helps to maintain soil fertility. Moreover, its utility is also being steadily evaluated in the use of biomass and agricultural waste, as well as in food processing systems, food packaging systems, and risk assessment (Floros et al. 2010). Recently, nanosensors have been widely applied in agriculture because of their strengths and rapid response for environmental monitoring of contamination in soils and in water (Ion et al. 2010).

Several sensors based on nanodetection technology—such as biosensors, electrochemical sensors, and optical sensors and devices—will be the main instruments for detecting heavy metals in the trace range (Ion et al. 2010).

New analytical methods need to be developed to detect, validate, and access the effects of each nanomaterial/nanofood in whole ecosystems. Life cycle analysis of nanomaterials/nanofoods should be done. Development of wide-ranging databanks—as well as international collaboration on policies, ideas, and regulation—are needed for manipulation of this knowledge. Additionally, authorities should provide clear guidelines and roadmaps for reducing the risks of use of nanotechnological products (Prasad et al. 2017).

Although a lot of information on individual nanomaterials is available, the toxicity levels of many nanoparticles is still undefined; thus, the application of these materials is limited by lack of risk assessment and lack of knowledge of their effects on human health. Development of comprehensive databases and alarm systems, as well as international collaboration on regulation and legislation, are necessary for exploitation of this technology (Prasad et al. 2017).

In addition, public perception of the various applications of nanotechnologies is a major factor determining commercial success in this field. Consumers' attitudes are particularly sensitive when it comes to the foods and beverages they consume. Whether the benefits that nanotechnologies offer outweigh the risks they present will dictate consumers' opinions and willingness to purchase. In one study, participants were hesitant to buy nanotechnology-related foods or foods with packaging enhanced with nanotechnologies (Siegrist et al. 2007).

It has been reported that public knowledge about nanotechnologies in general is limited in the USA (Cobb and Macoubrie 2004), but the results show that perceptions are generally optimistic. In Europe it has been found that perceptions are less positive (Gaskell et al. 2005).

## 9 Conclusion

Because of the limitations in the availability of purified water and land for farming, the development and application of nanomaterials in agriculture have a promising future, which includes nanofertilizers, nanoherbicides, nanopesticides, and nanosensors. Use of nanomaterials could bring about a revolution in agricultural practices, with various applications in soil remediation, pest control, minimization of chemical spread, nutrient distribution, water treatment, desalination, and disinfection, among others (Nuruzzaman et al. 2016). However, the current pace of development, lack of standardization, and indiscriminate use raise serious concerns regarding the effects on society and environment, because of the absence of appropriate in situ and in vivo studies capable of determining the appropriate doses and concentrations for each harvest to minimize their possible negative effects. Additionally, it is imperative to evaluate the release of nanomaterials into the environment, in order to determine the exposure levels of animals and humans, as nanoparticles can easily enter the respiratory, gastrointestinal, and dermal systems, causing various negative effects.

Finally, it is necessary to create and validate appropriate regulation protocols for each material, considering its synthesis, use, disposal, and recovery, especially if the nanomaterial will be used in agriculture, which has a direct impact on sustainable development.

**Acknowledgements** León-Silva, Sein received grant-aided support from Conacyt, Mexico.

**Competing interests** The authors declare that they have not competing interests.

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# Part II
# Fertiliszers and Plant Nutrients on Germination, Growth and Development of Crops

# Chapter 3
# Nanofertilizers and Their Controlled Delivery of Nutrients

**Fernando López-Valdez, Mariana Miranda-Arámbula, Ada María Ríos-Cortés, Fabián Fernández-Luqueño, and Verónica de-la-Luz**

**Abstract** Use of nanoparticles as nanofertilizers is a new research area, impacting crop science, environmental science, and agronomy—for example, the properties of the soil, its communities, and plant growth and development. Nanotechnology is now playing an important role because of the demand for high-quality and innocuous foods, and fertilizers with less impact or a neutral impact on the environment and on health. Nanofertilizers could be more stable and more efficient than conventional fertilizers. Nevertheless, nanoparticles could be important pollutant agents if we are not sufficiently well informed to apply or manage them correctly. In this chapter, we give a brief review of several important topics on use of nanoparticles as nanofertilizers, their formulations, and other important topics, such as the properties of ions and nanoparticles, materials for controlled delivery, plant cell processes, the entry of nutrients into plants, the advantages and disadvantages of nanoparticles, and other processes involved with them.

**Keywords** Controlled delivery · Nanofertilizers · Uptake · Adsorption · Nanoparticles

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# 1 Introduction

Worldwide, the demand for foods is increasing. Also, people have demands regarding the quality of their foods, such as organic origin and innocuousness (or safety). From this point of view, agricultural techniques are a questionable topic. In this new era, people are more conscientious about their environment, and they wonder what compounds are in their foods and how plant foods are cultivated. Chemical or synthetic fertilizers are like double-edged swords. On the one hand, they increase crop production; on the other hand, they disturb the soil mineral balance and decrease natural soil fertility over time, increasing soil erosion and damaging drinking water reservoirs. Given this concern, nanoparticles are playing a new and important role as a source of nutrients for plants through controlled delivery of those nutrients. Chemical fertilizers and nanoparticles can have the same origin but entirely dissimilar effects. In the first case, the delivery is total and exposed; in the second case, the release of nutrients is slow, depending on various factors such as the soil properties and the weather.

As can be seen, nanotechnology has played an important role in recent years, impacting several scientific fields, so we can talk about a new area of interest: agronanobiotechnology. We are discovering new properties of metals that are due to their size and ligands; moreover, their particle size offers an extended surface that can translate into minor losses of nutrients, less damage to the soil or any source of drinking water, slow or controlled delivery of nutrients, and only minor degradation of the fertilizer, among others. Certainly, the use of nanoparticles as nanofertilizers is a new field in which the major research has been done only at the laboratory scale so far. There are many questions to answer in several fields—such as agronomy, soil science, crop science, and environmental science—and also regarding social and economic aspects that may pose concern.

Behind the design and production of nanofertilizers, an ongoing theme is the controlled delivery of nutrients. In this chapter, we give a brief review of several important topics related to nanoparticles, such as their properties, materials for controlled delivery, the next generation of fertilizers, plant cell processes, the entry of nutrients into plants, the advantages and disadvantages of nanoparticles, and other processes involving nanoparticles.

# 2 Nanofertilizers: Some Concepts

Fertilizers are chemical compounds that play the main role in providing nutrients for plants. They can be natural or synthetic products applied to soil–crop systems to satisfy the need for essential nutrients. The first impression of fertilizers is of nonmetal fertilizers—e.g., nitrogen (N), phosphorus (P), and/or sulfur (S)—but metals are included in fertilizers too. It is well known that there are about 16 nutrient elements required for growth of plants, i.e., carbon (C), oxygen (O), hydrogen (H), nitrogen (N), potassium (K), phosphorus (P), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), manganese (Mn), boron (B), zinc (Zn), copper (Cu), molybdenum (Mo), and chlorine (Cl), as the main elements (Fernández-Luqueño et al. 2015). In addition, there are seven other elements—nickel (Ni), selenium (Se), vanadium (V), sodium (Na), silicon (Si), cobalt (Co), and aluminum (Al)—that are important elements for plants (Fernández-Luqueño et al. 2015); they increase plant growth as micronutrients and perform special functions as cofactors for enzymes. Of course, depending on the plant species, they may not require all of these elements and the necessary quantities may also vary. As mentioned by Pilon-Smits et al. (2009), there are beneficial effects of low doses of Al, Co, Na, and Se, but they have received little attention in comparison with the toxic effects of higher concentrations of these minerals.

A second point is that the term “nanoparticles” implies a metal particle size of less than $10^{-9}$ m (a billionth of a meter), where the scale is the most important factor as it provides a higher surface area to volume ratio (León-Silva et al. 2016). These nanoparticles reveal size-dependent properties. To control the size of the particles, nanofertilizers can be synthesized by physical, chemical, or biological approaches; the first of these is the one most commonly used. According to their properties, these particles can be classified into three categories: (1) *physical properties*: superconductivity, superparamagnetism, ultrahardness, and fluorescence; (2) *chemical properties*: high resistance to corrosion and photocatalytic capacity as semiconductors; and (3) *biological properties*: antimicrobial properties, antimicrobial coatings [e.g., silver nanoparticles (Ag-NP)], catalytic activity, and nonlinear optical behavior (León-Silva et al. 2016).

## 2.1 Some Characteristics of Nanoparticles and Their Effects

The main characteristics of nanoparticles are their size, shape, superficial charge, chemical composition, concentration, stability, and availability. These characteristics have effects on the properties of the nanoparticles, i.e., they should be taken into account in the exact applications and various uses of nanoparticles. For example, with regard to *size*, some studies of (spherical shaped) Ag-NP have suggested that particles measuring <40 nm can penetrate the skin, with a critical size of 70 nm, so bigger particles have been shown to be less toxic and cause less damage to the skin than smaller particles (Larese Filon et al. 2015). Carlson et al. (2008) tested Ag-NP sizes of 15, 30, and 55 nm, and they found that the smallest size increased the concentration of reactive oxygen species (ROS) in comparison with the other sizes. Choi and Hu (2008) found that nitrifying organisms were inhibited by use of 5 nm Ag-NP in suspension. These results suggest size-dependent toxicity and reactivity of smaller nanoparticles. With regard to *shape*, Pal et al. (2007), studied different shapes of Ag-NP with equal surface areas and found that truncated triangular nanoplates with a {111} lattice plane as the basal plane had higher reactivity than nanoparticles with fewer facets, such as spherical or rod-shaped particles. With regard to *surface charge*, according to Huk et al. (2015), a positive charge in nanoparticles may produce severe effects such as cytotoxicity, genotoxicity, and mutagenicity. Abdelmonem et al. (2015) stated that nanoparticles with a positive charge are more toxic than negatively charged ones. Therefore, this must be taken into consideration as an important factor when nanoparticles are released into the environment. The *concentration* seems to have an important effect on agglomeration/aggregation rates and particle stability, in conjunction with the surface charge; for example, a high concentration results in higher aggregation rates and greater stability of aggregate size than lower concentrations (Tourinho et al. 2012).

## 2.2 Physiological Functions of Minerals, Macronutrients, and Micronutrients (K, Ca, Mg, Cu, Zn, Mn, Fe, Ni, Mo, B, Al, Co, Na) as Potential Precursors of Nanoparticles

It is well known that plants need minerals, macronutrients, and micronutrients for their main processes of growth and development. The metallic macronutrients are K, Mg, and Ca, and the metallic micronutrients are Cu, Zn, Mn, Fe, Ni, Al, Co, and Na. These minerals are involved in any important processes such as activation of enzymes and catalytic active cofactors, enhancement of resistance to biotic stresses (phytopathogens) and abiotic stresses (drought and salinity), and charge balance (Karley and White 2009; Maathuis 2009). In the following subsections we show the importance of some of them.

### 2.2.1 Potassium

Potassium ($K^+$) is required by plants for metabolic reactions as an activator of multiple enzymes. The major chemical forms of $K^+$ are dehydrated and coordinated with oxygen atoms, and these forms are not available to plants. As reported by Maathuis (2009), the enzyme activation required between 50 and 80 mM $K^+$ was determined in in vitro conditions. The main roles of this mineral are turgor provision and water homeostasis, including stomatal aperture changes, with uptake and release of $K^+$ affecting plant water homeostasis; some of these processes are mediated by the vacuole. The $K^+$ ion plays an important role as a counterion for nucleic acids and proteins because of their total sum of negative charges (Maathuis 2009).

### 2.2.2 Calcium

The calcium ($Ca^2$+) ion is an important mineral and very abundant in the lithosphere, like potassium, but weather and soil conditions (negative charges) may lead to a deficiency of Ca, accelerated by the pH of the soil. The considerable electrochemical gradient of these ions, where concentrations of $Ca^{2+}$ in the rhizosphere environment solution are in the millimolar range, must be taken into account (Karley and White 2009). The main roles of $Ca^{2+}$ are structural and that of a secondary messenger, which remains sequestered in the vacuole (up to 1 mM) until its use. Because $Ca^{2+}$ readily forms insoluble salts and complexes (organic compounds with negative groups: phosphates, carboxyl groups in phospholipids, proteins, and sugars), the cytoplasm is an environment extremely low in $Ca^{2+}$, at around 100 nM $Ca^{2+}$. It has been found that some stimuli are responses to biotic and abiotic stress, stomatal regulation, and physical damage (Maathuis 2009).

### 2.2.3 Magnesium

Another macronutrient is magnesium (Mg), which has high leaching rates in the soil, so deficiency of this mineral is very common. Concentrations of Mg in soil solutions lie between 125 μM and 8.5 mM (Karley and White 2009). Its concentration in the cytoplasm is approximately 0.4–0.5 mM (Karley and White 2009; Maathuis 2009) and one of the important roles of magnesium is as the main component of the chlorophyll molecule. It also functions as an enzyme cofactor and plays a role in stabilization of nucleic acids and nucleotides. In enzyme reactions that involve energy transfer and phosphorylation/dephosphorylation [such as those of adenosine diphosphate (ADP) and adenosine triphosphate (ATP)], where energy is released by enzymes such as ATPases and phosphotransferases, the $Mg^{2+}$ ion is indispensable (Maathuis 2009).

Essential micronutrients are present in catalyzing, (co)activating, and/or structural functions. More than 1,200 proteins contain the metallic ions iron, copper, and manganese, and a smaller group contains molybdenum and nickel proteins.

### 2.2.4 Copper and Iron

Copper (Cu) and iron (Fe) are micronutrients of utmost important for life. Copper participates in important processes as an essential element in photosynthesis, mitochondrial respiration, C and N metabolism, oxidative stress protection, and cell wall synthesis processes. A deficiency of this mineral has consequences for the whole plant. Copper metabolism is closely linked to iron metabolism. Iron is an ion involved in photosynthesis, mitochondrial respiration, nitrogen assimilation, hormone biosynthesis, production and scavenging of ROS, osmoprotection, and pathogen defense, among other processes (Hänsch and Mendel 2009).

### 2.2.5 Manganese

Manganese (Mn) is an important element for plant metabolism and development. It is involved in around 35 enzymes in plant cells (oxidation states II, III, and IV). It participates as a catalytic active metal in proteins and exerts an activating role in enzymes—for example, enzymes of nitrogen metabolism, gibberellic acid biosynthesis, and RNA polymerase activation.

### 2.2.6 Molybdenum

The metallic ion molybdenum (Mo) is involved in nitrogen assimilation, sulfur metabolism, and phytohormone biosynthesis, mainly. For example, the last step of abscisic acid synthesis is catalyzed by the molybdenum enzyme aldehyde oxidase or sulfite oxidase, protecting the plant against toxic levels of sulfite such as those in acid rain (Hänsch and Mendel 2009).

### 2.2.7 Nickel

The metallic ion nickel (Ni) occurs in different states of oxidation: I, II, and III; state II is more common. This ion is related to urease activity in plant cells, and plants with a nickel deficiency show accumulation of urea, which is toxic to plants.

### 2.2.8 Zinc

The metallic ion zinc (Zn) is present as a component in some enzymes involved in protein synthesis and energy production. It is also responsible for maintaining the structural integrity of cell membranes and seed development, and plays other important roles too (Hänsch and Mendel 2009).

### 2.2.9 Boron

Boron (B) is a nonmetallic element and plays very important roles in plants as a micronutrient. Its main functions are in protein synthesis, sugar transport, respiration, carbohydrate metabolism, RNA, and hormone metabolism [indole-3-acetic acid (IAA)]. It is also involved in cell wall synthesis, lignification, and cell wall structures by crosslinking (polysaccharides of the cell wall) in structural membranes. The transport of phosphorus and chlorine is improved by plasmalemma ATPase induction, hyperpolarization of membrane potential by stimulation of proton pumping, and complexed proteins (rhamnogalacturonan II) (Hänsch and Mendel 2009).

Likewise, Al, Co, and Na are important micronutrients for plant metabolism, i.e., they can promote or stimulate plant growth and may be essential for some taxa (they are not required by all species of plant). Like other minerals, they are involved in stress processes such as drought, salinity, and nutrient toxicity or deficiency (Pilon-Smits et al. 2009). Plant requirements for these minerals can vary according to the plant species. Several studies have been conducted to establish their beneficial effects on plants through simple experiments such as comparisons of the presence and absence of the mineral in question. For example, aluminum has been reported to increase growth and may be related to increased leaf phosphorus levels in *Miscanthus sinensis*. It has also been shown to increase antioxidant enzyme activity, which may contribute to increased *Camellia sinensis* growth. Aluminum can enhance herbivore defense, can prevent Fe toxicity, and may stimulate P uptake in acidic soils (pH < 5.5) (Pilon-Smits et al. 2009). Cobalt presents a similarity to Ni; it may enhance herbivore defense and drought resistance, may retard leaf senescence via inhibition of ethylene biosynthesis, and is essential for rhizobacterial symbionts. The main beneficial effects have been reported in leguminous plants; pea plants showed increases in their growth, weight, and number of nodules when 8 parts per million (ppm) of Co were applied to the soil.

Sodium is an essential ion and chemically similar to potassium. It enters plants via nonselective cation transporters, mainly $K^+$ channels. Some typical examples of such plants are halophytic plant species that live in saline conditions. Sodium has also shown beneficial effects on plant growth in natrophilic species in conditions of $K^+$ deficiency or moderate drought stress (Pilon-Smits et al. 2009).

It is well known that these elements (ions) are very important for plant metabolism; nevertheless, their properties are completely different from those of nanoparticles, even in terms of the pathways used for entry into plants. The following point is made in order to invite reflection and research: if the ions are smaller than the nanoparticles, the differences between them are profound for instance, chemical properties, formation of aggregates, and electrical, paramagnetic, magnetic properties (physical properties). An interesting question is, Where are quantum characteristics shown more?

### *2.3 Mechanisms of Nutrient Uptake by Plants*

There are essential means of nutrient uptake by plants: via the roots, simple diffusion, facilitated diffusion, and active transport. In *simple diffusion*, nonpolar molecules flow according to the concentration gradient passively through the lipid bilayer membrane without protein transport being involved. In *facilitated diffusion* there is rapid movement of solutes or ion flow according to the concentration gradient, facilitated by transport proteins. In *active transport*, ions or molecules flow against the concentration gradient; of course, this process requires energy (ATP) to pump ions or molecules through the membrane. As is well known, not all molecules or ions are mobile in the same way; for example, boron is considered nonmobile via the phloem, and $Ca^{2+}$ shows slow mobility (or is relatively immobile). The aerial pathway is via the stomata on leaves.

## 3 Synthesis, Additives, Formulations, and Forms of Nanoparticle Application

There are two means of nanoparticle synthesis: natural and synthetic. The synthetic means applies to metal and metal oxide nanoparticles (ZnO, $TiO_2$, $Al_2O_3$, FeO, $Fe_2O_3$, etc.), and even nonmetal nanoparticles, usually called engineered nanoparticles (Husen and Siddiqi 2014). Many compounds may be used to achieve synthesis of nanoparticles; for example, extracts from plants that contain a wide variety of substances such as resins, latex, flavonoids, phenols, alcohols, and proteins—all in the presence of metal salts—can be used to produce metal nanoparticles. For this type of synthesis (of metal nanoparticles), microorganisms, algae, or plant extracts are used (Husen and Siddiqi 2014). On the other hand, for reuse of materials, biodegradable organic waste, plants, or fruit peel can be used in an alternative procedure for nanoparticle synthesis because of the presence of phenols, flavonoids, proteins, and reducing agents (Ghosh et al. 2017; Husen and Siddiqi 2014). Important quantities of organic waste are produced by aquacultural and horticultural activities; they offer biomolecules and bioactive compounds (as renewable sources) suitable for recycling and food waste utilization strategies (Ghosh et al. 2017) or for eco-friendly final disposal of organic waste. These types of process are easily and rapidly carried out in "normal" conditions [standard ambient temperature and pressure (SATP), such as room temperature and atmospheric pressure] and under eco-friendly conditions; this means that no toxic chemical and/or harmful solvents are involved. The nanoparticles are prepared with food extracts from food waste in aqueous conditions plus a source of metal ions, resulting in biosynthesis of nanoparticles (Ghosh et al. 2017).

According to Ghosh et al. (2017), in these processes it is possible to carry out the main steps (mechanisms) of metal nanoparticle biogenic synthesis: nucleation, nanoparticle growth, stabilization, and capping agents (enzymes, functional groups, proteins, etc.), resulting in capped and stable metal nanoparticles. The nanoparticles produced by this process include gold, silver, palladium, platinum, magnetic ferric oxide, cuprous oxide and cupric oxide, magnesium oxide, and manganese (II, III) oxide, mainly.

The herbs, shrubs, and trees that have been used in biogenic synthesis are *Cymbopogon citratus*, *Aloe barbadensis* (aloe vera), *Ipomea digitata*, *Mentha piperita*, *Jatropha curcas*, *Ginkgo biloba*, *Azadirachta indica*, *Cinnamomum camplora*, *Cinnamomum zeylanicum*, *Moringa oleifera*, *Pinus densiflora*, *Piper betel*, and *Santalum album*, among others (Husen and Siddiqi 2014).

### *3.1 Additives, Formulations, and Forms of Application*

Metal nanoparticles can be iron, cobalt, zinc, aluminum, nickel, gold, silver, copper, silicon, chromium, tin, titanium, lead, platinum, tungsten, palladium, rhodium, tantalum, ruthenium, or combinations or alloys of them. They can also be accompanied by additional nutrients (fertilizers) for plants, i.e., nitrogen, phosphorus, potassium, calcium, sulfur, magnesium, boron, iron, manganese, zinc, molybdenum, or chloride, or possible combinations of them. Also, the formula can include bioactive agents (antimicrobial agents such as bactericides), pesticidal agents (fungicides, insecticides, herbicides, acaricides, miticides, nematicides, and molluscacides), and other plant nutrients (phytohormones, plant growth regulators, or precursors of phytohormones) (Lillard et al. 2017; Nilanjan 2016).

Briefly, we describe the processing that take place to form metal nanoparticles, i.e., coating of the metal nanoparticle through salt reduction synthesis, solvothermal synthesis, ultrasonic irradiation, a reverse micelle process, photochemical reduction, bioreduction, electrochemical synthesis, or heat evaporation, among other processes, or combinations thereof.

Another important point that should be taken into consideration is the reducing agents that are used, such as sodium citrate, sodium borohydrite, hydroquinone, formaldehyde, ethanol, glycol ethylene, sugar pyrolysis radicals, hydroxyl radicals, *N*,*N*-dimethylformamide, other organic compounds with reducing characteristics, or combinations thereof. Also, some nanoparticle formulas require some sort of stabilizer such as polyvinyl alcohol, polyethylene glycol, dodecyl sulfate of sodium, polycaprolactone, carboxymethyl cellulose, citrate, cellulose, thiols or amines (both long-chain), bovine serum albumin (BSA), or combinations thereof (Lillard et al. 2017; Nilanjan 2016).

There are several forms of application; some of them come from hydroponic techniques, and others have been adapted to achieve efficient application of the product. These nanoparticle formulas are mainly prepared in an aqueous medium and can be applied by classical strategies such as spraying (of the foliage, stem, or plant roots directly), seed treatment, seedling root dipping (drench), direct soil application (precision farming or glasshouse farming), hydroponics, aeroponics, application in liquid media for tissue culture, in vitro culture, and the most common strategy: through irrigation water.

## 4 Nanoparticle Entry into the Vegetal System: Uptake of Nanoparticles

The potential benefits of nanoparticles depend on the scale of the nanomaterial, such as its size and/or surface to volume ratio. On the nanometric scale, we find colloids measuring 1–1000 nm, nanoparticles measuring 1–100 nm, and ultrafine particles measuring <100 nm (Anjum et al. 2016). On the nanoscale, properties such as plasmon resonance, quantum confinement, size/surface to volume ratio, surface functionalization, photocatalytic and redox activity, visible light photoreactivity, and superparamagnetism apply (León-Silva et al. 2016; Rodrigues et al. 2017). The main properties—size/surface to volume ratio, photocatalytic and redox activity, and visible light photoreactivity—could be useful for agro-food systems (Rodrigues et al. 2017).

### *4.1 Release of Nanoparticles into the Environment*

Nanoparticles can be released into the environment either deliberately or accidentally, and such releases may occur from anthropogenic sources (involving production of engineered nanoparticles and intentional release as waste) or natural sources of biological or physical origin. Both sources can cause nanoparticle release (called dispersion into the environment) into different ecosystems: the air, water (groundwater and, after that, superficial water), or soil (Anjum et al. 2016).

Finally, the receiving bodies of the nanoparticles—the entities that take up the nanoparticles—are microorganisms, plants, and animated beings (including human beings) exposed to single or aggregated nanoparticles, with subsequent bioaccumulation, adverse effects, and/or biodegradation of the nanoparticles (Anjum et al. 2016).

## 4.2 Plant Root Interactions with Nanoparticles

There is only sparse information in the literature concerning the interactions of nanoparticles within plants and their transport phenomena, the potential processes and mechanisms underlying nanoparticle uptake/accumulation, and root-harbored nanoparticle transport to leaves, and the mechanism involved in plant health are not yet understood (Anjum et al. 2016; Rodrigues et al. 2017).

Plant root interactions with nanoparticles occur in two principal ways: aerially and via the roots. The aerial way involves the leaves via use of leaf spray (entering through the stomata), injection, and atmospheric exposure (to natural sources or anthropogenic activities). Otherwise, the roots can be an important entry point for nanoparticles, particularly in plants grown in potentially contaminated soil. Depending on the size, type, chemical composition, and stability of nanoparticles, the processes involved in their entry into plants (and their modulation) can involve adsorption (including differential nanoparticle absorption), uptake, translocation, and accumulation of nanoparticles, mainly (Anjum et al. 2016).

## 4.3 Nanoparticle Absorption at the Root Level

Considering the high specific surface area of the roots and their reactivity with metal nanoparticles, these particles can be easily absorbed via the root interface. Control of the root interaction can be mediated by electrostatic adsorption, mechanical adhesion, and hydrophobic/hydrophilic affinity processes in the roots (Anjum et al. 2016). Zhou et al. (2011) have recommended distinguishing two important states: *adsorption* and *uptake/accumulation* of nanoparticles, as the adsorption of nanoparticles on root surfaces is every so often erroneously regarded as uptake, whereas adequate quantification of both is needed. They reported interesting results showing that copper oxide nanoparticles (CuO-NP) are strongly adsorbed on the plant root surface, partly by mechanical adhesion, and the amount of CuO-NP adsorption is always smaller than the amount of their uptake.

The transport phenomena can be explained with two models. The first one, foliar uptake, occurs via the stomata, providing access through the vascular system to the phloem, with mediated transportation to other parts. The second one, root uptake, occurs via the epidermis, then the endodermis, and then the xylem vessel, with mediated transportation to the aerial parts. For example, zinc oxide nanoparticles (ZnO-NP) can penetrate the root system through the epidermis and cortex, and then pass to the endodermis, followed by the xylem vessel, through the transpiration stream up to the aerial parts (Anjum et al. 2016). Reported examples of accumulation include Ag-NP accumulation in border cells, root cap, columella, and columella initials; and increases in the Cu content and CuO-NP percentage in *Oryza sativa* roots, associated with their mucilage and root exudate mixture.

### *4.4 Cellular Processes*

Cells can regulate the entry of nanoparticles; for example, nanoparticles have to interact with the plant cell wall to enter the cell or undergo intracellular transportation at the cellular level in roots.

In addition, inside a plant, there are two pathways: the *apoplastic* and *symplastic* routes. The apoplast is the space outside the plasma membrane, where materials or nanoparticles can diffuse freely. The apoplastic route facilitates the transport of water and solutes across a tissue or organ. In roots it is interrupted by the Casparian strips (which are formed from suberin and lignin, and are located in the transverse and radial walls of the endodermis, as the final apoplastic barrier between the outside and the vascular tissue, with relative permeability), by air spaces between plant cells, and by the plant cuticle. The apoplast is formed by the continuum of cell walls of adjacent cells, as well as the extracellular spaces, forming a tissue-level compartment comparable to the symplast (the cytoplasm of the cell).

As well, there is cellular uptake, characterized by size-based selection by the plant cell wall, the apoplastic route, and endocytosis or carriers (aquaporins, proteins, or ion channels) (Anjum et al. 2016). The pores of the cell wall restrict the entry of large aggregates or agglomerates of nanoparticles. Nevertheless, smaller clusters or aggregates and individual particles can enter the apoplastic/symplastic routes flowing in there, after diffusion through the pores. Also, interaction of nanoparticles with carrier proteins, ion channels, aquaporins, and organic substances can facilitate their entry into plant cells via the symplastic route. The apoplastic route is regulated by osmotic pressure or capillary forces, as well (Anjum et al. 2016).

## 5 Controlled and Targeted Delivery of Nanoparticles: Materials, Strategies, and Opportunities

Agriculture—particularly agroecosystems—requires efficient delivery of agrochemicals that improve crop yields with adequate release of nutrients, pesticidal agents, and/or bioactive agents (enzymes, DNA, amino acids, and proteins). As we can see, all of these offer opportunities leading to possible benefits such as targeted delivery, programmed triggers for active ingredient release, enhanced adhesion to biological surfaces, light-responsive agrochemical release, and high-performance catalysis, in order to increase the solubility and stability of active ingredients during their storage and application (i.e., nanoemulsions) and to prevent degradation, leaching, or volatilization (i.e., nanoencapsulation) (Rodrigues et al. 2017).

As mentioned before, nanoformulations can be very diverse, and a formulation can include multiple active ingredients and be synthetized and formulated for strategic, time-responsive, and stimulus-responsive release (using carriers with controlled mobility and target selectivity), using some important properties of nanomaterials, such as their high surface to volume ratio and their surface functionalization potential (Rodrigues et al. 2017). Formulations of metallic, oxide metal, or nonmetal nanoparticles of interest can include multiple ingredients such as nutrients (fertilizers), bioactive agents (antimicrobial agents or enzymes), pesticidal agents, growth promoters (phytohormones), and also reducing agents and stabilizers (Lillard et al. 2017; Rodrigues et al. 2017), according to the requirements of the final user.

The main objectives of targeted and controlled release are to make nutrient delivery efficient while at the same time diminishing the dosage and loss of nutrients, bioactive agents, and pesticides, and reducing soil and water pollution, in a way that is conducive to covering the most general features or necessities in the environmental, social, health, and economic areas. In terms of energy and materials, such approaches can decrease synthetic fertilizer or chemical application to crops, while reducing the need for irrigation as well (Rodrigues et al. 2017).

Additives (such as stabilizers) play an important role in nanoformulations, acting as controlled-release carriers, as protective/dispersing/biodelivery agents, or in photocatalysis. Another approach is use of emulsions (nanoemulsions, microemulsions, and nanodispersion) to increase the solubility of active ingredients—for example, Banner MAXX (by Singenta), a commercially available product (Rodrigues et al. 2017).

## *5.1 Advantages and Disadvantages*

Recent studies have described a variety of nanoparticle formulations used to cover many requirements such as formulations for agrochemical delivery. Nanoparticles have several advantages over conventional agrochemicals; it can be said that the disadvantages of conventional agrochemicals are advantages of nanomaterials. One example is size: a smaller size for a nanoparticle (on a nanometer scale) means a greater surface area, increasing the catalysis surface, reactivity, mobility, transportation, affinity, and in some cases even toxicity (León-Silva et al. 2016), in comparison with conventional agrochemicals. Another example is shape: nanoparticles come in several shapes, spherical and rod-shaped ones being the most common, whereas conventional agrochemicals may have several shapes in one formula, i.e., where the shape is not carefully controlled (in the formula, the stabilizer and/or thickeners are responsible for avoiding aggregation or agglomeration of the product).

## 6 Our Research Line as a Team: The Agricultural Biotechnology Group

We are interested in answering some fascinating questions, the first one being whether nanoparticles work as fertilizer, i.e., improve or favor crops. The second question is whether nanoparticles affect plant growth and development, germination, and crop yields, i.e., whether nanoparticles are toxic to plants. A further question is whether nanoparticles affect soil properties and soil microorganisms under different conditions (in incubation chambers, in greenhouses, and/or in the field). Additionally, we aim to study some metal nanoparticles (metal oxides) such as hematite nanoparticles ($\alpha$-$Fe_2O_3$-NP), ZnO-NP, and titanium dioxide nanoparticles ($TiO_2$-NP), which will be tested on *Zea mays* L., *Phaseolus vulgaris* L., and *Helianthus annuus* L.

## 7 Conclusion

We can conclude that there are many opportunities in the research area, including opportunities for innovation or for improving existing technology to create novel products. There are many possibilities for use of different combinations of potential elements for nanoparticle synthesis and their subsequent formulation, as well as broad possibilities for selection of stabilizers, bioactive agents, pesticide agents, reducing agents, and nutrients and/or plant growth–promoting agents. In addition, there is currently only minimal information available regarding the effects of nanoparticles on crops, soil properties, and living organisms, and their close interactions, in order to establish or confirm appropriate mechanisms of plant entry, material balance, and cellular entry, and how processes in plants are affected by the presence of nanoparticles. There is also a need to establish approaches to determine appropriate quantification of the processes of absorption, uptake, translocation, and accumulation of nanoparticles in plant tissues. Finally, there is a need to determine the effects of nanoparticles in order to ensure equilibrium in the most important aspects—environmental, social, health, and economic—through creation of energy, material, and economic balance in order to establish the real benefits of nanoparticles, as well their tangible advantages or disadvantages, in daily life.

**Acknowledgements** We would like to thank the Instituto Politécnico Nacional and CONACYT for their financial support (project number CB-2016-01 287225) and grant-aided support received by F.L.-V. and F.F.-L.

**Competing interests** The authors declare that they have no competing interests.

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# Chapter 4
# Incorporation of Nanoparticles into Plant Nutrients: The Real Benefits

**Edgar Vázquez-Núñez, Martha L. López-Moreno, Guadalupe de la Rosa Álvarez, and Fabián Fernández-Luqueño**

**Abstract** The nanosciences and nanotechnology have been the most novel and attractive fields in recent years; their applications have spread through different and diverse areas, i.e., medicine, chemistry, biology, agriculture, etc. In agriculture the possibilities for application and innovation are enormous, and these applications have resulted in essential improvements in central plant and crop aspects. The incorporation of nanoparticles into nutritional plants has increased the yield of nutrient values and also has played a vital role in developing improved systems for analyzing ecological conditions and increasing the capacity of crops to absorb nutrients or pesticides. This chapter discusses and summarizes some updated evidence regarding the effects of nanoparticles on the yield and quality of crops, and it highlights how nanoscience and nanotechnologies might revolutionize the nutrition of higher plants in the short term.

**Keywords** Crops · Nanoparticles · Nutrients · Field trials · Plant response

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F. López-Valdez, F. Fernández-Luqueño (eds.), *Agricultural Nanobiotechnology*, https://doi.org/10.1007/978-3-319-96719-6_4

## 1 Introduction

Nanosciences and nanotechnologies have been introduced into agricultural systems during the last decade, with the primary goals of increasing the crop yield and improving food quality. These goals can be reached through weed, pest, and disease control, application of slow-release nanofertilizers (NF), coating with genetic and organic or inorganic nanomaterials, nanosensors, etc. (Fernández-Luqueño et al. 2016; Khot et al. 2012). However, there are still some questions and concerns regarding the potential toxic effects of nanodevices (NDs) and nanomaterials (NMs) on environmental and human health (León-Silva et al. 2016). There is not enough published evidence regarding the absorption, uptake, and translocation of nanomaterials into plant cells or tissues, so more research at the field scale and over extended periods of time needs to be carried out expeditiously.

Macronutrients and micronutrients are already being delivered at the nanoscale level under field conditions, at the greenhouse scale, or in indoor agriculture. However, the economic, ecological, and technological benefits of nanoscience and nanotechnology in agriculture have been questioned because they are only emerging technologies; practically all of the physical, chemical, and biological processes involved in the uptake and transport of nanomaterials inside the plant are unknown, so these research areas need to be strengthened.

There are 16 chemical elements required to grow crops. These plant nutrients are well known: carbon, oxygen, hydrogen, nitrogen, potassium, phosphorus, calcium, magnesium, sulfur, iron, manganese, boron, zinc, copper, molybdenum, and chlorine. Additionally, there are seven chemical elements—nickel, selenium, vanadium, sodium, silicon, cobalt, and aluminum—that are known as beneficial elements for plants, i.e., they are not required by all higher plants, but they may increase plant growth and may be essential for some specific crops (Pilon-Smits et al. 2009). However, incorporation of engineered nanoparticles into the list of plant nutrients has not been considered yet, though there have been several attempts to demonstrate that some nanoparticles with specific characteristics can increase the yield and quality of crops. Notwithstanding this, it has been suggested that caution should be applied to use of some nanomaterials because they not only can remain in the soil for extended periods of time but also can be incorporated into plants or fruit, and the potential implications in upper-level trophic communities is unknown (de la Rosa et al. 2017).

Arnold and Stout (1939) defined the essentiality of chemical elements in plants. They stated that chemical elements are essentials for higher plants when each element fulfills three criteria: (1) the plant cannot complete its life cycle without the element; (2) lack of the element (deficiency) creates symptoms, which disappear upon addition of the element (i.e., the element is not replaceable by another element); and (3) the element plays at least one specific biochemical role in the plant. In this sense, the essentiality of nanoparticles, nanomaterials, and nanodevices has not been demonstrated yet, and maybe it never will be. Nanoparticles, nanomaterials, and nanodevices have not been considered as beneficial elements for plants either, but they might be considered as organic or inorganic amendments with specific benefits in some higher plants.

This chapter discusses and summarizes some updated evidence regarding the effects of nanoparticles on the yield and quality of crops, and highlights how nanoscience and nanotechnologies could revolutionize the nutrition of higher plants over a short period.

## 2 Nanodelivery Systems

Plant micronutrients (MiNs) can be incorporated directly into soils in the form of nanopowders and via foliar spraying of nanoemulsions. Figure 4.1 describes the use of nanoparticles in agriculture. Nanofertilizers can be applied as a source of macro- and micronutrients.

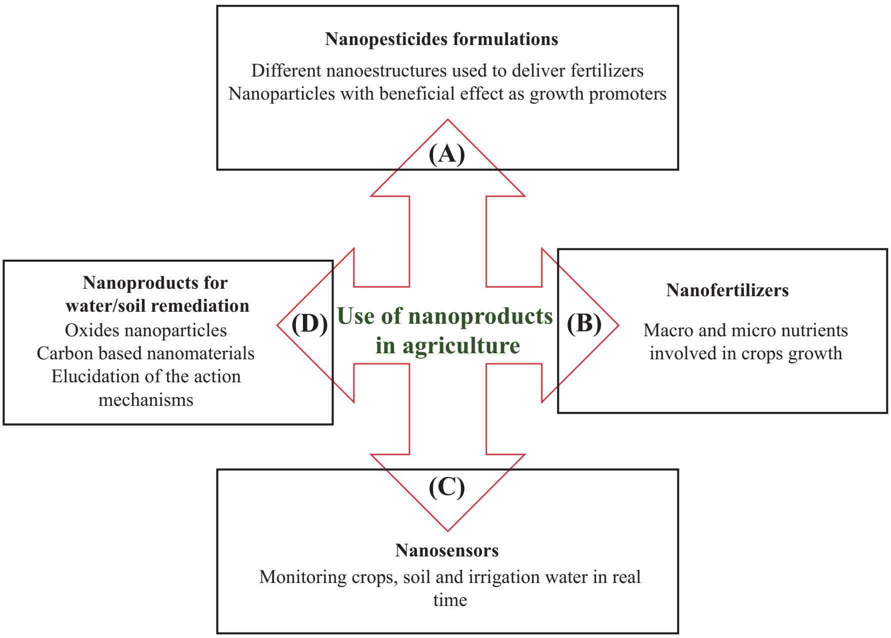


**Fig. 4.1** Use of nanoproducts in agriculture. (**a**) As components in pesticide formulations. (**b**). As components in nanofertilizers. (**c**) Devices (nanosensors) for monitoring crops, water and soil characteristics. (**d**) As part of nanotechnologies for remediating soil and water. (Modified from Iavicoli et al. 2017)

## 2.1 Nanopowders

One of the main disadvantages of bulk fertilizers is the variable solubility of chemical compounds. Bigger particles of some elements such as P are not readily available for plant root uptake mainly because of their interaction with inorganic (mineral) or organic (humic acid and fulvic acid) soil components. This fact entails the need to use more copious amounts of fertilizers to ensure sufficient delivery of the nutrients (Mikhak et al. 2017). Nanofertilizers such as nanozeolite and nanohydroxyapatite, synthesized by Mikhak et al. (2017), were tested on calcareous soils to determine P availability for chamomile plant growth. The authors reported a decrease in soil pH, as well as an increase in the availability of other nutrients such as Ca, due to the slow release of phosphorus. Plants grown in the presence of these nanofertilizers were taller and had more branches than control plants. Moreover, higher P concentrations in roots and shoots and greater flower fresh and dry weights were obtained when a mixture of nanozeolite/nanohydroxyapatite was applied to the soil. The greater active surface area of these nanoparticles allowed more P adsorption in plant roots, and the nanozeolite nanoparticle reactivity increased ion exchange reactions, decreasing soil pH and increasing P solubility. Greater dispersibility of nanoparticles, more P retention in soil pores, and better complexation to form orthophosphates is obtained when nanocalcium sulfate is added to soil (Chen et al. 2016). In addition to zeolite, other mineral compounds have been used not only as fertilizers but also to improve soil conditions. Liu et al. (2017) synthesized a nanomineral amendment from potassium feldspar, using a hydrothermal method. This nanopowder increased the soil pH and immobilized some heavy metals such as Al and Cd in a red soil in South China.

Depending on their solubility and their transport pathways, nanoparticles are sometimes modified and coated with compounds such as chitosan, citric acid, polyacrylic acid, zeolites, montmorillonite, or bentonite nanoclays (Morales-Díaz et al. 2017). One method used to encapsulate nanoparticles for fertilization purposes is the organic material intercalation and gelation process, which provides slow and controlled release of nutrients and improves the efficiency of nanofertilizers. Coating materials decrease the rate of dissolution of the nutrient nanoparticles, which are trapped inside pores in the modified film structures (Duhan et al. 2017; Liu et al. 2006).

Some researchers have designed polymer mixtures with crosslinked three-dimensional structures that allow more absorption and water-holding capacity (Qiao et al. 2016). Two-fold layers increase the release efficiency of nutrients because of the slow release of the compounds that are encapsulated.

## 2.2 Nanoemulsions

Nanoemulsions are the most common medium used to introduce nanoparticles as nanofertilizers. Nanoemulsions are solutions in which two or more nonmiscible compounds/substances are incorporated in such a manner that their drop sizes are in the range of 10–100 nm. Nanoemulsions can be synthesized using several techniques. The phase inversion temperature emulsification technique (PIT) is used to create long-term, more kinetically stable emulsions with smaller drop sizes. This method also offers the advantage of using lesser amounts of surfactants (from 5% to 10%) in comparison with the percentages needed to prepare microemulsions or regular emulsions (more than 10%) (Mashhadi et al. 2016). When nanofertilizers are sprayed on plant leaves, some nanoparticles get through the stomata of the leaves and are transported and become available to the plant (Sabir et al. 2014).

Liu et al. (2006) described a semiemulsification process in which nanometric particles were suspended in a mixture of an organic/inorganic solvent and a surfactant. The authors stated that some physical and chemical characteristics such as the size, shape, constitution, and structure of the nanoparticles were dominated by the proportions of the solvents/surfactants employed. Emulsions with coated nanoparticles have a longer shelf life than bare nanoparticles because ion charges and concentrations play an essential role in suspension stability (Duhan et al. 2017). Chitosan nanoparticles with polymethacrylic acid are being used to deliver NPK as a fertilizer for plant growth. However, the stability of these nanoparticles in a colloidal suspension is greater with the addition of 500 parts per million (ppm) of N (from urea) than with the addition of the same concentration but from a phosphorous source. On the other hand, Ghormade et al. (2011) pointed out that nanocoatings in nanofertilizers increase mineral uptake efficiency because these nanoparticles have greater surface tension than conventional fertilizers in the plant's adsorption/absorption mechanisms. Moreover, plant roots have better adherence to soil particles, and organic matter bonds with the nanoparticle coating surfaces, avoiding leaching of the nutrients (Dasgupta et al. 2015).

## 3 Bulk Nutrients Versus Nanonutrients

In recent years, and because of advances in nanotechnology, it has become more common to include nanomaterials and nanostructures in regular goods that society uses daily. One of the fields that nanotechnology has impacted is agriculture. It is well known that because of their characteristics, (i.e., their small size and enhanced surface area), nanomaterials are reactive with other surrounding materials, with the potential for detrimental effects on the environment and humans (Elsaesser and Howard 2012). In contrast to the first years of such research, positive effects of nanomaterials and their uses in agriculture have been studied, and it has been common to find applications for them in laboratory and field conditions (Chaudhry et al. 2008; Medina-Pérez et al. 2018, in press). There have been reports of numerous benefits to plants from the incorporation of fertilizers into nanostructures that allow slow delivery to crops (Prasad et al. 2014).

Recently, the interest in nutrient element nanomaterials has increased. Conventional fertilizers have low nutrient uptake efficiencies, with losses and also adverse impacts on the environment (Stark and Richards 2008). The use of nanofertilizers appears to be promising, reducing nutrient losses and increasing uptake by plants; however, their impacts on the environment are still unexplored.

Most studies of nanofertilizers have been focused on certain micronutrients such as zinc, copper, manganese, and iron (Mukherjee et al. 2016); however, to increase crop productivity, plants require large quantities of macronutrients (nitrogen, phosphorus, potassium, calcium, sulfur, and magnesium), so more research efforts have focused on these macronutrients than on analyzing and developing micronutrients.

## 4 Macronutrients in Nanofertilizers

Crop production around the world occurs in soil-based systems (Herrick 2000). The amounts of nutrients respond to specific requirements of specific crops and soil conditions, and this aspect makes it challenging to establish doses or nutrient concentrations in field conditions, since nanonutrient and nanofertilizer research has been carried out in artificial media (Dasgupta et al. 2015), in soil liquid extracts (Dimkpa and Bindraban 2017), and under controlled laboratory conditions. Because of the experimental setup of such studies, the time of exposure has been short and the concentrations of nanonutrients in the formulations have been high.

Besides the above considerations, it has been proved that the behavior of nutrients under those conditions is not the same as their behavior in agricultural field conditions; moreover, the different types of soil, the different types of crop, and the physical, chemical, and biological interactions of nanoparticles make it more complicated to establish generalized considerations (Tarafdar et al. 2015).

There have been extensive studies on micronutrients; in contrast, the scientific information available on macronutrients is limited, although these compounds drive global crop productivity.

### *4.1 Nitrogen*

Nitrogen (N) is among the vital elements needed for the survival of living things. Although this element is common and abundant on earth, sometimes its availability is limited for plants, depending on the physical and chemical conditions in the soil (i.e., pH, texture, electrolytic conductivity, etc.). This element is very reactive with other elements or compounds (e.g., ammonia, nitric acid, cyanides, and organic nitrates). Plants cannot take nitrogen from the atmosphere, so they must take this element from the soil in the form of ammonium and nitrate, and from commercial formulations such as urea (Masclaux-Daubresse et al. 2017).

N availability and losses in the soil are important factors in the mass balance. Zhu et al. (2011) evaluated the effects of application of nanourea on runoff losses in paddy fields. The study used urea as a control, and the measured parameters were the nitrogen concentration, nitrogen runoff losses, and grain yield. As was expected, the amount of N in the soil increased rapidly after fertilization in both treatment arms; however, the total nitrogen (TN) decreased more after nanourea treatment than after commercial fertilizer treatment. The authors observed an increment of drainage days with nanourea treatment compared with common urea treatment (12.5–17.3 days versus 11.5–15.9 days). Concerning agronomic productivity, the yield and agronomic efficiency were greater with nanourea treatment. The authors concluded that nanourea treatment increased the grain yield and N agronomic efficiency with less N loss.

Because of its high solubility, urea has been shown to be a nonsustainable delivered nutrient (Azeem et al. 2014). Some studies have focused on synthesis of materials that could provide stability with respect to long delivery times and physical and chemical structures in the soil. Hydroxyapatite has been studied as a component of nanohybrid structures such as nanourea–hydroxyapatite and tested widely in recent years (Kottegoda et al. 2017).

To increase N availability and slow the release of this nutrient in the soil, some experiments were carried out by Kottegoda et al. (2011), where the release of nitrogen in the soil was evaluated; the urea-modified hydroxyapatite nanoparticles were encapsulated, and the nanoparticle was compared with a commercial fertilizer in three different soils in Sri Lanka. The behavior of the nanofertilizer was like a burst at the beginning, and then the release was slow for 60 days; meanwhile, with the commercial fertilizer, sustained release occurred during the first 3 days.

Subbaiya et al. (2012) set up an experiment with the same formulation of nanourea–hydroxyapatite, and it was tested at different concentrations (10%, 20%, and 40%); the formulation was evaluated with green gram [*Vigna radiata* (L.) R. Wilczek] through both seed treatment and direct application to the soil. The seed germination rate was 100% with the urea–hydroxyapatite formulation, while the common urea treatment resulted in a 30% lower germination rate, and the plant height was shorter with the regular urea treatment. Application of urea–hydroxyapatite to the soil enhanced the utilization of the nitrogen source, reflected in better plant yield.

Some comparative studies were performed by Huang et al. (2015), in which conventional urea was compared with nanourea in rice crops. Increments in the accumulation of the element in the dry matter of the plant (leaves) and in the tiller were observed after nanourea treatment compared with conventional commercial urea. An important result of the same study was that the weight of grain harvested was higher in plants treated with nanourea; in general, it was possible to increase the agronomic efficiency by 44.5% and grain yield by 10%.

In 2017, Kottegoda et al. (2017) reported slow release of nitrogen in nanohybrid urea–hydroxyapatite structures. The primary aims of this work were to demonstrate sustained delivery of N and environmental friendly synthesis of the nanomaterials. The nanostructure was characterized, and the delivery of the N component was tested. It was confirmed that the molecule could be used as a platform of about 40% w/w of N and could maintain the slow delivery of this component.

## 4.2 Phosphorus

A critical characteristic of phosphorus (P) is its low availability due to its slow diffusion and high fixation in soils (Shen et al. 2011). Phosphorus also interacts in a synergic way with more than one nutrient in the soil, and its interaction depends on physical and chemical parameters in the soil—for example, the calcium content in soil; it has been demonstrated that calcareous soils facilitate the uptake of P in plants (Richardson 2001). Among the nutrients that interact with P fertilizers are Zn, Fe, Cu, Mn, Mo, and B (Murphy et al. 1981). However, the amount of P added to cultivars can paradoxically have a negative effect on plants; for instance, a large amount of P can induce Zn, Fe, Cu, and Mn uptake deficiencies (Murphy et al. 1981; Verma and Minhas 1987).

It is important to point out that commercial fertilizers have been designed and manufactured to include more than one nutrient (e.g., NPK), so it is complicated to measure the individual effect of only one component of them.

Like N fertilizers, fertilizers based on P are essential for agriculture. Most P fertilizers are applied as soluble phosphate salts (Nelson and Janke 2007). An excess of P in the dose applied to soils to provide sufficient amounts of nutrients can pose a risk of adverse environmental effects (eutrophication).

As an economical and environmentally friendly alternative, synthesis of apatite nanoparticles has recently emerged, and it is feasible for them to supply sufficient P to crops. Liu and Lal (2014) carried out an experimental procedure under greenhouse conditions, where soybean [*Glycine max* (L.) Merrill] was fertilized with synthetic apatite nanoparticles; after the experiment, it was observed that the growth rate and seed yield were increased significantly (by 32.6% and 20.4%, respectively) with apatite treatment compared with regular P fertilizer [$Ca(H_2PO_4)_2$]. The aerial and root biomass were measured and were found to be increased by 18.2% and 42.1% with apatite treatment. This experiment showed the potential use of synthetic apatite as a source of P that can agronomically enhance the yield of crops and reduce the risk of water eutrophication.

Some liquid formulations have been developed; for example, Sharonova et al. (2015) manufactured a nanostructured water–phosphorite suspension, and it was tested on morphological characteristics in seeds of wheat, rye, pea, barley, corn, buckwheat, tomato, small radish, and cucumber; the seed tests were carried out under laboratory conditions. The tests were grouped into a control treatment and phosphorite treatments at different concentrations (0.25, 0.50, 0.75, 1.25, 5, and 10 kg $ton^{-1}$). Mutagenic activity was evaluated as well by using a SOS-LUX test. In this experiment, average increments from 8.3% to 3.5-fold in plant morphometric indexes, fresh yield increases from 2.4% to 2.2-fold, and fruit yield increases from 14.5% to 24.1% were observed.

## 4.3 Potassium

Through its well-known role in plant metabolism and its availability in soils, potassium (K) contributes to stem and root growth and the synthesis of proteins (Mandal et al. 2007; Behera and Shukla 2015). Potassium is considered second to N in terms of the plant's requirements for adequate growth. In soil, potassium can be classified according to its availability to plants—i.e., unavailable K, fixed K, exchangeable K, and soil solution K; the latter is available and is quickly consumed by plants. Among the factors that can affect K uptake are the oxygen level, soil moisture, soil tilling, and soil temperature (Juan et al. 2011).

Currently it is possible to find patented commercial products that have shown positive effects on crop productivity and nutrient release under field conditions—for example, nanoleucite and potassium aluminum silicates [$K(AlSi_2O_6)$]; besides showing sustained release of nutrients, they are eco-friendly materials. Among their properties are an excellent cation exchange capacity (CEC); also, their nutrient-holding capacity can be increased by salt occlusion (Farrukh and Naseem 2014).

Rostami Ajirloo et al. (2015) measured the effects of application of biofertilizers (humic acids and nitrogen fertilizer) and nanofertilizers (K fertilizer) on tomato plants (*Lycopersicon esculentum* Mill.) during a complete growing season (2013–2014). Application of humic acid and nitrogen fertilizer resulted in significant differences in all tomato traits, but the effect of humic acid on fruit length was not significant. Higher plant height and greater stem diameter were obtained when the K fertilizer was added at a ratio of 300 kg $ha^{-1}$. The best yield and yield components were observed with conjugated application of both K and N fertilizer.

As a new strategy to facilitate the release and uptake of K by plants, some strategies based on nanotechnology have been developed. Rajonee et al. (2017) evaluated the efficacy of incorporation into plants of P–K nanoparticles carried by zeolite. The experiment was carried out in in vitro conditions for 30 days and cultivated *Ipomoea aquatica* Forssk. The results showed higher content of K and P in plants fertilized with the nanofertilizer than in those managed conventionally. The authors suggested the use of different carriers to elucidate the release rate and its effect on the fertilization effect.

Mala et al. (2017) evaluated not only the release of nutrients by nanostructures of nanophosphate and potash fertilizer but also the soil fertility, yield, and nutritional profile of *V. radiata* (L.) Wilczek; the fertilizer was prepared as a nanoemulsion by blending of the components with neem cake and plant growth–promoting rhizobacteria (PGPR); this formulation is the only one patented and tested so far. The stimulation of germination and biochemical characteristics (specific activity of enzymes, carbohydrates, protein, photosynthetic pigments, number of root nodules, and microbial population) of *V. radiata* (L.) Wilczek also confirmed the positive yield attributes after application of the nanoemulsion compared with the individual treatment components (i.e., neem cake, chemical fertilizer, PGPR, and the nanoemulsion).

### 4.4 Calcium

Calcium (Ca) is an essential plant nutrient, which plays a structural role in the cell wall and regulates plant growth (Helper 2005). As a macronutrient, calcium also acts in a part of the cell wall and gives strong structural rigidity by forming cross-links within the pectin polysaccharide matrix. This nutrient enhances resistance to diseases (bacterial and viral) in plants (Usten et al. 2006).

Application of calcium at the nanoscale level could enhance properties in a biological system, including its mobility, and could possibly have positive effects on the development and growth of the plant. There have been some studies on the effects of nano-Ca on plants and their implications. Liu and Lal (2014) developed Ca and P hydroxyapatite nanoparticles, and they found that application of these nanoparticles to soybean [*G. max* (L.) Merrill] increased the seed yield and growth rate by 20% and 33%, respectively, in comparison with conventional phosphorus. Several reports have shown that soybean plants incorporate apatite as a useful P nutrient but, in addition, this nanoparticle may also supply Ca (Liu and Lal 2017). Several authors have reported the benefits of nano-Ca compared with CaO and $CaCO_3$. Deepa et al. (2015) reported increased Ca accumulation and promotion of root development in peanut treated with 10–1000 mg $L^{-1}$ of nano-CaO in comparison with bulk CaO and $CaNO_3$; furthermore, they confirmed greater entry of nano-CaO into leaves and stems through the phloem in comparison with bulk calcium sprayed on groundnut. Yugandhar and Savithramma (2013) compared nano-$CaCO_3$ with $CaCl_2$ at 10 mM in seed treatment of *Vigna mungo* (L.) Hepper and found that it improved root and shoot growth and fresh biomass production in comparison with the conventional Ca source. Liu et al. (2005) reported that application of nano-Ca and humic acids at the same time resulted in maximum seedling growth in peanut (a 30% increase in comparison with the control). According to these authors, it was clear that the plant roots could absorb nano-Ca as a Ca source and transport Ca from the roots to the shoots, and the total percentages of Ca content in seedling stems and roots were 3.04% and 1.58%, respectively, compared with 0.58% and 0.43%, respectively with no-Ca control treatment. Given the above, it is clear that Ca-NP have an enormous potential as fertilizers in the field.

### 4.5 Magnesium

As a macronutrient, magnesium (Mg) plays an essential role in plants. It is among the seven mineral elements that are lacking in human diets (White and Broadley 2009). This element is related to plant enzymatic activities: ATPases, RNA polymerases, etc. Changes in the content of magnesium could alter plant metabolism in different ways, i.e., an excess of Mg may alter the photosynthetic system, but its deficiency reduces the photosynthesis rate (Delfani et al. 2014). Saad and El-Kholy (2000) reported that foliar application of this macronutrient increased the seed yield and crude protein content in plants. Other studies have shown that in comparison with conventional Mg, as a consequence of crop productivity the use of nano-Mg could provide information about application of nano-Mg as a pesticide because it improved protection of tomato against wilt infestation at a nano-MgO rate of 0.1–1.0% (Dimkpa and Bindraban 2017; Imada et al. 2016). Delfani et al. (2014) reported that foliar application of nano-Mg (0.5 mg $L^{-1}$), in comparison with MgO, promoted photosynthesis, growth, and yield in cowpea. These authors developed magnesium nanoparticles as an alternative form of Mg, and they observed increments in seed weight, stem Mg content, plasma membrane stability, and chlorophyll content at 2.5 ppm. Similarly, they observed the highest yield of black-eyed pea [*Vigna unguiculata* (L.) Walp.] with application of 0.5 g $L^{-1}$ of regular Fe salt and 0.5 g $L^{-1}$ of Mg-NP; this experiment showed a 13.4% yield increase in comparison with the control treatment. Therefore, these authors suggested that an increase in photosynthetic work occurred when they used foliar application of these nutrients, and they observed that Mg-NP improved the uptake of Mg in plant stems and leaves.

## 5 Micronutrients in Nanofertilizers and Their Impacts on Crop Nutritional Quality

Successful application of nanofertilizers to crops requires optimization of several parameters related to the uptake, transport pathways, accumulation, interactions, and fate of nanofertilizers in soils and water. Optimization of crop growth conditions and risk assessments is needed to ensure the safety and security of crops and fruit. Modeling of these and other parameters is difficult because there is only sparse information available on the immediate, medium, and long-term effects of nanofertilizers on different crops, and on the risks associated with bioaccumulation of these nanomaterials in the environment and in food chains (Morales-Díaz et al. 2017). New regulations regarding agricultural systems for food production in the USA and public perception of the safety of nanofertilizers in crop cultivation are some challenges that need to be overcome. Figure 4.2 shows the main application routes for nanofertilizers and the relationship between nutrient release and environmental conditions.

Micronutrients have been incorporated into nanofertilizers to potentiate the effects of fertilizers on crops by increasing the availability of nutrients. The low release of agrochemicals allows us to obtain higher crop yields and avoids fertilizer leaching. Micronutrients can be absorbed, translocated, and accumulated more easily in the form of nanoparticles than in the form of microparticles or bulk particles. Micronutrients play an essential role in growth, and nutrient uptake could be greater through plant leaves (Duhan et al. 2017).

The main means of nanoparticle application have been described. The time of exposure and application must be considered critical, considering soil parameters and environmental conditions; the presence of nutrients in soils is crucial in the design of strategies in field trials.

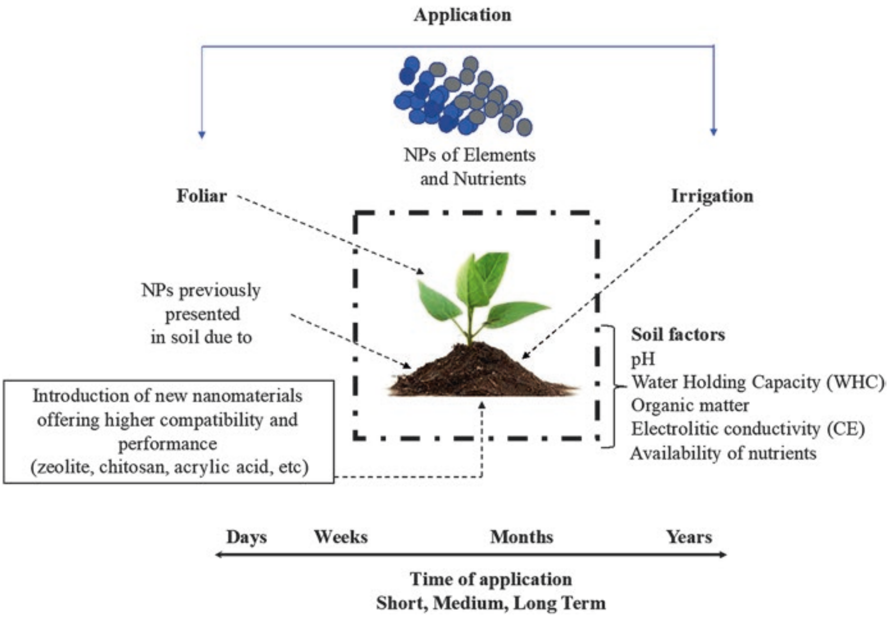


**Fig. 4.2** Use of nanofertilizers in crops. NP: nanoparticles

## *5.1 Iron Nanoparticles*

Iron nanoparticles (Fe-NP) have been used as a source of Fe for plant nutrition. It is well known that Fe is necessary for the synthesis of chlorophyll in plants. A deficiency of this mineral causes leaf chlorosis. There have been several reports on the effects of Fe-NP on crops. Coated and bare $Fe_3O_4$-NP have been evaluated in *Triticum aestivum* L. (Iannone et al. 2017). The germination of seeds, chlorophyll content, and shoot length were not affected by exposure to 20 mg $L^{-1}$ of $Fe_3O_4$-NP, but the root biomass increased by approximately 20% in comparison with control plants. The Fe content in the roots was five times higher than in control plants, but Fe was not translocated to the aerial parts of the plants. Activity from oxidative stress enzymes [catalase (CAT), superoxide dismutase (SOD), ascorbate peroxidase (APOX), and glutathione peroxidase (GPOX)] was probably increased because of the high Fe concentration in the plant roots, but there was no evidence of cell damage or lipid peroxidation inside the plant tissues. The authors stated that the increase in antioxidant enzyme activity may have prevented oxidative damage to the plants. Suresh et al. (2016) described the effect of $Fe_3O_4$-NP on *Arachis hypogaea* L. plant leaves. These researchers found that presoaking of peanut seeds with 500 ppm of $Fe_3O_4$-NP increased the protein and carbohydrate content in the peanut leaves. Higher concentrations (more than 500 ppm) of $Fe_3O_4$-NP were shown to have negative effects on the growth and development of peanut plants. Rui et al. (2016) reported significant increases in root and shoot biomass, as well as in the branching of *A. hypogaea* L. plants. The chlorophyll content and antioxidant enzyme levels were also higher than in control plants. These researchers compared the effects of bare $Fe_3O_4$-NP and ethylenediaminetetraacetic acid (EDTA)–chelated $Fe_3O_4$-NP, and the effects of bare $Fe_3O_4$-NP were more beneficial for plants. In addition, the researchers pointed out that $Fe_3O_4$-NP modified synthesis of the phytohormones gibberellin (GA), zeatin riboside (ZR), dihydrozeatin (DHZR), indolepropionic acid (IPA), and abscisic acid (ABA). Lower concentrations of ABA were found in plants treated with $Fe_3O_4$-NP, while the concentrations of the other phytohormones (which promote growth and development of plants) were increased. The authors suggested that $Fe_3O_4$-NP could be a potential fertilizer because of their ability to adhere to soil particles and to prevent the mobility of other nutrients in sandy soils.

Li et al. (2016) reported that -$Fe_2O_3$-NP promoted germination of corn seeds and increased root growth by about 10%. Nanoparticles were found to accumulate in the vacuoles, but there was no translocation of nanoparticles to the shoots. Wang et al. (2016) found that -$Fe_2O_3$-NP promoted *Citrullus lanatus* (Thunb.) Mansf. growth and chlorophyll content in a long-term study. Plants were exposed in a range of concentrations (0–100 mg $L^{-1}$) without showing toxicity symptoms.

### *5.2 Zinc*

As a micronutrient, zinc (Zn) plays an important role in tryptophan synthesis and photosynthetic activity, and it is a crucial cofactor for the activity of several enzymes (dehydrogenases, aldolases, isomerases, etc.). A long-term study performed by Davarpanah et al. (2016) described the effect of foliar application of Zn-NP on *Punica granatum* L. cv. Ardestani plants. Treatments were applied using Zn and a mixture of zinc–boron nanoparticles (Zn-B-NP) at 60 and 120 mg $L^{-1}$. Trees were sprayed with different treatments once per season, and fruit were harvested after the first and second seasons. The results showed that the fruit yield was significantly higher (63–66 fruit per tree) with application of the Zn-B-NP mixture and higher concentrations; the control tree yield was 51 fruit per tree. Both elements (Zn and B) play roles in pollen germination, tube elongation, and flowering. Larger fruit were also observed with these treatments. The juice pH, total soluble solids (TSS), titratable acidity (TA), and maturity index (TSS to TA ratio) were also measured. The TSS value was increased by 4.4–7.6% and the TSS/TAA ratio values were 20.6–46.1% higher than those in control fruit. The phenolic content of the fruit did not differ significantly between the treatments. On the other hand, the total sugar and anthocyanin values were increased and the fruit quality was improved.

Bradfield et al. (2017) grew *Ipomoea batatas* L. Poir. in soils amended with Zn-NP at concentrations of 100, 500, or 1000 mg $kg^{-1}$ of dry weight (DW). The yields obtained with the control, 100, and 500 mg $kg^{-1}$ DW Zn-NP treatments did not show significant differences. The tuber biomass, number of tubers, mass per tuber, tuber water content, and tuber diameter were evaluated. However, the 1000 mg kg$^{-1}$ DW treatment resulted in a decrease in the number of tubers harvested, lower tuber biomass, and smaller tuber diameter. Although the concentrations of treatments applied to soil are higher than those reported with foliar treatment, it is clear that the availability of Zn-NP is different when they are applied to the soil. A hormesis effect on the Zn content in unpeeled and peeled tubers was observed, where the Zn concentration was higher in tubers exposed to 100 mg kg$^{-1}$ DW of Zn-NP than in those exposed to 500 or 1000 mg kg$^{-1}$ DW of Zn-NP.

Zn-NP synthesized from flower extracts were tested for their impact on *Solanum lycopersicum* L. plants. Singh et al. (2016) evaluated the effects on tomato seed germination of a common Zn supplement ($ZnSO_4$) and Zn-NP in a concentration range of 1.2–6.1 mM. The effects observed with nanoparticles and the common salt $ZnSO_4$ were concentration dependent, and lower concentrations of Zn-NP increased germination and the seedling vigor index after 8 days. The authors stated that the nanoparticles could penetrate the seed coat better than the Zn ions, promoting a positive response in embryo development. The protein and sugar content were also increased in tomato plants; however, long-term studies need to be done to determine if the quality of the fruit is better than that of tomatoes grown with $ZnSO_4$. On the other hand, Yoon et al. (2014) reported contrary effects on *G. max* (L.) Merrill growth when these plants were grown in soil containing 50 or 500 mg kg$^{-1}$ of ZnO-NP. The plants were cultivated for 8 weeks; those treated with 500 mg kg$^{-1}$ of ZnO-NP were harvested on day 57 after treatment, and control plants were harvested on day 65. The authors stated that the highest concentration of nanoparticles inhibited soybean stem growth. The control plants and those grown in 50 mg kg$^{-1}$ and 500 mg kg $^{-1}$ of ZnO-NP developed trifoliate leaves, blooms, and pods after 14 days; however for plants exposed to 500 mg kg$^{-1}$ of ZnO-NP it was not possible to observe any signal of reproductive stage, showing stoppage in the developing process. The soybean roots were significantly affected by the ZnO-NP. In comparison with control plants, the root length in plants exposed to 500 mg kg$^{-1}$ of ZnO-NP was decreased by 90%, and accumulation of Zn in the roots, stems, and leaves was also greater with this treatment.

## 5.3 Manganese Nanoparticles

Manganese (Mn) is also a micronutrient, which is essential to complete oxidation–reduction reactions in the photosynthetic process. It is the second most essential micronutrient for plant growth. This element participates in electron transfer and activates more than 35 enzymes (Mousavi et al. 2011). Studies on the use of Mn-NP in agriculture are scarce, and there is not enough information about the effects of these nanoparticles on crops. Pradhan et al. (2013) compared the effects of Mn-NP and $MnSO_4$ salt on *V. radiata* (L.) R. Wilczek plants in a concentration range of 0.05–1.0 mg L$^{-1}$ and found that the root and stem lengths of the plants were increased with the nanoparticles in comparison with the Mn salt. Transmission electron microscopy (TEM) studies showed accumulation and deposition of Mn-NP on the chloroplast surface. It seems that nanoparticles at a dose of 1 mg $L^{-1}$ are more beneficial to plants than Mn salt because nanoparticles favor electron transport and increase the activity of the CP43 protein from photosystem II.

Liu et al. (2016) reported the effects of Mn-NP on *Lactuca sativa* L. plants. Mn-NP promoted the growth of lettuce plants at concentrations less than 50 ppm. $MnSO_4$ salt was selected for comparison with the effects of the nanoparticles. Germination of seeds was not affected by Mn-NP, seedling growth was enhanced, and no signs of toxicity were found. The authors suggested use of Mn-NP to improve agronomic production of crops.

## 5.4 Copper Nanoparticles

Copper (Cu) is a very important micronutrient, which regulates the rate of many biochemical reactions in plants. Like Zn, Cu is an essential element for enzymatic activity. It also participates in chlorophyll synthesis, as well as in the production of seeds. Cu nanoparticles have been studied for their higher availability in media in comparison with regular salts. Bradfield et al. (2017) exposed *I. batatas* L. Poir. plants to 100, 500, and 1000 ppm of Cu-NP. Tubers were allowed to grow for 130 days, and the results showed decreases in the tuber biomass, number of tubers, tuber water content, and tuber diameter and length when plants were exposed to 1000 ppm of Cu-NP. Moreover, Cu content in tubers was higher with all nanoparticle treatments in comparison with control plants and plants exposed to Cu from salts. However, there was less translocation of Cu (from the tubers to the high parts of plants) than in the controls. The authors stated that the solubility and stability of Cu-NP played an essential role in the availability of Cu for plant uptake. Regardless of the chemical form of Cu applied, the results showed that there are beneficial effects of applying this micronutrient in the form of nanoparticles at concentrations up to 500 ppm.

Zhao et al. (2017) studied the nutritional quality of *Cucumis sativus* L. with Cu-NP exposure. The authors reported valuable information about metabolite concentrations in fruit after exposure of plants to 200, 400, and 800 ppm of Cu-NP. Fruit were harvested at fruit maturity (68 days). The sugar and carbohydrate content and the concentrations of amino acids, fatty acids, myo-inositol, nicotinic acid, and lignoceric acid were evaluated. The values were higher than those in control fruit, and the metabolite content was dose dependent, increasing as Cu-NP concentrations increased in the soil. The authors suggested that Cu-NP change the nutritional quality of fruit and can be used as an alternative to improve fruit quality in crops while minimizing the amount of fertilizers applied. Cu-NP have been studied not only for their use as fertilizer but also as an alternative to pesticides. Several such studies have been reported in the literature; however, that topic is beyond the scope of this chapter.

### 5.5 Molybdenum Nanoparticles

The role of molybdenum (Mo) in plants is to fix nitrogen through bacteria found in plant roots. Mo is also required for the synthesis of an enzyme called nitrate reductase, which reduces nitrate to nitrite. This process is crucial for protein synthesis in plants (Singh et al. 2010). Mo-NP have been studied as a fertilizer for crops. Adhikari et al. (2013) performed a study in *Oryza sativa* L. plants. Mo-NP were applied in a concentration range from 0 to 600 ppm (0, 1, 5, 10, 15, 20, 100, 200, 400, 600 ppm). Rice seeds were placed in Mo-NP suspensions for germination, and all treatments resulted in 90–95% germination. The authors suggested that Mo-NP did not cross the seed coat and never reached the embryo. However, after germination, the seedlings were in contact with Mo-NP, and the root tips were affected by the 50-ppm treatment. The only treatment of 5 ppm increased the root and shoot biomass of rice plants. To the best of our knowledge, there have been no short- or long-term studies reported on the use of Mo-NP as a fertilizer. Taran et al. (2014, 2016) reported use of these nanoparticles, but they studied their effects on microbial composition and the oxidative stress response of *Cicer arietinum* L. to Mo-NP and a microbial preparation.

## 6 Plant responses to Other Nanoparticles Used as Potential Nanofertilizers in Crops

In addition to micronutrient nanofertilizers, another type of nanoparticle has been investigated and reported in the literature for its possible role in agriculture. $CeO_2$-NP have been studied and found to promote plant growth and development, nutrient uptake, and fruit yield in some plants.

Barrios et al. (2016) reported the impacts of bare and coated $CeO_2$-NP on *S. lycopersicum* L. plants at different concentrations (0–500 mg $kg^{-1}$). The fruit were collected after 210 days. Plants cultivated in soils amended with bare and coated $CeO_2$-NP at 500 mg $kg^{-1}$ showed 9% and 13% increases in stem elongation, respectively, in comparison with control plants. The coated nanoparticles did not have any significant effects on chlorophyll content or nutrient uptake. However, treatments with coated $CeO_2$-NP increased the content of Al (a nonessential element) in the roots and leaves significantly. The fruit yield was not affected by the presence of bare or coated $CeO_2$-NP.

The effects of $CeO_2$-NP have also been studied in second-generation *T. aestivum* L. plants (Rico et al. 2017). The authors reported that Ce accumulation in plant tissues was greater in the roots and shoots of the second generation, but no Ce was present in the grains. These authors also found that the first generation of plants treated with $CeO_2$-NP at 125 and 500 mg $kg^{-1}$ had decreased uptake of Fe (49% and 58%, respectively) and Mn (34% and 41%, respectively) in their roots in comparison with control plants. A concentration of 125 mg $kg^{-1}$ of $CeO_2$-NP in the second generation decreased the nutritional (macronutrient) quality in the grains. Plant height was increased in the second generation. However, there was no correlation with the $CeO_2$-NP concentration in the soil. This was a long-term study, but it should be noted that environmental conditions, as well as the properties of the soil matrix, play decisive roles in the availability, uptake, and translocation of nanoparticles inside plant tissues.

Antisari et al. (2015) reported significant changes in nutritional quality in tomato plants exposed to 20 mg $kg^{-1}$ of $CeO_2$-NP. Uptake of macronutrients (Ca, K, Mg, and P) in roots was increased, but there was no translocation of these elements to leaf tissues. Also, the nutrient content in the fruit was lower than that in fruit from control plants. These authors also observed that the macronutrient content in fruit from plants exposed to nanoparticles of Ag, Co, Ni, $SnO_2$, and $TiO_2$ (20 mg $kg^{-1}$) was lower than that in control fruit. The authors related the translocation of nutrients to the capacity of plants to absorb water and nutrients through their roots, which is greater in plant species with high water transpiration. The authors also stated that there was competition between nanoparticles and nutritional elements taken up by plant tissues; some of them were stored or accumulated in vacuoles and other plant compartments rather than being transported into the fruit.

Carbon-based nanomaterials (CBNMs) have been reported to promote germination and seedling growth in several plant species. Ratnikova et al. (2015) described the effects of time and different concentrations of CBNMs and ultrasonic irradiation on *S. lycopersicum* L. plants. Seed germination and seedling growth were increased in comparison with control plants. The authors stated that oscillations from ultrasonic irradiation disrupted cell membranes in seeds, removing parts of the seed coat, and CBNMs penetrated the embryo. Seedling weight and length were also increased in *S. lycopersicum* L. plants after exposure to CBNMs. Kole et al. (2013) evaluated the effects of carbon-based nanoparticles (fullerol) on *Momordica charantia* L. seeds. Five concentrations in a range of approximately 1–50 nM were tested. Fullerol nanoparticles were found in the roots, stems, leaves, and fruit, and their distribution was observed by Fourier-transform infrared spectroscopy (FT-IR) analysis. The fruit yield, water content, lycopene content, charantin content, and cucurbitacin B content were increased with all treatments. More research is needed to determine if another type of nanoparticle can be used to promote crop growth and nutritional quality.

## 7 Scale Approaches for Nanoparticle Uptake by Plants: Short-Term and Long-Term Effects

To compare the short- and long-term effects of nanofertilizer use on different plant parameters, definitions of these models should be provided. Unfortunately, to the best of our knowledge, no consensus exists to define these concepts. Different authors have reported data where long-term and short-term expressions were presented; however, the definitions were not precise or even not specified. This may have led to subjective interpretations, which contradict scientific objectivity. For example, Dobermann et al. (2005) reported the results of annual and cumulative yield responses of cotton, soybean, rice, and corn to application of different nutrients. According to their publication, "short-term" related to annual observations whereas "long-term" implied cumulative responses after two or more years of treatment. Earlier experiments provided a different context.

The first long-term experiment was initiated in 1843 at Barnfield, with the aim of performing yearly measurements of N, P, K, Na, and Mg content in wheat, as well as the yield at different times. The plants were supplied with different types of manure (Rothamsted Research 2006). Similar experiments were initiated later, and some of them are still running: barley at Hoosfield (1852); hay at Park Grass (1856); wheat at Broadbalk (1844); garden clover since 1954; and wheat and fallow since 1851 (Rothamsted Research 2006). More recently, Ferguson et al. (2005) reported that in a long-term experiment, corn yield was measured on a yearly basis after different treatments of beef feedlot manure were applied at different rates.

According to Knapp et al. (2012), short-term experiments are set up in conditions where data on the effects are gathered at the time of plant manipulation. On the other hand, if the data enable interpretation of the system's response in complete cycles, it is said that a long-term experiment has been set up. In 1980, the US National Science Foundation (NSF) created the Long Term Ecological Research Network (LTERN) with the aim of investigating environmental topics that cover extended geographical areas and last for decades (LTER 2017). With this in mind, and considering resource limitations, Knapp et al. (2012) suggested that a long-term experiment is one that exceeds 6 years, which reconciles the need to obtain data on the basis of the temporal dynamics of the system and resource use efficiency.

## 8 Long-Term and Short-Term Aspects of Acquisition, Transport, and Utilization of Mineral Nutrients in Plants

Plant nutrition is based on different processes that are fundamentally similar in all living organisms. In the case of mineral elements, these are taken up by plants mostly from the soil or water in which they set up their roots. The mechanism by which plants take up, transport, store, and use mineral nutrients has been a subject of in-depth research in recent decades. We now know that different molecules are responsible for these mechanisms. Other factors, including solubility and elemental speciation, are also determinants.

In the case of nanofertilizers, the processes should be similar to the additional component of the nanofertilizer interaction with the environment where the plant and the nanomaterial are present. In this context, solubility and bioavailability determine the way in which nanofertilizers will interact and, in the process, they affect plant development. Also, short- and long-term exposure of plants to the nanofertilizers will be influenced by these factors.

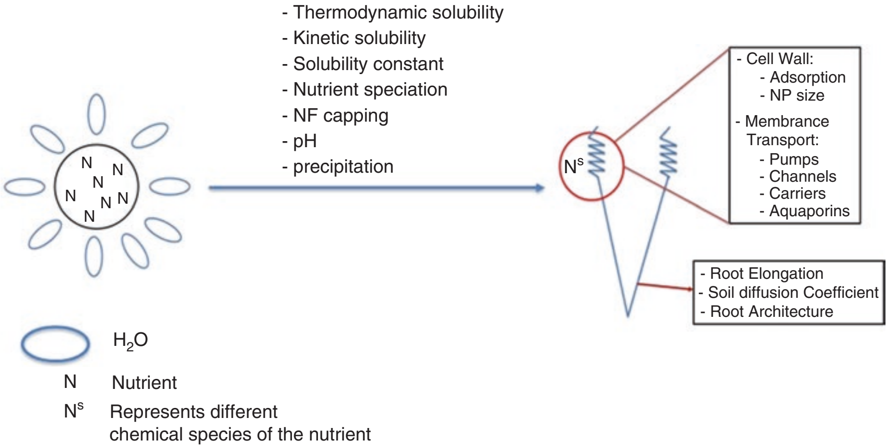


**Fig. 4.3** Different parameters influence nanofertilizer (NF) solubility and nutrient bioavailability, which in turn affect nutrient transport, absorption, and translocation in the root system. *NP* nanoparticle

Figure 4.3 shows a graphic explanation of selected parameters that may influence the extent to which nutrients present in the nanofertilizers will be delivered, solubilized, absorbed, and eventually transported into the root system. When the nanofertilizer is placed in contact with the medium, solubility factors determine the effective concentrations of the nutrients in the short-term context. Eventually, when the nutrient reaches the root, these same parameters, in addition to size and speciation, influence its interaction with membrane transporters and components of the cell wall. It is likely that depending on the physicochemical characteristics of nanofertilizers, phenomena such as channel clogging, complexation, and reaction with other elements of the system dictate the fate of the nutrient.

## 9 Short-Term Experiments to Study the Effects of Nanofertilizers in Plants

On the basis of the definitions provided above, it seems that no long-term experiments to determine the effects of nanofertilizers on plants have been conducted. Herein we present selected data obtained in short-term experiments. By comparing the data, it may be possible that some conclusions can be reached if extrapolation is applied with care. In any case, formal long-term experiments are required because in some cases, short-term data are not consistent with long-term data (Sainju et al. 2006).

Hassani et al. (2015) compared the effects of supplying peppermint (*Mentha piperita* L.) with macro- and micronutrients in the forms of either chemical fertilizer or nanofertilizer. The yield was determined after 7 days of treatment application by analysis of the dry and wet weights of the stems, the leaves, and the complete plant, as well as the number of branches, leaves of branches, and nodes. In general, the results demonstrated positive effects of Zn, Fe, and K nanofertilizers on peppermint growth.

Rui et al. (2016) compared the effects of $Fe_2O_3$-NP and complexed bulk Fe fertilizer on the development and growth of peanut [*A. hypogaea* (L.)]. They determined that $Fe_2O_3$-NP were adsorbed to the soil, unlike the chelated Fe (Fe-EDTA), which was leached. Measurements were performed after 38 days of treatment. No significant differences were observed in comparisons of the dry weight, number of branches, shoot height, and root length of plants treated with either $Fe_2O_3$-NP or Fe-EDTA. Still, the use of $Fe_2O_3$-NP may be preferable, as it avoids Fe leaching. Chlorophyll production was not affected by the different treatments, as the values were between 30 and 35 Soil Plant Analysis Development (SPAD) units, with no significant differences. Also, POD, SOD, CAT, and MDA activity were measured. The results indicated that production of stress enzymes was not affected in the shoots. In the roots, no trend was observed. Unfortunately, no data on the bioavailability of Fe in the treatments was provided by the authors. Thus, the comparisons performed in this study might not have been valid.

Mikhak et al. (2017) performed experiments with chamomile at a research field in Esfahan, Iran, in 2015, using soil treatments containing nanohydroxyapatite (nHA) 25–50 nm as a source of phosphorus. The experiments were continued from seeding to full plant maturity, which took 187 days. The data obtained indicated that nHA, in combination with ammonium sulfate and rock phosphate, significantly increased plant height, branch and subbranch numbers, chamanzulene content, flower numbers, root and shoot P content, flower fresh and dry weight, and shoot fresh and dry weight.

Moghaddasi et al. (2013) produced Zn nanofertilizer from waste tire rubber with the aim of determining the performance of cucumber when it was supplied with either the nanofertilizer or $ZnSO_4$ in a hydroponic system. These researchers compared root and shoot dry weight, as well as fruit weight (fruit yield), with the different treatments. Biomass production was evaluated after 28 days of treatment and fruit yield 32 days after seeding. The data suggested that the Zn-NP from waste tire rubber significantly improved biomass production and fruit yield in comparison with $ZnSO_4$ treatment.

Foliar application of Zn chelate and B chelate nanofertilizers (50 nm) in different concentrations was performed in pomegranate [*P. granatum* (L.) cv. Ardestani]. In this research, fruit yield (numbers) and quality (length, fruit and calyx diameters, peel thickness, and nutrient concentrations in leaves, among other parameters) were determined (Davarpanah et al. 2016). Zn chelate nanofertilizer was applied at rates of 0–120 mg $L^{-1}$ Zn and B nanofertilizer at 0–6.5 mg $L^{-1}$ before blooming. Both nutrients increased the number of fruit per tree; however, physical characteristics, antioxidant activity, and anthocyanin production were not affected. In addition, the maturity index and TSS values were increased. These parameters are related to nutrient quality. In this case, the experiments were carried out over a period of 2 years.

## 10 Planning of Long-Term Experiments to Determine Benefits and Risks of Nanofertilizer Use in Plants

To the best of our knowledge, long-term experiments to determine the benefits and risks of nanofertilizer use in plants have not been performed so far. Both short and long-term models are required to predict elementary plant physiology and the responses of whole plants to environmental changes. Given the complexity and variety of ecosystems, it seems that modeling may be an appropriate approach to predict the behavior of different crops when nanofertilizers are applied. From the agronomic perspective, long-term experiments are needed if, for example, advice on fertilization is required (Le Bot et al. 1998). These models provide the basis for prediction of nutrient requirements by crops, and other decision-making tools.

In crops, the yield is probably the ultimate goal, and there is a strong relationship between the yield and nutrient acquisition, which in turn is related to fertilizer application and efficiency (Le Bot et al. 1998). This is the reason for stating the importance of performing long-term experiments (considering whole plants and field experiments) using nanofertilizers. Final crop yield models have been published since 1841, when Von Liebig provided the "Law of the Minimum" model, in which he explained how the most limited nutrient directly affects the yield (Von Liebig 1841). In this case, the model considers only one nutrient. More complex models have followed, and a review of these has been published by Le Bot et al. (1998).

Given the number of nutrients that are essential for plant development, data on nutrient management at the field level is beneficial. However, performing experiments to model all necessary nutrients seems like a task that is rather complicated with many variables. Angus et al. (1993) suggested applying prioritization by considering the price ratio of the nutrient and the product in relation to the yield obtained when that specific nutrient is applied to the crop. According to different data analyzed by those authors, priority has to be given to N, followed by P, K, Mg, S, B, Fe, Mn, Cu, Zn, and Mo, in that order. Since the physicochemical behaviors of nanofertilizers are expected to differ from those of traditional forms of fertilization, this list of priorities may change, considering that before being present in the soil solution, nutrients need to be made available from nanoparticles to the surrounding environment. This is one of the steps in crop simulation–calibration of additional parameters and adjustment of models (Angus et al. 1993).

In summary, models that consider the physicochemical behavior of nanofertilizers in addition to nutrient uptake by plants are required in order to provide a more systemic view and analysis of the impact of using these materials on a long-term basis.

## 11 Conclusion

It has been shown that every plant responds differently to nanofertilizer treatment; this is because of their biochemistry and physiology, even depending on the nature of the nutrient (i.e., whether it is a macro- or micronutrient) and soil characteristics.

Although many experiments have been carried out with different crops, most of them have explained the behavior of the response under laboratory or controlled conditions. This has made it complicated to describe the particular effects of specific nutrients, carriers, and doses of application on the physiology and biochemistry of crops, consequently generating the notion about possible toxic effects of these compounds. It is necessary to conduct more medium- and long-term field experiments, considering as many variables as possible.

It is important to point out that the soil matrix where the nanofertilizer is delivered plays an important role—for example, in terms of its pH, organic matter, and electrical conductivity; therefore, these factors must be analyzed. This entails analysis of the effects of the soil type on the development of plants, but also the impact of the addition of nanofertilizers on soil aggregation and modification of chemical properties.

Given the importance of the NPK nutrients, every year more and more research has been conducted to develop sustainable strategies for the incorporation and assimilation of these nutrients at the nanoscale level. The effects of the carriers and the impacts of the environmental conditions, crop necessities, and costs of the compounds have also been investigated to allow these fertilizers to be made available in an affordable way. The application of micronutrients in nanofertilizers and the carriers must be explored further and investigated in field conditions, as the optimum concentrations for application and their possible effects after release are still unknown.

Short- and long-term experiments must be carried out in the coming years to determine the real benefits and drawbacks of nanoscience and nanotechnology in agriculture worldwide. Also, new technologies to characterize the changes at the cellular and tissue levels have to be incorporated into this research. Other techniques to quantitate the concentrations of nanomaterials in the plants or fruit, and to obtain micrographs of the highest quality with advanced equipment, have to be incorporated into this research as soon as possible. Engineering of nanoparticles improves some biological characteristics of crops, increases yields, and improves the quality of fruit. However, additional information on how nanoparticles are taken up by the roots and how they are transported throughout cells and tissues is needed. Also, the effects of nanoparticles on human and environmental health need to be studied because it is well known that engineered nanoparticles not only may remain in soils for extended periods of time but also could be incorporated into plants or fruit, and potential consequences in upper-level trophic communities are still unknown but likely to occur.

## 12 Remarks and Future Actions

- More research must be conducted to compare the effects of nanofertilizer carriers on the release effect and its impact on soil characteristics, plant biochemical and physiological responses, and crop yields under field conditions.

- As is well known, the multivariability in agricultural and field conditions is extensive; however, the inclusion of more environmental variables in research must be considered and analyzed—i.e., soil pH, texture and aggregation of soils, intensity of agricultural practices, irrigation, and water quality, among others. These factors not only will provide information about benefits but also could be useful to exclude some possible adverse effects due to undesirable interactions of nanofertilizers and components of the soil system, as mentioned above.
- Elucidation of the mechanisms involved in nutrient uptake and their effects on crop improvement is necessary to establish experimental setups oriented to molecular analysis of soil microbial communities and proteomic levels, i.e., protein expression and regulation.
- It is essential to include life cycle analysis (LCA) tools to estimate the environmental impacts of application of nanofertilizers in agricultural practices and to define mechanisms to mitigate the possible effects.

**Acknowledgements** Edgar Vázquez Núñez acknowledges financial support received through project ID PRODEP UGTO-PTC- 571 and thanks BV Furlong for her assistance. Guadalupe de la Rosa Álvarez acknowledges support received from Universidad de Guanajuato (DAIP-UG 1,014/2016, ETAPA 2; Dirección de Apoyo a la Investigación y al Posgrado; Rectoría Campus León). Martha López-Moreno and Fabián Fernández-Luqueño received no specific financial support for this work.

**Competing interests** The authors declare that they have not competing interests.

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

**I. Vera-Reyes, Edgar Vázquez-Núñez, R. H. Lira-Saldivar, and B. Méndez-Argüello**

**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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F. López-Valdez, F. Fernández-Luqueño (eds.), *Agricultural Nanobiotechnology*, https://doi.org/10.1007/978-3-319-96719-6_5

# 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

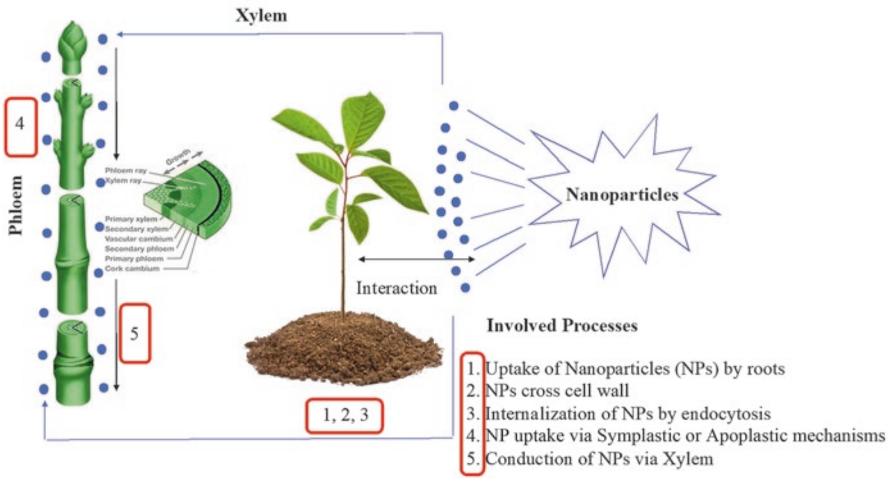


**Fig. 5.1** Mechanisms involved in nanoparticle transport through a plant. After plant exposure to nanoparticles, these nanostructures pass vegetal barriers; some specific mechanisms are triggered, and some critical effects can be observed

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).

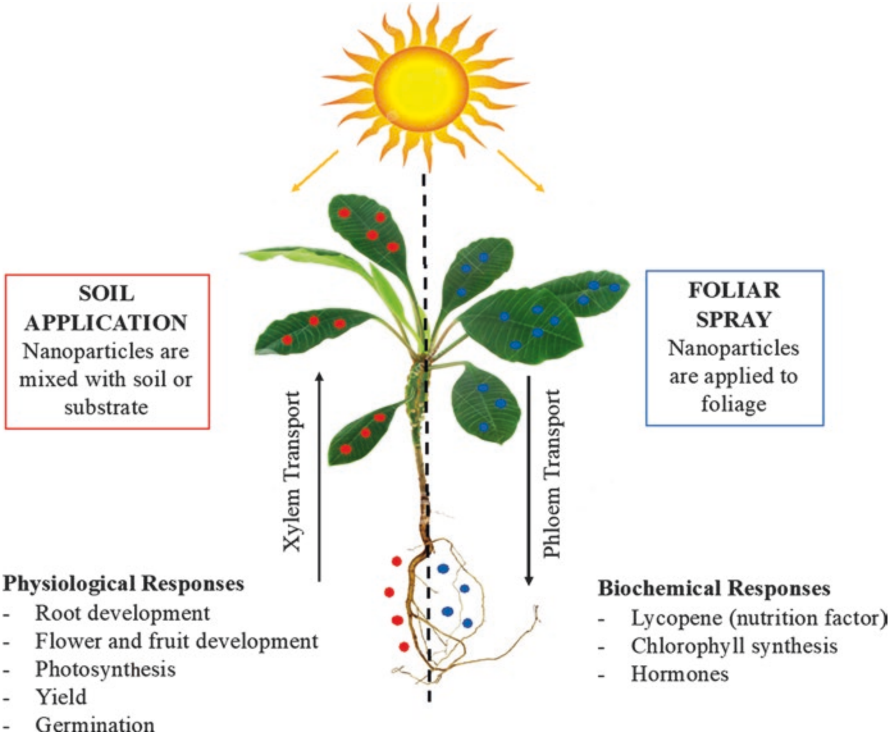


**Fig. 5.2** Positive and negative responses in plants after exposure to zinc oxide nanoparticles. Plants can show physiological and biochemical responses observed in the flowering time, yield, expression of genes involved in the biosynthesis of chlorophyll, etc. The interpretation of these responses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

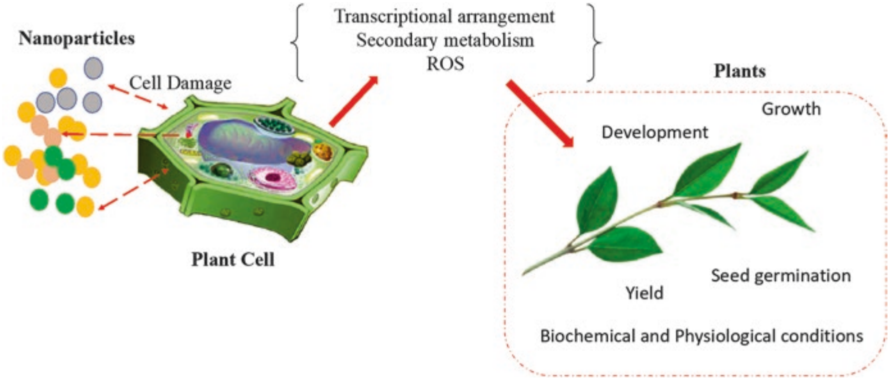


**Fig. 5.3** Effects of nanoparticles on plant cells. Most of the mechanisms involved in the responses to nanoparticle exposure are related to oxidative stress. *ROS* reactive oxygen species

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.

**Acknowledgements** E. Vázquez-Nuñez thanks the Universidad de Guanajuato for the support he has received, B.V. Furlong and AFLI Institute for the technical support. Méndez-Argüello and Vera-Reyes thank CONACYT-Mexico, for the postdoctoral fellowship (230282) and the research fellow project CONACYT-CIQA (Project 1333), I. V.-R., B. M.-A. and R.H. L.-S. wish to acknowledge for the financial support through the project number 268 from Fronteras de la Ciencia-CONACYT (Mexico).

**Competing interests** The authors declare that they have not competing interests.

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# Chapter 6
# Effect of Nanoparticles on the Growth and Development of Crops for Indoor Agriculture Applications

**Jaeyun Moon and Erick R. Bandala**

**Abstract** In this work, a review of the effect of nanoparticles on the growth and development of crops, particularly in indoor agriculture applications, is reported. Historically, the usual information of nanoparticles accidentally arriving into agricultural sites has been reported with negative or catastrophic effects for the crops cultured in the affected areas. In the last few years, however, the use on purpose of nanoparticles (NPs) particularly for indoor agriculture (IA) practices is a growing field with several different potential branches including their use as growth enhancers, soil surrogates, or pest controllers or in the improvement of inlet and/or outlet water quality. Despite the exciting results reported frequently in literature, more care is needed to assess the potential drawbacks associated with this practice before it may become a common place for food production. The scientific task involving the gathering of information and analysis of data is paramount in order to ensure the proper public judgment by the final consumers as well as informed-based decision-making by corresponding authorities. This chapter reviews all these novel, and apparently, successful applications of nanoparticles, explores the further gaps in the knowledge, and analyzes potential obstacles related with the effect of nanoparticles on the growth and development of crops.

**Keywords** Nanoparticles · Crop development · Agriculture · Indoor agriculture

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F. López-Valdez, F. Fernández-Luqueño (eds.), *Agricultural Nanobiotechnology*, https://doi.org/10.1007/978-3-319-96719-6_6

## 1 Introduction

Agriculture has supported civilization evolve since early crops allowed humans to create a more dependable food supply. Nowadays, farming is one of the most important industries with over 570 million farms around the world, over 90% of them managed by an individual or a family producing 80% of the global food (FAO 2014). Only in the USA, the average farm totals 178.4 ha in size, and family farmers grow 84% of the country's domestically grown crops, utilizing 78% of the total farmland and yielding $230 billion in annual sales. In developing countries, farming is also a very important activity. In Latin America, farm size averages 111.7 ha, and in sub-Saharan Africa and Asia, the mean farm size is less than 2 ha (FAO 2014). Despite the size of the industry, large gaps between current and potential yields for main crops are identified, and the hope for increased cultivation through productivity growth on family farms remains along with the development of new farming practices and innovative technologies that contribute to increased productivity (FAO 2014).

The combination of population growth, urbanization, and climate change have affected traditional agriculture and threatened global food supply (Platt 2007). According to the United Nations World Food Programme, nearly one billion people worldwide are undernourished (FAO 2012a, b). It is expected that by 2050, the world's growing global population will require an estimated 60% more food than produced today (Alexandratos and Jelle 2012), including the 1.3 billion tons of food lost or wasted annually (FAO 2011). While demand for food is increasing, land and water resources are finite. Currently, 11% of the world's total land surface is used as arable land (FAO 2011), and global projections show that up until 2040, agricultural land capacity can only be increased by another 2% until the earth runs out of space (FAO, 2012a). In the near future, farmers will need to grow significantly larger amounts of food, mostly on land already in production.

Along with overall increases in population, the number of people living in urban areas is expected to rise to over six billion people by 2050, 90% of whom are expected to live in developing countries (UN 2014). In 2000, the world's megacities took up just 2% of the earth's land surface, but they accounted for roughly 75% of industrial wood use, 60% of human water use, and nearly 80% of all human-produced carbon emissions (UN 2008). As human populations continue to concentrate in cities, intensive urban farming techniques have been proposed as a way to increase production in land-constrained areas (Ackerman 2012).

In agreement with FAO/WHO (2013), nanoparticles (NPs) are those materials produced intentionally with structure features between 1 and 100 nm that possess properties different from their conventional counterparts. Because of their extremely small size, NPs present greater surface area than the equivalent mass of microscale materials, and quantum effects are more important in determining their properties and characteristics leading to the development of materials with different properties. The market for nanotechnology has reached multibillion US$, and the expectation is to grow to billion US$ within the next 5 years. NPs are used in a wide variety of products and a significant number is in the pipeline. For the formers, nanoscale metal oxides (e.g., $TiO_2$, iron and aluminum oxides), nanoscale polymers, and polymeric nanocomposite materials are manufactured and applied in greatest quantities (i.e., kilograms to tons), and other emerging NPs are being reported (Aitken et al. 2006). Due to the diversity of materials included in the NPs group, predicting the long-term global trends for the industry is complex and inaccurate. Some reports, however, bet on the development of accessible materials that can be produced in large quantities as the development of new uses for not accessible NPs is expected difficult and discouraging. Despite the wide amount of information for NPs application and research and development (R&D), relatively few is reported on agricultural use of NPs, and even fewer has been reported related with the enhancement of agriculture by using this novel field of knowledge (Mukhopadhyay 2014). The aim of this work is to develop a review of the main opportunities, challenges, and expectations related with the effect of NPs on the growth and development of crops.

## 2 Indoor Agriculture (IA)

As the most efficient use of resources becomes more important for food production worldwide, highly efficient, cost-effective approaches have been emerging as interesting alternatives for conventional agriculture practices; IA is by far the one with the highest interest in the last few years. IA involves hydroponic greenhouse systems on and in mixed-use buildings that do not use farmland or open spaces leveraging synergies with the building environment. Production types are numerous and include rooftop gardens, rooftop greenhouses, edible green walls, indoor farms, or vertical greenhouses (Specht 2014). IA has the potential to produce food on a larger scale using less resources (Despommier 2011), improving the resilience of the food supply and generating significant value to the agricultural industry and the global economy reducing negative environmental effects of agriculture, as greenhouse gas emissions and soil degradation, and the protection of water supplies and biodiversity.

IA more efficiently uses land and resources, has higher year-round yield production, is safe from severe weather events, enables food security, limited use of pesticides or fertilizers, saves water (70–90% less) and energy, and reduces logistical costs (Despommier 2011; Heath et al. 2012). By restoring and more efficiently using natural systems, IA could help slow some adverse effects of climate change and possess potential to contribute to a greater reabsorption of carbon dioxide from the atmosphere in the form of carbon reserves (Platt 2007). Reduction of water use is another important benefit of IA; the possibility of capturing evaporated water from the greenhouse atmosphere with cooling traps and returning it to the system, conversion of graywater into irrigation water, and the application of hydroponic systems lead to significant water savings. It has been suggested that each hectare of recirculating hydroponic greenhouse could replace 10 ha of rural land and save 75,000 tons of fresh water annually (Specht 2014). Finally, significant energy savings can be achieved if IA is integrated into buildings with other uses (up to 41% for combined building/greenhouse in heating compared to stand-alone greenhouses and buildings) (Specht 2014). Rooftop greenhouses, for example, can provide additional passive-insulating benefits to the building, and low-energy cooling methods such as ventilation and evaporative cooling can result in energy savings vs. conventional air conditioning (Ackerman 2012). NPs are particularly linked with IA technologies, and its application is widely considered with more positive than negative impacts as detailed in the following sections.

## 3 Indoor Agriculture-Related Applications of Nanoparticles

Figure 6.1 depicts some of the most important applications of NPs in the indoor farming industry. In the following sections, a detailed explanation of the main findings and R&D developments related is provided along with some examples of field and lab-scale uses, NPs employed, and results obtained.

## 4 Nanofertilizers and Growth Rate Enhancers

Since indoor farming usually does not include the use of soil, all the nutrients required for plant development should be provided. This situation makes the use of micro- and macronutrients a very important issue. NPs have been used successfully

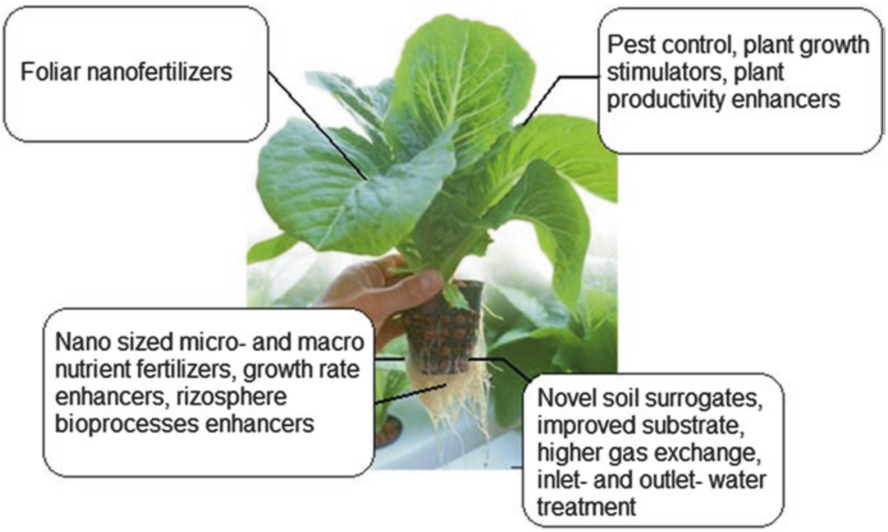


**Fig. 6.1** Application of nanoparticles in the indoor agriculture industry

to serve as both micro- and macronutrients with the advantage to directly enter the plant cells enhancing plant uptake and growth. Table 6.1 shows a compilation of the NPs used in both cases, along with a brief description of the plant species tested, method and medium used, as well as some additional comments on the observed enhancements (Liu and Lal 2015).

Different NPs can contribute to ameliorate plant growth by enhancing the uptake and use of nutrients (Khot et al. 2012). However, this effect has been demonstrated

**Table 6.1** Nanoparticles used as micro- and macronutrients for indoor farming applications

| Nutrient (type) | NP type, size, concentration | Test plant, method, medium | Main results | Reference |
|---|---|---|---|---|
| P (macronutrient) | Nano-apatite ($Ca_2(PO_4)_3OH$, 16 NP, 21.8 mg $L^{-1}$ as P | Soybean, house test, 50–50 perlite-peat moss, nutrient solution | 6.5 times more ground biomass, twice growth rate, 5.4-folds yields | Liu and Lal (2014) |
| Ca (macronutrient) | Nano-calcite, $CaCO_3$, 20–80 NP, 160 mg $L^{-1}$ as Ca | Peanut, greenhouse test, sand medium, nutrient solution | 1.2 times aboveground biomass, increased content of Ca in stems and roots, increased soluble sugar and protein | Liu et al. (2005) |
| Fe (micronutrient) | Nano $Fe_3O_4$, 18.9–20.3 NP, 30–60 mg $L^{-1}$ | Soybean, 7-days greenhouse test, perlite medium, nutrient solution | 10% increased chlorophyll content | Ghafariyan et al. (2013) |
| | $Fe_2O_3$-NPs, 50 NP, 100, 150 and 200 mg $L^{-1}$ | Spinach, house test, sawdust and coco peat, solid hydroponic medium | Increase in 30–500% biomass, increased Fe concentration in plant, increased size and growth rate in stems and root | Jeyasubramanian et al. (2016) |
| Mn (micronutrient) | Metallic Mn, 20 NP, 0.05–1 mg $L^{-1}$ | Mung bean, 15-days growth in chamber, nutrient solution | Increased rood length, shoot length, dry weight, chlorophyll and carotenoid content | Pradhan et al. (2013) |
| Zn (micronutrient) | Nano ZnO, 20 NP, 1–200 mg $L^{-1}$ | Mung bean and chickpea, 60-h in incubator, agar medium | Increased shoot height and biomass, root length, fruit starch, and glutelin | Mahajan et al. (2011) |
| Cu (micronutrient) | 70–30 CuO-$Cu_2O$, 30 NP, 0.025–5 mg $L^{-1}$ | *Egeria densa* planch, 3-days incubation, water | Increased photosynthesis rate | Taran et al. (2014) |

being highly depending on NP composition, concentration, size, surface charge, and physical or chemical properties and plant species susceptibility (Jeyasubramanian et al. 2016; Lambreva et al. 2015; Ma et al. 2010). The successful application of NPs as growth rate enhancers is usually related with the interaction between hydroponic conditions in indoor agriculture applications and the capability of the NPs for being released and efficiently uptake by the plant. In a very recent report, Jeyasubramanian et al. (2016) found that the addition of $Fe_2O_3$ nanoparticles enhanced biomass production and roots and shoots length for spinaches culture via hydroponic method. They found that iron coming from the NP reacted with dihydrogen monoammonium phosphate added as the source of nitrogen and phosphorus to the hydroponic medium to generate iron phosphates, and these components are then translocated into roots, stems, and leaves of the spinach, increasing the biomass and iron concentration in a dose-dependent effect.

Other reports suggest that low concentrations of iron-based NPs significantly increased the chlorophyll contents in subapical leaves of soybeans in a greenhouse test under hydroponic conditions (Ghafariyan et al. 2013). They suggested that soybean could use this type of NPs as source of Fe and reduce chlorotic symptoms of Fe deficiency. The impact of using NPs was similar to that of an effective Fe source for the plants, Fe-EDTA at concentrations 45 mg $L^{-1}$ as Fe. Delfani et al. (2014) reported that a foliar application of 500 mg $L^{-1}$ Fe-NPs to black-eyed peas significantly increased the number of pods per plant (by 47%), weight of 1000 seeds (by 7%), Fe content in leaves (by 34%), and chlorophyll content (by 10%) over those of the controls. Application of Fe-NPs also improved crop performance more than that by application of a regular Fe salt. The abovementioned parameters were increased by 28%, 4%, 45%, and 12%, respectively, under the Fe-NP treatment compared with these under treatment with a Fe salt. In addition, Fe-NPs significantly improved the beneficial effect of other nanofertilizers (Mg-NPs) on black-eyed peas (Liu and Lal 2015).

## 5 Soil Surrogate Improvers

In indoor farming the use of soil is not the rule, but the exception; as a result the search for materials with the proper characteristics to serve as soil surrogate is an important issue. Sustainable intensification is a concept commonly used by indoor farming, meaning the increase of system yield production cultivating the same agricultural area without adverse environmental impact (Fraceto et al. 2016). It allows to evaluate the selection of the best conditions for agricultural production considering biophysical, social, cultural, and economic situation (Garnett and Godfray 2012). NPs based on inorganic, polymeric, and lipid nanoparticles have been developed to successfully taking the role of the soil with an increased productivity. They have been used to enhance the immobilization and release of nutrients to the plant, minimizing leaching and improving nutrient uptake by plants (Liu and Lal 2015). The use of hydrogels, nanoclays, and nanozeolites is reported with enhanced water-holding capacity (Sekhon 2014), saving water usage by acting as a slow release source of water.

## 6 Plant Disease Controllers

As closed environments, indoor farming facilities are usually very sensitive to plant diseases with the consequent interest in the development of NPs that may serve to control it without the risk of threatening the health of the final consumers. The use of NPs improves the performance and acceptability of conventional plant disease controllers by increasing effectiveness, safety, and patient adherence and ultimately reducing health-care costs (Srilatha 2011).

Many different NPs have been reported with the capability to control pests and diseases in plants. Copper, for example, have been used for the control of vineyards from fungal diseases. Recent work has found that the amount of copper to be applied can be reduced significantly by the use of Cu hydroxide NPs with an additional increase in the efficiency against phytopathogens (Gogos et al. 2012). Colloidal Ag is another example of well-known antibacterial material (Baker et al. 2005; Nowack et al. 2010). Ag NPs have been tested as antifungals (Jo et al. 2009) and powdery mildew being successful in the disease control at lower doses and higher efficiency (Kim et al. 2008).

## 7 Inlet and Outlet Water Treatment

The quality of the inlet water in an indoor agriculture system and the proper treatment of the wastewater effluent generated are another very significant consideration when using this technology that NPs have the potential to improve. Many technological approaches for improving water quality have been developed over the last few decades with an increasing emphasis placed on sustainability. Technological solutions are currently evaluated not only by their cost-effectiveness but also by their ability to withdraw pollutants from the environment without generating by-products and, preferably, by their use of renewable sources of energy.

The use of NPs to promote advanced oxidation processes (AOPs) has recently emerged as a very interesting alternative for application in the treatment of inlet and outlet water from indoor farms. AOPs are defined as processes involving the generation of highly reactive oxidizing species able to degrade organic substances and considered physical-chemical processes with high thermodynamic viability and the ability to produce deep changes in the chemical structure of contaminants as a result of the participation of free radicals in redox reactions. AOP-generated free radicals, involved in the degradation process, are produced by photochemical and non-photochemical procedures as widely reported previously (Quiroz et al. 2011). In particular, photochemical AOPs have generated great interest in the last decade since these procedures have led to the use of renewable sources of energy to promote the chemical procedures involved. Solar radiation has been identified as a potential source for driving photochemical AOPs with interesting potential for real applications, specifically for water detoxification and disinfection (Aurioles-Lopez et al. 2016; Bandala and Bustos 2015).

The use of NPs for the enhancement of water quality involves the generation of hydroxyl radicals ($HO^{\bullet}$), chemical species possessing inherent properties that enable them to mineralize dissolved organic pollutants (Castillo-Ledezma et al. 2015a). Several different types of organic pollutants have been tested for the application of NPs-based degradation processes including pesticides, dyes and textile wastewater effluents, surfactants, algal toxins, bacteria, viruses, pathogens, and highly resistant microorganisms, among many others (Castillo-Ledezma et al. 2015b: Lopez-Ayala et al. 2015; Ramirez et al. 2015). Colored wastewater, dyes, and pigments have been remediated with good results using NPs (Bandala and Raichle 2013). Several other different NPs are reported for use as AOPs for the removal of organics in water alone or coupled with other processes in the past (Tuerk et al. 2010; Rodriguez et al. 2010; Bandala et al. 2011).

## 8 Food Supply Chain Improvement

The NPs are applicable for quality control, for biosecurity, and/or in agriculture but also along the food supply chain (Valdes et al. 2009; Aragay et al. 2010; Yao et al. 2014). NPs in nanosensors, to mention one application, having sensing dimension less than 100 nm, can help for monitoring physical-chemical properties in places otherwise inaccessible. Several different NPs shapes (e.g., nanotubes, nanowires, nanoparticles, or nanocrystals) may be used to improve transduction signals from sensing elements to better respond to chemicals having similar size (Scognamiglio 2013). In the indoor farm arena, where controlling the different conditions is basic for the proper development of the product, NPs in nanosensors may help to the users in maintaining the required precise control and report (Mousavi and Rezaei 2011), accurate analysis of nutrients in subtract, or maximizing water use efficiency. Also, they can be of great use managing all the phases of the food supply chain, from crop cultivation and harvesting to food processing, transportation, packaging, and distribution showing higher sensitivity and specificity compared to the conventional sensors (Scognamiglio 2013). NPs can be also used to create cost-effective sensors to ensure food quality, safety, freshness, authenticity, and traceability along the entire food supply chain.

## 9 Gaps and Obstacles

Despite the wide applicability of NPs for indoor farming improvements, it is necessary to consider also some of the main feedbacks potentially produced for these materials after its use. Little is known yet about the toxic effects of NPs in plants as they have the trend to accumulate essential and nonessential elements, in many cases beyond the lethal threshold for non-tolerant species. After accumulation, NPs may enter the food chain and reach higher organisms (Grover et al. 2012). The effects of exposure to engineered NPs is expected to be different from these produced by naturally occurring nanoparticles. Engineered NPs have been suggested passing through the body's defenses because of their size or protective coatings, making health and environmental risks due to the exposure to engineered NPs, a field needing further study since nanoscale materials are likely to be more toxic to biological systems than bulk ones (Prasad et al. 2014). Deeper analysis on total lifecycle of NPs and any related product is needed, and the results should be seriously considered by researchers, entrepreneurs, manufacturers, consumers, and policy makers.

Only few examples of regulations on production, use, labeling, and disposal of NPs are available worldwide (FAO-WHO 2013) with the consequent lack of knowledge on potential side effects of their and concern on the unknown export of waste NPs in several countries since these materials may not be degradable and capable to interact with other compounds in the environment (FAO/WHO 2012). Some places like Australia and New Zealand have recently launched food standard codes for food substances manufactured using NPs (FZANZ 2011). However, no information is included on how to proceed in the case of food materials growth using NPs. The same happens in the case of Canada where only food materials prepared using NPs are considered (Health Canada 2011), where only the presence of engineered NPs in foods is considered (EU 2011). Few other efforts on the generation of regulation for the use of NPs in food productions are reported in Brazil, Indonesia, Japan, Malaysia, Mexico, Korea, Russia, South Africa, and Switzerland with the same outcome (FAO-WHO 2013).

Another important issue to consider is the identification and quantification of NPs in the products, since food and agricultural samples are considered complex systems where the mixture of engineered and natural NPs may change their physical and chemical characteristics, making its separation and characterization a very complex task (Badyopadhyay et al. 2013). These lacks of information could open a whole new research area devoted to the development of analytical methods and models to characterize, localize, and quantify NPs in plant or food materials (Fraceto et al. 2016).

## 10 Conclusions

It is clear that the use of NPs in aid of crop growth for food production appears as an intriguing alternative in effort to fill the gap existing between the need and the offer of commodities for the population. In this report we have reviewed a significant amount of newly highlights on the significant potential showed by some NPs for increasing crop yields and pet control, producing good quality of water, or assisting the monitoring of optimal conditions for food production in indoor agriculture environments.

Despite all the interesting features reported for all those nanoparticles, we think more detailed research is needed not only to assess their application at real scale but also in preventing environmental or even human health effect risks down the road favored by its misuse or overuse in agricultural practices.

For example, systematic analysis on lifecycle of NPs is among the major needs which may led to proper regulations and proper decision-making, based on the proper knowledge of their side effects. Nevertheless, relatively few countries have seriously considered the potential risks and prepared the normative mark that may allow the use of resources in order to gather the information needed to properly assess potential impacts of the use of NPs in general and their application in food production in particular.

From our point of view, the scientific community is carrying out a significant effort by testing and identifying the characteristics and potential uses of NPs, as well as alerting also of their potential drawbacks under specific conditions. Additional effort, however, is needed from stakeholders, decision-makers, and final users in order to ensure the adequate operation rules and avoid the abuse of this resource in detriment of the environment as occurring in the past with other technology solutions as synthetic fertilizers or chlorinated pesticides. The final decision, thought, is in all of us.

**Acknowledgment** This material is based upon the work supported in part by the National Science Foundation (grant IIA-1301726).

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# Part III
# Improving the Soil and Water Quality

# Chapter 7
# Nanomaterials: New Agrotechnology Tools to Improve Soil Quality?

**Erick R. Bandala and Markus Berli**

**Abstract** Engineered nanomaterials (ENMs) are proposed as a new tool to enhance the quality and characteristics of agricultural soils. ENMs are under high scrutiny because of the controversial information about their potential benefits and risks. A significant part of the scientific community considers ENMs within the same group than naturally produced nanomaterials (NPNMs), which have interacted with plants, animals, and microorganisms since ancient times. While, others consider ENMs as a threat with unpredictable consequences if used without the proper regulations and specifications. This chapter reviews recent studies on the application of ENMs in soils and assesses advantages and disadvantages, challenges, and perspectives as well as scientific knowledge of ENM applications for food production and to improve soil quality.

**Keywords** Engineered nanomaterials · Soil · Naturally produced nanomaterials · Food production

## 1 Introduction

Sustainable food production is of global concern in the face of a growing population as well as to further alleviate hunger and poverty (Friedrich et al. 2012). Increasing food production competes with limited natural resources such as land water, energy, nutrients, and land (Friedrich et al. 2012; Tilman et al. 2011). Experience shows that intensifying agriculture (i.e., increased use of water, energy, fertilizer, and pesticides) can lead to negative effects on essential natural resources such as water and biodiversity as well as soil and its associated ecosystem services (e.g., effects on nontarget species, eutrophication, desertification) (Tilman et al. 2011). Therefore, assessing the benefits and risks of new technology prior to being applied to agriculture should be a priority to avoid adverse effects on human health and the environment.

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F. López-Valdez, F. Fernández-Luqueño (eds.), *Agricultural Nanobiotechnology*, https://doi.org/10.1007/978-3-319-96719-6_7

In agreement with FAO (2011), sustainable agriculture should prioritize increased and cost-effective food production and, at the same time, contribute positively in harnessing ecosystem services. Soil care is a fundamental subject for sustainable agriculture, so agriculture development will have to go hand in hand with sustainable soil use and management. The importance of healthy soils has often been a second-tier priority leading to soil deterioration, loss of productivity, and ecosystem services (Montanarella et al. 2016).

Nanomaterials (NMs) are currently discussed as a means to improve the quality of agricultural soils and subsequently foster sustainable agriculture. Due to their small size and large surface area, NMs are very reactive and have a variety of properties (e.g., enhanced cation exchange capacity, long-lasting nutrient release, nutrient delivering) potentially feasible for application in soils. So far, NMs have been successfully applied to solve soil restoration problems (Tuhl et al. 2013). Various engineered nanomaterials (ENMs) have demonstrated direct effects on plant growth and productivity (Liu and Lal 2015; Mukhopadhyay 2014; Rai and Ingle 2012), nevertheless their effect on real ecosystem where plants and microbes are in association is mostly unknown (Montanarella et al. 2016; Gardea-Torresdey et al. 2014). It has been argued that applying ENMs to soils is posing a possible risk for soil and human health, generating concerns about the consequences of uncontrolled use of ENMs for food production as it happened in the past for the use of chlorinated pesticides. There is a growing body of studies dealing with the toxicity of ENMs to soil bacteria and the impact of EMSs on other environmentally important soil processes and properties (Mendez-Rojas et al. 2014; Frenk et al. 2013; Gardea-Torresdey et al. 2014; Dimkpa 2014; Bakshi et al. 2015). However, many of these reports are not conclusive and, in some instances, even contradictory (Karu and Duborguier 2010; Tuhl et al. 2013).

The aim of this chapter was to review the state of knowledge on ENM applications to soil with a special focus on soil quality. We tried to address the currently known benefits and challenges of ENM when applied to soils and identified the main gaps in knowledge as well as the opportunities for further research in the field. The overarching goal was to shed some light on potential and limitations of ENMs as an agro-technology tool to improve soil quality.

## 2 Natural and Engineered Nanomaterials in Soil

Nanostructured materials (or nanomaterials, NMs) such as clays, fine ash, ferrihydrite, and hydrous sulfate, among others, occur naturally and are involved in a variety of environmental processes including soil formation and erosion, forest fires, and volcanic eruptions, just to mention some (Sharma et al. 2015). Several different kinds of organic and inorganic naturally produced nanomaterials (NPNMs) exist in the environment with a wide variety of particle shapes and sizes as well as physical and chemical properties. As a result of their small size (characteristic diameters ranging from 1 to 100 nm) and having high surface area and defects and dislocations, NPNMs are highly reactive toward external molecules and easy to transport through many of the natural filters and barriers. NPNMs are often monodisperse, low or nontoxic, water and hydroxyl groups rich, aggregated, and devoid of specific ligands bound to the surface (Bakshi et al. 2015).

In soils, NPNMs play an important role in the form of clay minerals, which influence chemical as well as physical properties of the soil. For example, clay minerals govern cation exchange capacity (CEC) of the soil, a key parameter for soil fertility and hence productivity (De Boodt et al. 2013). Besides food production, human kind has been taking advantage of clays since ancient times in the form of ceramic, building materials, and other applications. Although living organisms have been exposed to NPNMs for centuries, the overall impact of NPNMs on organisms is not well known (Bakshi et al. 2015). Some authors have suggested that the apparent lack of NPNMs toxicity for plants and animals is encouraging for the perspective of using nanomaterials as soil amendments, but that further research is needed (Gardea-Torresdey et al. 2014).

The ENMs are artificially produced nanomaterials with specific chemical characteristics designed for very specific applications (Fig. 7.1). ENMs possess high surface area, unusual phase transformation, defect stabilization, surface strain, and controlled aggregation (Waychunas 2009) and, depending on the conditions, occur as dispersed particles or aggregates and possess novel physical, chemical, mechanical, or optical properties. ENMs are produced in a wide variety of types, sizes, and shapes and are added to soil for a variety of reasons such as to improve plant growth, increase soil water and nutrient holding capacity, increase the amount of biosolids (e.g., the release of wastewater sludge in agricultural fields) to agricultural fields, or to clean up and restore soil after accidental spills (Gardea-Torresdey et al. 2014).

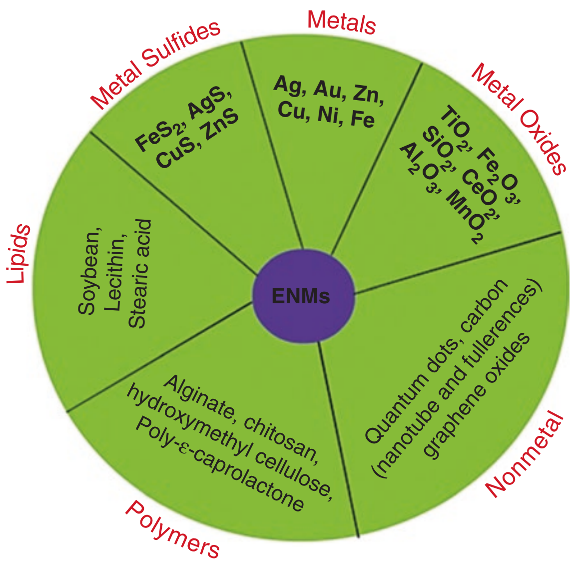


**Fig. 7.1** Nature of engineered and natural nanomaterials; bolded represents typical NPNMs (Sharma et al. 2015)

There is a significant amount of publications on the interaction between ENMs and soil addressing ENM *adsorption*, *translocation*, *accumulation*, and *biotransformation*, indicating that ENMs can have beneficial and harmful effects on agricultural activities. Gardea-Torresdey et al. (2014), for example, found some positive effects of ENM applications to soil such as improved photosynthetic processes, antioxidant activity, radical scavenging activity, and gene expression of edible plants. Zheng et al. (2005) and Gao et al. (2008) reported beneficial effects of ENMs on plant growth depending on soil type, improved physiological and growth response of certain crops or increased photosynthesis as well as growth stimulation by ENMs. However, other studies found that ENMs can damage root cell membrane as well as impair cell division, seed germination, root elongation, and plant biomass (Dimkpa 2014; Collins et al. 2012; Frenk et al. 2013). ENMs have also been reported as effective plant disease controllers or able to improve the performance of conventional plant disease controllers by increasing their safety, adherence, and other basic characteristics (Srilatha 2011; Gogos et al. 2012; Baker et al. 2005; Nowack et al. 2010; Jo et al. 2009; Kim et al. 2008; Mishra and Singh 2015).

A significant concern of ENM applications to soil is related to the effect of ENMs on soil microbial communities as the latter is responsible for various highly important biogeochemical processes, such as nutrient mineralization and nitrogen and organic carbon metabolism. A variety of studies addressed the lethality of ENMs for specific soil microorganisms (Frenk et al. 2013; Ge et al. 2012; Collins et al. 2012) finding that ENMs pose a significant threat for the microbial community and all these studies agree that further research is needed to properly understand the observed effects, specifically for different soil types.

The controversy about NPNM and ENM applications in soils revolves around the potential negative consequences of NMs for sustainable agriculture. This review indicates that more systematic research is needed related to exposure conditions, biotransformation, and speciation of both NPNMs and ENMs in soil and after their interaction with plants and other soil organism in order to generate a better understanding of the basic processes occurring to reduce uncertainty and produce more accurate information on potential effects of the massive implementation of ENM use in agriculture.

## 3 Nano-Based Soil Restoration Technologies

Soils can be contaminated with a wide variety of pollutants that may pose significant restrictions for further use, particularly for sites where industrial or military activities have occurred or farmlands where accidental spills have been registered. In order to remediate contaminated soils for further use (e.g., commercial, urban development) or to restore farmlands to their productive characteristics, NMs have been used as alternative to traditional remediation practices when these become unfeasible due to environmentally disruptive and cost-prohibitive behaviors on

**Table 7.1** Use of nanomaterials for soil restoration

| NM type | Soil application | Notes | Reference |
|---|---|---|---|
| Natural iron oxide and silver NPs | Metal removal (Pb, Cu, Sb) | NMs were tested jointly with biochar for soil restoration | Rajapaksha et al. (2015) |
| SAMMS[a] | Extraction of PAHs | The sequestration of PAHs in soil using SAMMS was demonstrated | Brandl et al. (2015) |
| Emulsified zerovalent iron (ZVI) NPs | Trichloroethylene (TCE) removal | TCE ranging 0.439–1.18 mg $L^{-1}$ was removed 65–85% in 90 days | Virkutyte and Varma (2014) |
| ZVI NPs | Hg, Ni, Cd, Pb, and Cr removal | Nano ZVI was found able to reduce and adsorb metals from soil | Rabbani et al. (2015) |
| Colloidal ZVI | Cd removal from aqueous soil solution | Use of carboxymethyl cellulose stabilized ZVI to improve colloid stability | Nasiri et al. (2013) |
| Iron nanooxides | As removal | Nanogoethite, nanomaghemite, and nanomagnetite were used to trap As in soil samples | Zhang et al. (2010) Shipley et al. (2011) |
| Nano manganese oxides | As removal/oxidation | Different Mn oxides were used for As removal/oxidation in soil | Watanabe et al. (2013) Villalobos et al. (2014) |
| Metal-NPs | Organic and inorganic pollutants removal | Hetero- and homogeneous systems are used for abiotic soil remediation | Floris et al. (2017) |
| Other NMs | Cr adsorption and reduction | Cr and As are immobilized/reduced in soil | Martinez-Fernandez et al. (2017) |

[a]Note: *SAMMS* self-assembled monolayers on mesoporous supports

large scale (Rajapaksha et al. 2015). The information of some selected works related to the use of NMs for soil restoration is summarized in Table 7.1.

From Table 7.1, it can be seen that removal of metal ions is one of the most common problems addressed using NMs (particularly nanoparticles, NPs) in soil. Several different types of metal/metalloid pollutants have been successfully removed using an interesting variety of NMs, *zerovalent iron* (ZVI) among them, one of the most frequently cited. ZVI has received the attention of the scientific community for soil and groundwater restoration accounting, in agreement with some authors, for over 90% of the work done in the area (Yan et al. 2013). It is an effective technology that has been applied in different forms for the construction of permeable barriers or the treatment in situ of soil for the removal of a wide variety of contaminants (Cecchin et al. 2017). Nano-sized ZVI is also reported as highly effective for the removal of organic compounds, specifically chlorinated solvents (e.g., TCE) in soil and groundwater for real-scale applications in different military-related sites along the United States and Europe (Virkutyte and Varma 2014).

Of particular interest for organic pollutant removal from soils are the so-called self-assembled monolayers on mesoporous supports (SAMMS) which are nano-structured materials capable of removing contaminants by sequestration highly efficient in the extraction of heavy metals from aqueous and nonaqueous liquids and recently reported in the removal of hydrophobic pollutants (e.g., polyaromatic hydrocarbons, PAHs) from soil (Brandl et al. 2015). Besides ZVI, other NMs are reported for the restoration of contaminated soil including silver-, iron-, and manganese-oxides with interesting capabilities for metal/metalloid removal. For the latest, its capability for immobilization of metals has been suggested as highly interesting related to its large specific surface and low value of pH at point of zero charge. However, manganese oxides are also reported possessing strong oxidative properties that may restrict their application in some cases where reduced chemical species are preferred (e.g., Cr(III) vs Cr (VI)), but highly desirable in the treatment of other pollutants with oxidized species that are more convenient for environmental purposes (e.g., As(III) vs As(V)) (Watanabe et al. 2013; Villalobos et al. 2014). Manganese- and other metallic-based (e.g., Fe, Ag, and Cu) nano-oxides have been reported from biogenic processes (Zhou et al. 2015) with scarce reports for its use in soil restoration. The application of biogenic NMs in the restoration of soil is, nevertheless, a highly interesting field of research as the application of these bionanotechnologies in the production of NMs will generate products mimicking natural oxides and pose a lower concern for its release into the environment.

Use of nanotechnology for soil restoration is predominantly used in saturated soils for both laboratory- and fiel-scale applications, few works are available reporting the use of NMs for soil restoration in the unsaturated zone (Kern et al. 2011; Tosco et al. 2014; Cecchin et al. 2017). Because the behavior of the target pollutants and the NMs may be different when interacting in unsaturated and saturated soil, this lack of information is a significant gap that deserves further research.

## 4 Agricultural Applications

The use of NMs as fertilizers and plant growth enhancers is discussed in detail elsewhere in this book. It is worth, however, to mention that the direct use of NMs to promote biomass production in crops is not the only approach reported in literature for NMs as soil improvers (Liu and Lal 2015). Figure 7.2 depicts the most common functions on NMs in agricultural applications.

Table 7.2 shows a summary of studies reporting the use of NMs for soil applications. The use of nanoscale biopolymers has been reported as a versatile class of materials used for different applications including soil conditioners (Mohammadi and Khalafi-Nezhad 2012). Also, in the same way, nano-sized sulfonated polyaniline (nSPANI) has been reported as an interesting alternative to controlling soil surface crust formation in arid and semiarid regions.

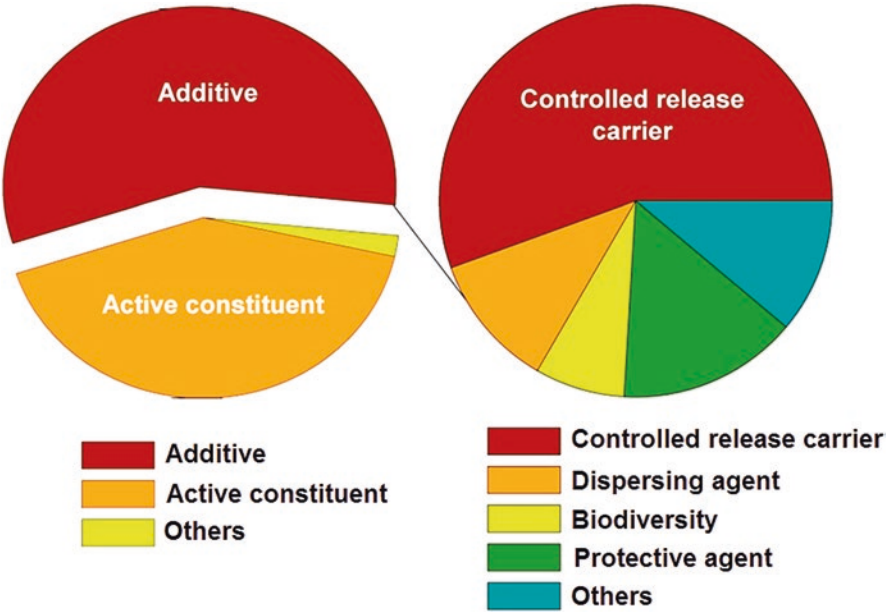


**Fig. 7.2** General functions of NMs in agricultural applications (modified from Gogos et al. 2012)

**Table 7.2** Selected applications of NMs in soil

| NM type | Soil application | Notes | Reference |
|---|---|---|---|
| nSPANI | Soil surface crust formation control | nSPANI delays crust formation with no impact in crop germination | Mohammadi and Khalafi-Nezhad (2012) |
| Nano-clays | Grown media additive in small-scale cultivation | Able to stabilize sandy soil | Boroghani et al. (2011)<br>Oztas et al. (2002) |
| Chitosan NPs | Carvacrol encapsulation | Bioactive compound found in thyme with bactericidal activity | Keawchaooon and Yoksan (2011)<br>Higueras et al. (2013) |
| Nano-clays | Thymol encapsulation | Insecticide and bactericide activity | Lim et al. (2010)<br>Guarda et al. (2011) |
| Zein NPs | Eugenol and curcumin encapsulation | Insecticide, nematicide, and bactericide activity | Gomez-Estaca et al. (2012)<br>Zhang et al. (2014) |

In agreement with these reports, the use of nSPANI has been capable to delay the process of formation of a compact layer of soil particles at the soil surface (a soil surface crust) that would result in decreasing infiltration, increasing runoff, and subsequent erosion. Lab toxicity tests carried out with nSPANI on earthworms and mice showed $LC_{50}$ values 1.13 and 206.6 mg $kg^{-1}$ (for earthworm and mice, respectively), considering nSPANI as low and moderately toxic, respectively (El-Din et al. 2016). Nano-clays have been used as grown media additive in pot plants and small-scale cultivation (Boroghani et al. 2011) or to stabilize sandy soil to maintain water and control erosion (Oztas et al. 2002).

In another interesting approach, nanoparticles of different nature have been reported as carriers, suitable for encapsulation of insecticides (e.g., azadirachtin, rotenone, carvacrol, thymol, eugenol, and curcumin) and its further release under controlled conditions for increasing agricultural productivity and reducing impacts on the environment (De Oliveira et al. 2014).

In most of these applications, the lack of information related to the scaling up of the technology is probably the main significant gap. Estimating the scalability of nanocarrier production for the development of commercially available products for full-scale application is a very interesting research area that deserves attention.

## 5 Nanomaterial Toxicity in Soil

The contamination of food supply chain via the use of nano-enabled agricultural and soil restoration technologies for crop production is one of the main concerns of the application of NMs in soil (Gardea-Torresdey et al. 2014). Some nanostructured materials with highest environmental and health impact are metal semiconductors and carbon nanotubes due to their extended use (Mendez-Rojas et al. 2014). These nanostructured materials are, however, less likely to end up in the food chain since they are not used as soil amendments and enter the natural environment only through accidental release. In order to determine whether or not a specific NM is toxic, rigorous characterization of its physical and chemical characteristics is needed as well as an accurate understanding of its biological activity. Plenty of reports exist related to the negative impacts of NMs to plants (Dimkpa 2014), soil biodiversity (Suppan 2013; Frenk et al. 2013), or the final consumers (Handford et al. 2014) and, at the same time, on the positive achievement of its use for a wide variety of improvements in the agri-food industry such as desert reclamation (El-Din et al. 2016), the improvement of nutrient quality and use (Pulimi and Subranian 2016; Mukhopadhyay 2014), or the proper management of pest (Rai and Ingle 2012). To the light of these controversial results, it is clear that a scientific gap exists in the understanding of the behavior and effects and its relation with the properties of NMs that deserves immediate attention considering the potential risk related. Also, only limited information exists about the amount used and exposure of NMs in soil, food, and food-related products.

The interaction between NMs and biological systems has been suggested very complex involving several different events with considerable difficulties in the monitoring of systemic and physiological effects occurring in vivo and measured in vitro. In many cases, toxicity assays used for measuring the effect of NMs on different living systems tend to oversimplify the events measured (Mendez-Rojas et al. 2014). As a result, the development of new methods for accurately measuring biological impacts of NMs is a research task with outstanding further interest as the controversy on the beneficial or undesirable consequences of NM use in soils remains. Particularly, generation of inexpensive, simple, and quick methods capable to correlate physical or chemical properties in the NMs with biological activity is not only an interesting research line but also a suitable business opportunity.

## 6 Challenges and Perspectives

As the production of food coming from agricultural land becomes restricted by several different variables and threatened as a result of climate change or population growth scenarios, the alternative of improving soil quality for an increased production becomes more tempting. The implementation of the so-called smart agriculture is significantly based on the modern application of agro-nanobiotechnologies able to provide keener solutions for the current problems in the field (Rameshaiah et al. 2015). However, more work is needed in order to clearly assess the real benefits of NMs in agricultural soil applications and the need of emerging methodologies to evaluate risk and determine benefits.

Probably, one of the main challenges is related to the growth and move toward commercial NM application. Despite the reported benefits of nanotechnology to increase crop yield and agricultural productivity to meet the challenges in food security (Rohoni et al. 2015), the widespread use of NMs is expected to face several different constrains related to regulations, intellectual property rights, the lack of investment support, or even the low appeal of technology investment (Gruere 2012). Using increased productivity as the rational to increase NM application likely does not suffice, and special care is in order before further decisions can be made.

Another very significant challenge is related to the potential risk posed for consumers and environmental health involved in the use of NMs in agricultural soils. Although NPNMs are common part of soil, concerns related to the application of ENMs have started to include also those NPNMs which, for some authors, may not being properly characterized for their health risks (Gardea-Torresdey et al. 2014). Furthermore, the range of applications of ENMs in agriculture goes far beyond the discussed uses for soil improvement and includes promotion of seed germination, plant growth, and nutrient fixation besides other food chain-related applications as food additives, packaging materials, and health supplements, among many others (Liu and Cohen 2014), with the consequent emerging of normativity for the different applications in many countries (EFSA 2009: FAO-WHO 2013: FSANZ 2011).

Another important challenge is related to the ethical and social implications of NMs and the public acceptation of products generated in farmlands where NMs have been used for soil improvement. In the early 2000s, NSF proposed ethic principles and societal implications of nanotechnology including how to accelerate its advantages while minimizing the risks or improving education and research related to nanotechnology (Khan 2012). Unfortunately, it is also very well-known that multiple reports on NM applications in soils lack scientific rigor on toxicological studies which have not followed accepted and recognized protocols with the consequent generation of questionable results (Reich 2011; Gruere et al. 2011). The public perception about nanotechnology is generally positive, but it may change as a result of the growing awareness and the role of the media (Dudo et al. 2010). Besides, some civil society groups have fixed strong position related to the risk posed by NM use in soil for food production and the ban of NMs in agro-food products. Unfortunately, an increased knowledge gap has been identified between educated and non-educated public as well as the potential for highly volatile responses when acute events occur (Gruere 2011).

From a research perspective, the most interesting aspects are related to the development of more accurate and sensitive methodologies for assessing the toxicity of NMs in soil including their effect on soil microorganisms, plants, and other nontarget organisms, as well as the search of specific knowledge on different processes related to the trend, behavior, and dispersion of NMs after their release or use in agricultural soil. Lack of information on accuracy, sensitivity, and replicability on NM risk assessment methodologies poses an unacceptable uncertainty for decision-making creating undesirable extreme approaches, where excessive caution may discourage innovation, investment, and consumers' benefit, whereas excessive confidence may lead to severe threats for consumer's health.

There are some other opportunities of improvement such as increasing the leverage by the governments for the proper investment devoted to support basic research and technology development on NMs in agricultural applications. Securing private investment for the continued development of new technology is another governance exercise that may generate fruitful results in medium-long term by creating the human resources opportunity and the adequate political, under legal and social environments for business generation.

Finally, moving toward appropriate normativity, using scientific-based decision-making, for nano-enabled product use and release, is a highly desirable opportunity. To date, a number of OECD countries have taken the governance challenge, but most others remain without decision if and/or how to regulate NM-related products and their use in soil or any other food-related system (Gruere 2012), giving place to a wide variety of approaches ranging from absolute ban to very simplistic requirements that increase the complexity or the problem.

## 7 Conclusions

The actual trends, technology development, and scientific gaps on the application of NMs for soil quality were reviewed including an address of the currently known benefits and challenges of ENM applications in soils. The following were the main findings:

A highly controversial debate is currently ongoing related to the environmental and health-related implication of the use of ENMs to improve soil quality, no matter what the final soil use is intended. From the information reviewed, a fair amount of uncertainty remains about the benefits of NMs over conventional soil amendment technologies. There are also concerns about the potential negative impacts of

NM. Available information is insufficient to carry out a solid risk-benefit analysis indicating a need for more research.

The comparison between naturally and engineered NMs has just added more confusion into the discussion as the characteristics and properties of both material types may not allow the comparison at all and might lead to unfair outcomes with the consequent regrettable decision-making. Besides, while the necessary information is generated, other significant bottleneck operations impeding fundamental soil-related activities, such as food production, should be reviewed in order to eliminate them from the discussion. For example, there is a long-standing debate whether food production or distribution is the limiting factor and, therefore, key challenge for food access in the next decades. We think that addressing the food production versus distribution question may be equally if not more important than the application of NMs with their potential benefits, but also risks.

Finally, ethical and social implications were considered of great importance for the debate as the public acceptation of the use of NMs for improving soil quality is the ultimate barrier to be faced by the technology. Based on past experiences with new technology entering agronomy, public acceptation may be high initially, but the trend to go back to the basics has showed to prevail after all, as demonstrated by the actual tendency by the public to use organic products or to avoid genetically modified organisms (GMO), just to mention two examples. There is, however, an urgent need to provide the public with the proper information in order to avoid unfair manipulation, or the access to reports lacking of the proper scientific rigor, that may be intentioned to bias the public opinion.

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# Chapter 8
# Agronanobiotechnologies to Improve the Water Quality in Irrigation Systems

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**Abstract** Several international studies have shown that the performance of watering practices and irrigation equipment are still too low, while the water quality and availability are increasingly scarce worldwide. Consequently, there are reductions in crop yields and a waste of water resources. The objectives of this chapter are (1) discussing some bibliographic evidence regarding the availability of agronanobiotechnologies to improve the water quality and watering efficiency in agricultural irrigation systems and (2) describing some technological developments used in the design of cheap and eco-friendly filters with natural or engineering nanomaterials and organic wastes. It has been found that groundwater irrigation has grown rapidly

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F. López-Valdez, F. Fernández-Luqueño (eds.), *Agricultural Nanobiotechnology*, https://doi.org/10.1007/978-3-319-96719-6_8

over the past 50 years and now supplies over one-third of the world's irrigated area. Water management emerged as a strategic resource, not only in many arid and semi-arid countries, but also in humid climates, because of its capacity to support intensive land use and high-value agriculture. However, effective governance of watering water and the implementation cutting-edge technologies are critical and urgent challenges. It is required to critically examine the various approaches that different technologies have proposed for taking advantage sustainably about irrigation water and assessing their wider applicability for promoting its responsible use worldwide, while better water technologies and management are urgent and critical for productivity, equity, and sustainability.

**Keywords** Crop water requirements · Engineering nanomaterials · Irrigation and drainage · Rainfall harvesting · Runoff and evaporation · Low-cost irrigation techniques · Nanofilter · Water supply

## 1 Introduction

Water scarcity and the little availability of good quality water are global problems for human consumption or agricultural irrigated land. During the last years, high attention has started being paid on environmental analyses with multiple goals: quantifying environmental impacts of processes, identifying environmental hotspots, and suggesting mitigation strategies to reduce the impact of anthropogenic productions on the environment (Lovarelli et al. 2016).

Global consumption of freshwater resources has grown more than sixfold in the past century, and local water consumption has accumulated as a global problem (Luan et al. 2018). In addition, human impact on the environment has grown much more and faster than what was expected, and humanity consumes more resources (e.g., land, water) than what Earth is capable of regenerating (Galli et al. 2012).

Nowadays water scarcity is a major issue for present and future generations. It is well known that globally less than 10% of collected wastewater receives any form of treatment. Concomitantly, agriculture is the largest water user in most countries, representing 70% of total global freshwater withdrawals (Thebo et al. 2017). However, drought and inadequate water management are the predominant causes of low yields worldwide so that there is an urgent need for more water-efficient cropping systems facing large water consumption of irrigated agriculture and high unproductive losses via runoff and evaporation. Consequently, identification of yield-limiting constraints in the plant-soil-atmosphere continuum is the key to improved management of plant water stress (Bodner et al. 2015). Nevertheless, it has to be remembered that other strategies such as deficit irrigation have been widely investigated as a valuable and sustainable production strategy in dry regions, while limiting water applications to drought-sensitive growth stages aims to maximize water productivity and to stabilize—rather than maximize—yields (Geerts and Raes 2009).

Despite technological efforts by the specialists from different knowledge areas, water scarcity, water pollution, runoff, and evaporation are main problems which link to the use of water in agricultural systems. In addition, water is becoming scarce not only in arid or drought-prone areas but also in regions where rainfall is abundant: water scarcity concerns the quality of resource available and the quality of the water because degraded water resources become unavailable for more requirements (Pereira et al. 2002). Pereira et al. (2002) also stated that the sustainable use of water (resource conservation, environmental friendliness, appropriateness of technologies, economic viability, and social acceptability of developments issues) is a priority for agriculture in water-scarce regions. Imbalances between availability and demand, degradation of surface and groundwater quality, inter-sectorial competition, and interregional and international conflicts often occur in water-shortage regions. Therefore, innovations are required mainly relative to irrigation management and practice since the agriculture sector is far ahead in demand for water in those regions.

The objectives of this chapter are (1) discussing some bibliographic evidence regarding the availability of agronanobiotechnologies to improve the water quality and watering efficiency in agricultural irrigation systems and (2) describing some technological developments used in the design of cheap and eco-friendly filters with natural or engineering nanomaterials and organic wastes.

## 2 Irrigation Versus Rain-Fed Agriculture

There are two main ways to use agricultural water to cultivate crops: (1) rain-fed farming and (2) irrigation. Rain-fed farming is the natural application of water to the soil through direct rainfall. Rainfall reduces the contamination of food products but is open to water shortages when rainfall is scarce. On the other hand, artificial applications of water increase the risk of contamination by heavy metals, organic or inorganic pollutants, or pathogen microorganisms (Table 8.1; Fernández-Luqueño et al. 2013). Irrigation is the artificial application of water to the crops through systems of tubes, pumps, and sprays. There are many types of irrigation systems, in which water is supplied to the entire field uniformly.

Irrigation water can come from groundwater, surface water, or even other sources, such as treated wastewater or desalinated water. As a result, it is critical that farmers protect their agricultural water source to minimize the potential for contamination. It is well known that rainfall generally is uncontaminated and it could be stored throughout rainfall harvesting for later use or used without any previous treatment. However, frequently the water stored, treated, or extracted for irrigation purposes requires several treatments to decrease the pollutants, salts, or pathogens, so that several novel materials with specific characteristics never seen before (Table 8.2) have been synthesized by nanotechnologies and they could be used to improve the irrigation water quality (Fig. 8.1).

**Table 8.1** Main characteristics that affect the quality of agricultural irrigation water

| Pollutant | Problems | Reference |
|---|---|---|
| Salinity | Salts in soil or water reduce water availability to the crop and cause a slow rate of growth, along with a suite of metabolic changes caused by water stress, including premature senescence | Munns (2002) |
| Ion toxicity | Sodium, chloride, and boron ions from soil or water accumulate in a sensitive crop to concentrations high enough to cause crop damage and reduce yields. It is usually first evidenced by marginal leaf burn and interveinal chlorosis | WHO (2006) |
| Pathogens | Diseases such as diarrhea, cholera, hepatitis A, and typhoid fever can be transmitted through direct physical contact of farmers with wastewater or by consumption of products irrigated with contaminated ground or water | Minhas et al. (2006) Hanjra et al. (2012) |
| Nutrients | High nitrogen concentrations in the water which supplies the crop may cause undesirable vegetative growth, delayed crop maturity, and reduced crop quality | Qadir et al. (2010) |
| Suspended solids | Organic and inorganic sediments cause problems in irrigation systems through clogging of gates, sprinkler heads, and drippers. Sediments also reduce water infiltration rate of an already slowly permeable soil | WHO (2006) |
| Heavy metals | Heavy metals accumulated in the edible parts of leafy vegetables. Consumption of heavy metal-contaminated food can cause a decrease in immunological defenses, intrauterine growth retardation, impaired psychosocial behavior, disabilities associated with malnutrition, and a high prevalence of upper gastrointestinal cancer | Arora et al. (2008) |

## 3 Types of Irrigation Systems

There are many different types of irrigation systems, depending on how the water is distributed throughout the field. In addition, some modern technologies to watering in cropped soils are described in Table 8.3, while some common types of irrigation systems include:

1. Surface irrigation: water is distributed over and across land by gravity, no mechanical pump involved.
2. Localized irrigation: water is distributed under low pressure, through a piped network and applied to each plant.
3. Drip irrigation: localized irrigation in which drops of water are delivered at or close the root of plants.
4. Sprinkler irrigation: water is distributed by overhead high-pressure sprinklers or guns from a central location in the field or from sprinklers on moving platforms.
5. Center-pivot irrigation: water is distributed by a system of sprinklers that move on wheeled towers in a circular pattern. This system is common in flat areas.

**Table 8.2** Properties of the main nanomaterials (NM) used for wastewater treatment

| NM | Application | Mechanism of action | Reference |
|---|---|---|---|
| Cu | The use of copper nanoparticles in paper filters for water purification contaminated with bacterial activity | The CuNP papers with higher copper content showed a high bacteria reduction of for *Escherichia coli* | Dankovich and Smith (2014) |
| $TiO_2$ | Textile-wasted water contaminated with methylene blue | $TiO_2$ nanoparticles degraded methylene blue from the solution due to the high photocatalytic activity | Hossain and Hossain (2015) |
| CuO | To purify seawater contaminated with oil | The use of CuO demonstrates that it could find promising application in oil-water separation and offshore oil spill cleanup | Kong et al. (2015) |
| Magnetic nano-adsorbent | Wastewater contaminated with $Pb^{2+}$ | It improves 80% removal efficiency | Khani et al. (2016) |
| $Fe_3O_4$ and $\gamma$-$Fe_2O_3$ | Wastewater contaminated with mercury | It removes mercury by 70% | Vélez et al. (2016) |
| Zeolite materials obtained from fly ash | Wastewater contaminated with $Pb^{2+}$ | Improves >80% removal efficiency | Visa (2016) |
| $TiO_2$/CuO nanoneedle arrays (NNA) | Industrial water contaminated with oil | The nanostructure $TiO_2$/CuO NNA dual-coated meshes are potentially useful in practical oil/water separation | Yuan et al. (2017) |

6. Lateral move irrigation: water is distributed through a series of pipes, each with a wheel and a set of sprinklers, which are rotated either by the hand or with a purpose-built mechanism.
7. Subirrigation: water is distributed across land by raising the water table, through a system of pumping stations, canals, gates, and ditches.
8. Manual irrigation: water is distributed across land through manual labor and watering cans.

## 4 The Value of Irrigation

Irrigation systems allow primary producers to grow more crops and to have more flexibility in their productive processes as the ability to access water at times when it would otherwise be hard to achieve good plant growth due to a deficit in soil moisture. Producers can then achieve higher yields and meet market demands especially if rainfall events do not occur to produce higher-quality crops as water stress can dramatically impact on the quality of farm produce to lengthen the growing

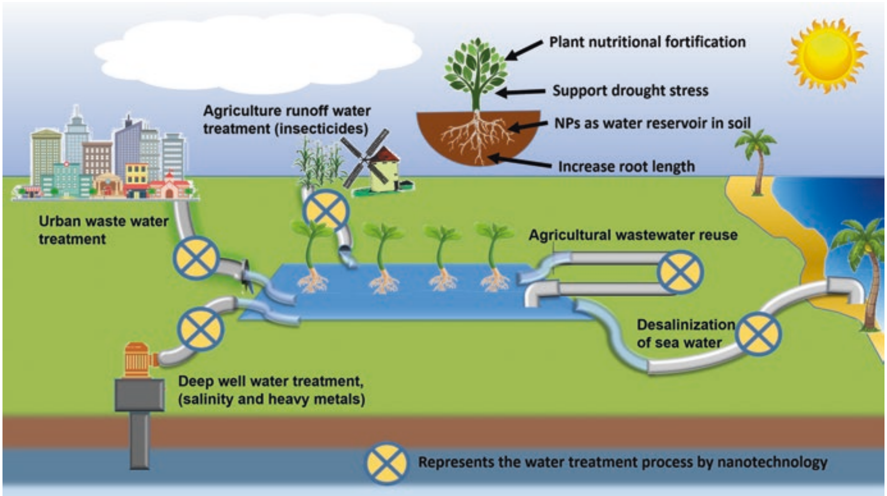


**Fig. 8.1** Some of the possibilities where nanotechnology has been involved in irrigation water. Different sources of water, such as urban wastewater, salt water, deep well-contaminated water, or agricultural runoff waters, could be treated by nanotechnology to be used in agriculture. This nanotechnology includes nanomembranes and metal-based, carbon-based, or polymeric nanoadsorbents. Some of the contaminants which could be handled by nanotechnology are heavy metals, hydrocarbons, organic pollutants, and insecticides. Apart from water treatment, some nanomaterials applied by irrigation could have a positive impact in plant development or their quality. Examples are the increase in root area and length by Ag-NP, increased support to drought stress by maghemite nanoparticles, and fortification of plants for human consumption by Se-NP, while during drought conditions, calcium pectinate NP could act as a water reservoir

season to have "insurance" against seasonal variability and drought. Irrigation systems, wastewater management, and water store systems (Fig. 8.2) in cropped lands have several technical and financial benefits such as:

1. To stock more animals per hectare and practice tighter grazing management due to the reliability of pasture supply throughout the season.
2. To maximize benefits of fertilizer applications. Fertilizers need to be "watered into" the ground in order to best facilitate plant growth.
3. To use areas that would otherwise be "less productive." Irrigation can allow farmers to open up areas of their farms where it would otherwise be "too dry" to grow pasture/crops. This also gives them the capability to carry more stock or to conserve more feed.
4. To take advantage of market incentives for unseasonal production.
5. To have less reliance on supplementary feeding (grain, hay) in grazing operations due to the more consistent supply and quality of pastures grown under irrigation.
6. To improve the capital value of their property. Since irrigated land can potentially support higher crops, pasture, and animal production, it is considered more valuable. The value of the property is also related to the water licensing agreements or "water right."

**Table 8.3** Modern systems for irrigation in agricultural production

| Main argues and findings | Reference |
|---|---|
| Precision irrigation strategies, including variable rate irrigation, are useful approach for irrigation management to save water and reduce deep percolation losses. | Gonzáles-Perea et al. (2018) |
| Aerial sensor, with multispectral and infrared thermal imaging sensors, is a potential tool for remote crop stress monitoring. Green normalized vegetation index, canopy cover, and canopy temperature were able to differentiate crops with full and deficit irrigation at different growth stages. | Zhou et al. (2018) |
| Subsurface drip irrigation in rice cultivation produces similar grain yield compared with puddle-transplanted rice, with 50% lower N applications and 32% of water savings. | Rajwade et al. (2018) |
| Aquaponics is an integrated fish and plant production in a recirculation system. It has a hydroponic component which directly influences the water quality and consumption. The plant species influenced the daily water loss, whereas no effect was exerted by the water flow or type of hydroponics. | Maucieri et al. (2018) |
| Plant factories use the hydroponic techniques which have been used to increase the efficiency of protected horticulture. The hydroponic systems adopted in plant factories can circulate water and fertilizers within the systems. | Kikuchi et al. (2018) |
| Drip irrigation could reduce water consumption to 70% compared with conventional flood irrigation. Pressure compensate drip emitters to maintain a constant flow rate under variations in pressure have been designed and optimized empirically. A model to design new drip emitters with attributes that improve performance and lower cost is presented. | Shamshery et al. (2017) |
| Aeroponic system is a soilless culture system, where roots are kept in a dark environment saturated with aerosol of nutrient solution. Potato minituber production with this system resulted in a two to three times greater compared with the traditional method. | Rykaczewska (2016) |
| With the nutrient film technique, plants are grown directly in a circulated thin film of water containing a dissolved nutrient solution. This technique is easy to manipulate for toxicity test. The use of biochar filters reduced the Ni uptake in tomato plant growth with this technique. | Mosa et al. (2016) |
| Water productivity is increased by reducing non-beneficial use or by other agronomical practices such as engineering solutions that reduce the use of irrigation water. Agronomical solutions such as regulated deficit irrigation are directly linked to basin water conservation with little or no yield penalty. | Mateos and Araus (2016) |

7. To cost save/obtain greater returns. The cost benefits from the more effective use of fertilizers and greater financial benefits as a result of more effective agricultural productivity (both quality and quantity) and for “out-of-season” production are likely.

## 5 Irrigation and Environment

Drainage facilities, in delta areas in particular, are considered as a form of flood protection. In conjunction with irrigation, they also prevent waterlogging and salinization. The area salinized by irrigation covers over 37 million ha worldwide, thereby reducing productivity. The use of urban wastewater in agriculture is a

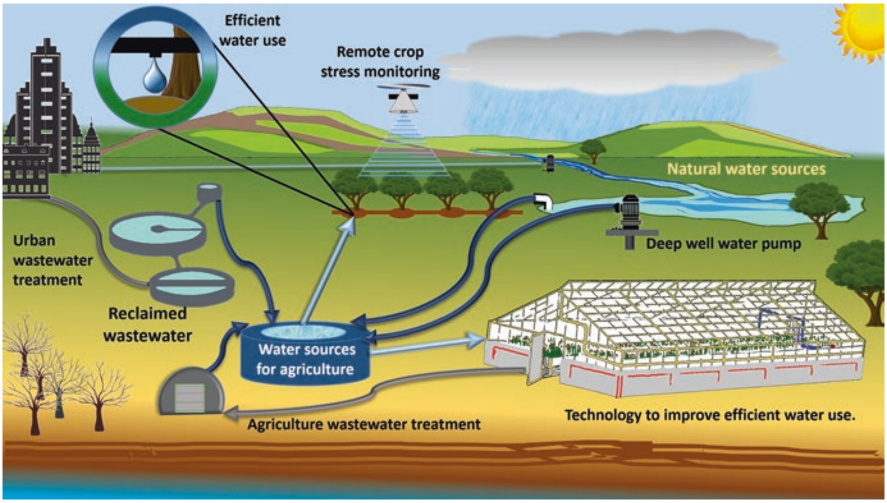


**Fig. 8.2** Irrigation systems, wastewater management, and water store systems could improve the human well-being. To deal with food production and water scarcity, new technologies are emerging in water treatment and agricultural recirculation systems, as well as efficient water use. Reclaimed water from urban areas or agronomical activities could be a good water source together with natural water resources. Regulated deficit irrigation supported with remote crop stress monitoring is a promising emerging technology, while micro-irrigation systems in the field allow to give the amount of water that a plant needs by dripping water directly to the root zone. In protected agriculture, hydroponics and their variables increase the water use efficiency in crops and allow to recover the excess of water to be treated and recirculated into the production system. These are some of the actual approaches and future perspectives to deal with water scarcity and food production

century-old practice that is receiving renewed attention with the increasing shortage of freshwater around the world.

Irrigation of crops with wastewater is a common practice in urban and suburban farming communities where wastewater is often the only water source for agriculture. Additionally, wastewater contains important nutrients, such as inorganic N, P, micronutrients, and organic matter, which favor crop growth, but irrigating crops with wastewater might increase human viral and bacterial infections and contamination of the environment with toxic substances. In Latin America more than 500,000 ha arable land is irrigated with wastewater, of which 350,000 ha in México. In the valley of the Mezquital in the state of Hidalgo (México), 145,000 ha are irrigated with wastewater from Mexico City. This has favored the development of the region, but 1,200 ha have already been lost as agricultural land due to increased soil salt contents (Fernández-Luqueño et al. 2010).

Overexploitation of groundwater when water withdrawal exceeds water recharge—and its subsequent lowering of water tables—is a recurring problem in several cropping lands. In some countries the overpumping due to subsidizing electricity has lowered the water level by 25–30 m in one decade.

Fortunately, almost 155 million ha are under conservation agriculture worldwide. This technique enhances water use efficiency in rain-fed conditions due to minimum soil disturbance, soil cover, and appropriate crop association.

Some wetlands and inland valley bottoms are cultivated with minimum disturbance to the environment, as they have no or limited (mostly traditional) equipment to regulate water and control drainage. In addition, flood recession cropping is another traditional water management technique with relatively low environmental impact, where cultivation occurs along rivers in the areas exposed as floods recede and where nothing is undertaken to retain the receding water. It is well known that over 8.6 million ha worldwide are cultivated with these water managements.

However, there are also some examples of environmental problems regarding improper irrigation system management such as the drying up of the Aral Sea in Central Asia. It is one of the most dramatic examples of environmental tragedy caused by the mismanagement of irrigation where the sea level dropped by 17 m and the shoreline moved 70 km since 1960. This is due to the large diversions of water for irrigation of cotton and electricity production, resulting in little water reaching the Aral Sea. However, on a positive side, without the high productivity permitted by irrigation, at least an additional 500 million ha would be needed to reach the current agricultural production.

Temperate or humid areas allowing rain-fed production are often already densely populated or environmentally disturbed, therefore having no additional land for agriculture available anymore. Unfortunately, countries reaching their limit of cultivated areas already buy or rent large areas in other less developed countries, also known as land grabbing, i.e., they destroy and buy more cropping soil but do not improve technologies to take care the environment; they only look for economic benefits. In addition, globally more than one-third of the food is lost between field and fork, and thus also a large amount of water and energy, needed to produce the food. While in poor countries, most losses occur due to postharvest losses, in rich countries losses are mainly due to throwing away the food that is not consumed.

More reclaimed water is expected to be used for agricultural irrigation as the conventional water supply is becoming increasingly limited. The increasing concern of environmental risk caused by irrigation with reclaimed water and its complexity requires continuous monitoring and more research on the negative influences resulting from reclaimed water irrigation. To face these problems, the cutting-edge knowledge has been ahead, and new agronanobiotechnologies and/or biotechnologies have been developed during the last years in order to increase the yields and quality of harmless food (Tables 8.4 and 8.5).

According to Wang et al. (2017), extensive research regarding the extensive use of reclaimed water has shown a positive effect of reclaimed water irrigation on crop growth and yield with acceptable product qualities, although a reduction in the crop yield and quality and the ornamental performance of landscapes, as well as soil deterioration, have been occasionally reported. At present, there are some issues of great concern that should be addressed for the sustainable use of reclaimed water irrigation such as (Wang et al. 2017) (1) updating of the standards of reclaimed

**Table 8.4** Agronanobiotechnologies to improve the water quality in agriculture irrigation systems

| Main argues and findings | Reference |
|---|---|
| To use municipal wastewater for irrigation, it needs to be treated with plant growth-promoting rhizobacteria (PGPR) and Ag-NPs prior to be used for irrigation.<br>Silver nanoparticles though suppressing the growth-promoting potential of PGPR increases their bioremediation potential for Pb, Cd, and Ni. Ag-NPs enhanced root area and root length by PGPR isolates. | Khan and Bano (2016) |
| Selenium NP uptake by wheat seedlings is dependent on nanoparticle size and synthesis method in hydroponic experiments. The selenium NP uptake is energy independent. | Hu et al. (2018) |
| Calcium pectinate nanoparticles function as water reservoirs to provide sustained irrigation in areas where water is scarce. | Sharma et al. (2017) |
| Maghemite nanoparticles delivered by irrigation support drought stress management through enzymatic activity in *Brassica napus.* | Palmqvist et al. (2017) |
| Main applications of nanotechnology in water bioremediation are as uranium remediation, hydrocarbon remediation, groundwater and wastewater remediation, and heavy metal remediation. | Dasgupta et al. (2017) |
| A hybrid system of forward osmosis and nanofiltration (FO-NF) for agricultural wastewater reuse was developed. FO-NF permeate showed a high-quality water for irrigation in a long-term period. | Corzo et al. (2018) |
| Low-quality waters can be filtered using nanotechnology applications allowing the removal of salts and other micropollutants. This water could be used for agricultural production. | Bueno et al. (2017) |
| Nanohexagon NiO sheets can potentially remove hydrophilic and hydrophobic insecticides such as carbamates and organochlorines, respectively, from agriculture wastewater. | Derbalah et al. (2015) |
| Wastewater and desalination for a more sustainable agriculture could be accomplished by nanomaterials science. | Villaseñor and Ríos (2018) |

**Table 8.5** Applied biotechnology to improve irrigation water

| Main argues and findings | Reference |
|---|---|
| Two *Pseudomonas protegens* strains were isolated from an agricultural water well contaminated with heavy metals. The isolates show mycelial growth inhibition against some pathogenic fungus and have a potential as beneficial bacteria for agriculture applications even in metal-polluted soils. | Bensidhoum et al. (2016) |
| This study highlights the potential benefits that plant growth-promoting microorganisms may confer to plants grown in hydroponic systems, particularly when cultivated in extreme environments. | Sheridan et al. (2017) |
| From 48 bacterial strains isolated from agricultural water well, 4 shows the ability to express plant growth-promoting traits and inhibition of mycelia growth to *Botrytis cinerea* and *Aspergillus niger.* | Tabli et al. (2018) |
| Microalgae *Chlorella* sp. in aquaponics system is able to remove ammonia and balance pH drop caused by nitrifying bacteria. Algae prefer ammonia nitrogen over nitrate nitrogen. | Addy et al. (2017) |
| *Stevia rebaudiana* showed increase production of stevioside when treated with purple phototropic bacteria. Foliar treatments combined with treatments through rhizosphere irrigation showed best results. | Wu et al. (2013) |

water for irrigation, (2) better understanding of the mechanisms of the migration, transformation, accumulation, and diffusion of various contaminants, (3) determining the technical parameters of irrigation systems to enhance the safety and effectiveness of reclaimed water irrigation, (4) making a risk assessment for continuous reclaimed water irrigation, (5) promoting local and global policies for developing reclaimed water irrigation, and (6) developing and evaluating new technologies that guarantee better performance of irrigation techniques without jeopardizing the sustainable development.

## 6 Design and Manufacture of Low-Cost and Environmentally Friendly Filters

Our research team has been working with the synthesis and evaluation of new materials to increase the performance of environmentally friendly water filters.

### *6.1 Methodology*

*Aspergillus niger* strain (ATCC 9642) was obtained from the National Collection of Microbial Strains and Cell Cultures of Cinvestav Zacatenco, Mexico. It was subcultivated every month in malt extract agar. A Tween 80 (20% v/v) sterile stock solution was used for the spore dispersal. 2.5 mL spore suspension of *A. niger* ATCC 9642, obtained from a 14-day agar growth, was inoculated into 250 mL malt extract broth medium in a 500 mL Erlenmeyer flask. The cultures were cultivated at 30 °C and pH 4 for 6 days in an orbital incubator. Mycelium was recovered through filtration using filter paper (Whatman No. 2), washed repeatedly with distilled water until a clear filtrate was acquired, and dried for 3 h at 80 °C. Fungal biomass was homogenized using an Agate mortar and deproteinized with 15 mL 1 M NaOH treatment for 2 h at 90 °C. The alkali insoluble fraction was recovered by centrifugation (15,000 × *g*, 15 min), washed with distilled water, and recentrifuged until it reached a neutral pH. Finally, fungal biomass was dried and ground with Agate mortar.

Montmorillonite clay was extracted from 20 kg of vertisol soil by the test tube method. 50 g of soil, previously sieved in a 30 mesh, were air dried and placed in a 1-L test tube. 10 mL of sodium hexametaphosphate (5 g per 100 mL) were added and after 5 min stirred, and the test tube was left to settle for 24 h.

## 6.2 Adsorption Experiments

The adsorption of arsenic (As), lead (Pb), carbonate calcium ($CaCO_3$), and sulfate ($SO_4^{-2}$) ions was evaluated using produced fungal biomass, montmorillonite clay, and TiO2, $Fe_2O_3$, ZnO nanoparticles as adsorbents in aqueous solution. Adsorption experiments were conducted in a batch mode as a function of time (0–480 min) and concentration at neutral pH and 25 °C. A known weight of adsorbent (0.1 g) was added to 25 mL of composite solution containing equimolar concentrations of each compound in the range of 1–50 mg $L^{-1}$. The residual ion content was determined by inductively coupled plasma, and the capacity of adsorption ($Q_e$) was calculated according to the following equation:

$$Q_\mathrm{e} = \frac{\left(C_\mathrm{o} - C_\mathrm{e}\right) * V}{m}$$

where "$C_\mathrm{o}$" is the initial concentration (mg/L), "$C_\mathrm{e}$" the equilibrium concentration (mg $L^{-1}$), "$m$" the weight of used adsorbent (g), and "$V$" the volume of the solution (L).

## 6.3 Application of the Adsorbents in a Filter

A PVC cylinder (30 cm of height and 2.4 cm of diameter) was designed and loaded with the five adsorbents to be applied as a filter. Contaminated water with As, Pb, $CaCO_3$, and $SO_4$ ions was passed from the bottom of the filter and released from the top at a continuous flow. Experiments were conducted in triplicate, and samples were collected each 2 h. Efficiency of the filter was evaluated by determining the pollutant concentration in the water release (Fig. 8.3).

## 6.4 Characterization

The physicochemical characteristics of the five adsorbent materials (fungal biomass, montmorillonite clay, and $TiO_2$, $Fe_2O_3$, and ZnO nanoparticles) were evaluated by Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction, X-ray fluorescence, and scanning electron microscopy (SEM).

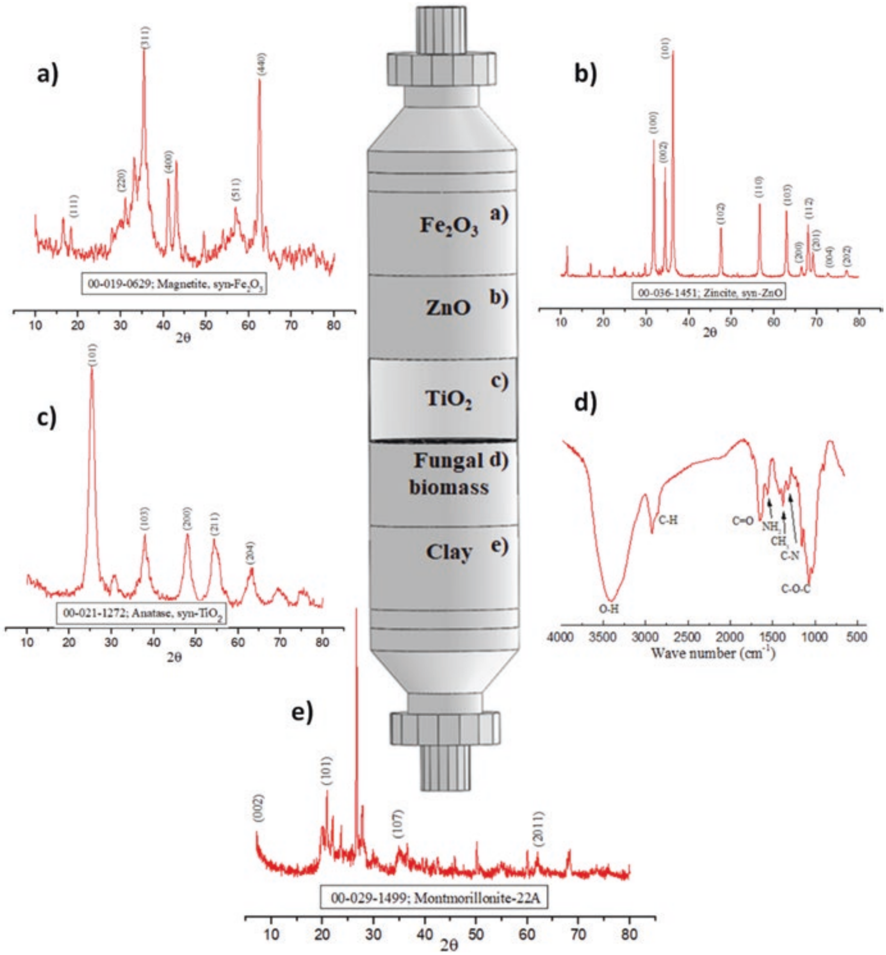


**Fig. 8.3** Filter prototype with XRD diffractograms of (**a**) $Fe_2O_3$, magnetite, (**b**) ZnO, zincite and (**c**) $TiO_2$, anatase, (**d**) IR spectrum of fungal biomass, and (**e**) XRD diffractogram of montmorillonite clay

## 6.5 *Adsorption Yields*

Once the batch tests for each adsorbent have been carried out, it has been found that the adsorption equilibrium is reached after 2 h of contact between adsorbent and adsorbate. Regarding the removal efficiency of the pollutant mixture, taking into account an initial concentration of 25 mg $L^{-1}$ of each one, a neutral pH, and a temperature of 25 °C, the lead ion has decreased by 89% and 98% using montmorillonite clay and the three nanoparticles, respectively. On the other hand, As concentration has been diminished by over 90% using the nanoparticles of ZnO (93%) and $TiO_2$ (98%), while the removal of $CaCO_3$ has only been favored with the nanoparticles of $Fe_2O_3$ in a 90%. The removal of the sulfate ion is very low, since none of the five adsorbents obtained a yield greater than 10%.

Our research team is also working on a low-cost solution for household water purification by a manufactured filter with engineering nanoparticles, soil-natural clays, and recycled materials. The goal of this research is to design, build, and evaluate a cheap water filter for the low-income household which is being manufactured with engineering nanoparticles (NP), natural soil NP, and recycled materials. In the present study, water filters were developed with Ag-NP, $TiO_2$-NP, coffee waste, and natural soil NP. Soil NP and residues of coffee-supported Ag-/$TiO_2$-NP (soil NP/coffee waste/Ag/$TiO_2$-NP) were prepared through step by step. First, the preparation of the coffee waste and the extraction of soil NP were made. After that, coffee residues and the soil NP were sifted, mixed, and dispersed in 25 mL of ethanol under continuous stirring until a suspension was formed. Then 0.2 g of $AgNO_3$ was dissolved in the suspension with stirring, followed by the addition of 1.5 mL of tetrabutyltitanate. After stirring for 2 h, the mixture was heated at 160 °C for 30 h, centrifuged, and calcined at 500 °C for 5 h to firmly attach among themselves. Powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) showed that the Ag-NP coated with $TiO_2$-NP is well-dispersed on the surface of soil NP and recycled materials. This nanomaterial, i.e., soil NP/coffee waste/Ag/$TiO_2$-NP, had proper recycling, increased the surface area, and facilitated the water purification.

## 7 Conclusion

Suffering from severe water scarcity, several countries have been using wastewater for irrigating cereal, fiber, and vegetable crops. However, rarely both quantities and qualities have been enhanced from raw wastewater, i.e., the common procedure is to have irrigation system watering crops without any previous or minimum treatment.

The importance of promoting local and global policies for developing reclaimed water irrigation must be recognized worldwide. In addition, as integral parts of wastewater reclamation policy frameworks and its use and management in land watering systems, several regulations should be developed and improved worldwide.

Effective governance of watering and the implementation of cutting-edge technologies are critical and urgent challenges. It is required critically to examine the various approaches that different technologies have proposed for taking advantage sustainably about irrigation water and assessing their wider applicability for promoting its responsible use worldwide, while better watering technologies and management are urgent and critical for productivity, equity, and sustainability.

The synthesis of new materials for treated wastewater or freshwater with potential use in irrigation systems has to be promoted but also the long-term studies to know the potential human or environmental harm. The humanity needs more water, energy, and food, but also needs a comfortable and safe site to live and thrive. Otherwise, the sustainable development will be jeopardized.

**Acknowledgments** This research was founded by "Ciencia Básica SEP-CONACyT" projects 151881 and 287225, the Sustainability of Natural Resources and Energy Programs (Cinvestav-Saltillo), and Cinvestav Zacatenco. G.M.-P., H.P.-H., G.S.-H., A.Z.-C., and V.U.-I. received grant-aided support from "Becas Conacyt." F.F.-L., F.L.-V., E.V.-N., and S.L.-S. received grant-aided support from "Sistema Nacional de Investigadores (SNI)," México.

**Conflict of interest** The authors declare no conflict of interest.

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# Part IV
# Environmental Topics

# Chapter 9
# Effects of Nanoparticles on Plants, Earthworms, and Microorganisms

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**Abstract** The synthesis of engineered nanomaterials (ENMs) has increased in recent years because novel and unexpected properties and applications have been found to such a degree that hundreds of scientists have published concerns and evidence regarding the toxicology of ENMs. However, most of the reported findings have been inconsistent, so more research is needed, but also long-term in situ field trials are required, while the standardization of tests, chemical reagents, and methodologies must be strengthened and regulated in accordance with scientific advice or international organizations. This chapter discusses new findings published during

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F. López-Valdez, F. Fernández-Luqueño (eds.), *Agricultural Nanobiotechnology*, https://doi.org/10.1007/978-3-319-96719-6_9

the last 5 years regarding the advantages and disadvantages of ENMs, as well as findings obtained in our laboratories and greenhouse. We found that ENMs have favorable effects on some crops and biological systems. Consequently, ENMs have potential industrial applications in the agricultural sector, with biological, environmental, and ecological advantages. Nevertheless, the effects of ENMs depend on the kind of ENM, exposition period, concentration, substrate or soil type, kind and age of organisms, biotic and abiotic interactions, etc.; i.e., a specific test has to be carried out for each particular condition, and generalizations regarding the effects of ENMs should be avoided, otherwise human and environmental health—but also sustainable development—will be compromised.

**Keywords** Engineered nanomaterials · Human and environmental health · Sustainable development

## 1 Introduction

Nanomaterials are classified as naturally occurring, incidentally synthesized, and intentionally manufactured. Since engineered nanoparticles (ENPs) have been developed for use in industry and human commodities, it is common to find them in waste and by-products of industrial chemical reactions, but it is also possible to find incidental nanoparticles (NPs) in the environment (Medina-Pérez et al. in press). Despite that, nanotechnology has been recognized by the European Commission as one of its six "Key Enabling Technologies" that contribute to sustainable competitiveness and growth in several industrial sectors (Parisi et al. 2015).

According to Terekhova et al. (2017), ENPs can enter the soil through atmospheric precipitation, through sedimentation in the form of dust and aerosols, through direct soil absorption of gaseous compounds, through abscission of leaves, or as a result of anthropogenic activity, etc. After ENPs get into a water system through sewage or industrial emissions, nanoparticles can accumulate in plants (e.g., in algae), as well as in invertebrates (plankton, benthos, crustaceans) that are the primary links of a food chain, and then they can pass into water vertebrates that form part of the human food chain (Terekhova et al. 2017). In a land ecosystem, ENPs can accumulate in soil, vegetation, surface water, sewage, landfills, and groundwater.

The current challenges of sustainability, food security, and climate change are engaging researchers in exploring the field of nanotechnology as a new source of key improvements in the agricultural sector (Parisi et al. 2015). However, because of the rapid advent of nanotechnologies, great attention is being paid to the effects of engineered nanomaterials (ENMs) on living organisms, while concerns are rising in the scientific community worldwide.

Despite the numerous potential advantages of nanotechnology and the growing trends in publications and patents, agricultural applications have not yet made it to the market, but several factors could explain the scarcity of commercial applications, such as the high production costs of nanotechnological products, unclear technical benefits, and legislative uncertainties, as well as public opinion (Parisi et al. 2015). Nevertheless, the research and development landscape regarding ENMs is very promising, and the possibilities offered by nanoscience and nanotechnology in various agricultural applications will continue to be actively explored. In addition, the rapid progress of nanotechnology in other key industries may, over time, be transferred to agricultural applications as well, and facilitate their development (Parisi et al. 2015).

This chapter discusses new findings published during the last 5 years regarding the advantages and disadvantages of ENMs, as well as findings obtained in our laboratories and greenhouse.

## 2 Environmental Behavior of Engineered Nanomaterials at Various Trophic Levels

Despite the wide applications of ENPs in several areas, limited data are available on their behavior at various trophic levels. Rocha et al. (2017) stated that the current knowledge indicates the existence of important accumulation and ecotoxic effects of Cd-based quantum dots (QDs) on microorganisms, aquatic invertebrates, and vertebrates (fish) in freshwater and seawater.

It has to be acknowledged that there is an urgent need for development of analytical methods for detection and quantification of ENMs in environmental matrices, as well as a need to establish guidelines for experimental design and development of new end points/biomarkers for ecological risk assessment of ENMs. In addition, the ecotoxicology of ENMs in environmentally relevant exposure conditions, such as micro- and mesocosms, has not been investigated yet, while chronic and long-term ecotoxicity tests have been limited (Rocha et al. 2017). Entry, migration, transformation, or degradation of ENPs in different ecosystems (Fig. 9.1) have been reported by Cornelis et al. (2012), Keller and Lazareva (2014), Gokhale (2016), and Song et al. (2017).

According to Karimi et al. (2018), despite the wide application of nanoparticles in different sectors of the food industry and the benefits that nanotechnology offers in achieving better quality, safety, efficiency, and food-processing techniques, human exposure to nanoparticles through trophic transfer and possible adverse health effects on the human body seem to be inevitable. They also stated that toxicology of nanoparticles suffers from severe limitations in the certified assessment approaches and contradictions in the stated data, and that consideration should be given to screening of nanoparticle-containing foods in a set of long-term studies conducted in large groups of people to consider all of the related issues before those foods rapidly occupy the market.

Most nanoparticles have been traced in different plants, crops, bacteria, algae, protozoa, fungi, crustaceans, annelids, platyhelminths, nematodes, bivalves, gastropods, and fish, reported in several updated reviews (Tangaa et al. 2016; Rocha et al.

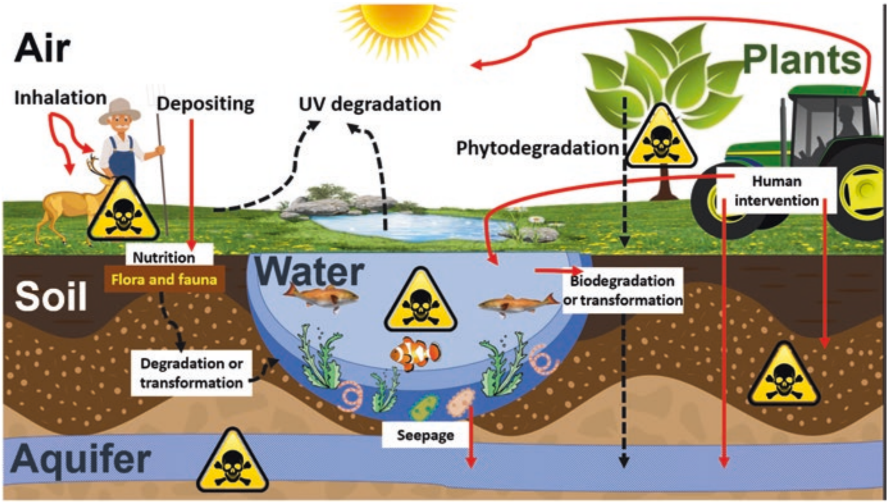


**Fig. 9.1** Entry or migration (*solid red lines*) and transformation or degradation (*dashed black lines*) of engineered nanoparticles (ENPs) in different ecosystems. The *danger symbols* denote organisms or systems for which evidence regarding nanoparticle toxicity has been reported (see Tables 9.1, 9.2, and 9.3). *UV* ultraviolet

2017; Karimi et al. 2018; Tan et al. 2018). It is suggested that precise and standard tests should be utilized to assess the long-term effects of acute and chronic exposure to different ENMs existing in food systems before mass production. Overall, the available knowledge indicates an urgent need to study the effects of ENPs on humans and on the environment, in order to develop environmentally sustainable nanotechnologies.

## 3 Effects of Engineered Nanomaterials on Plants

Reports indicate that ENMs affect plants differently at the physiological, biochemical, nutritional, and genetic levels, while effects on growth, physiological and biochemical traits, production, and food quality, among other things, have been reported. However, our understanding of the dynamics of interactions between plants and ENMs is not clear enough yet (Rajput et al. 2018; De la Rosa et al. 2017; Rizwan et al. 2017; Zuverza-Mena et al. 2017). This review clearly confirms the existence of toxic effects of ENMs on cultivated crop plants through inhibition of seed germination, decreases in root and shoot lengths, reductions in photosynthesis and respiration rates, and morphological as well as enzymatic changes (Table 9.1). However, benefic effects of ENMs on plants have also been reported (Table 9.2).

**Table 9.1** Negative effects of different engineered nanoparticles (ENPs) on plant species

| Types and sizes (nm) of ENP | Species | Effects | Reference |
|---|---|---|---|
| $CeO_2$ (8) | *Triticum aestivum* | Root changes; decreased chlorophyll content and starch grain size in endosperm | Du et al. (2015) |
| CuO (100–200) | *Lactuca sativa* | Effects on seed germination, vigor index, and fresh weight; root length reduced by 49% | Hong et al. (2015) |
| CuO (0–80) | *Coriandrum sativum* | Effects on germination rate and shoot elongation | Zuverza-Mena et al. (2015) |
| CuO (<1200 to >2100) | *Daucus carota* | Reduced shoot biomass and restricted Cu accumulation in taproot periderm | Ebbs et al. (2016) |
| NiO (<100) | *Hordeum vulgare* | Decreased leaf surface, chlorophyll, and carotenoids | Soares et al. (2016) |
| ZnO (15) | *Triticum aestivum* | Reduced photosynthetic efficiency, inhibited antioxidant activity | Tripathi et al. (2017) |
| Ag (12 ± 9) | *Capsicum annuum* | Decreased plant growth | Vinkovic et al. (2017) |
| $AgNO_3$ (61.2 ± 33.9) | *Nicotiana tabacum* | Oxidative stress and changes in chloroplast size | Cvjetko et al. (2018) |
| CuO (<50) and ZnO (<100) | *Raphanus sativus* | Reduced root length, shoot length, and biomass | Singh and Kumar (2018) |

**Table 9.2** Positive effects of different engineered nanoparticles (ENPs) on plant species

| Types and sizes (nm) of ENP | Species | Effects | Reference |
|---|---|---|---|
| $TiO_2$ (25) | *Solanum lycopersicum* | Promoted plant height, root length, and biomass | Raliya et al. (2015) |
| Ag (200–800) | *Trigonella foenum-graecum* | Enhanced plant growth and diosgenin synthesis | Jasim et al. (2016) |
| $Fe_3O_4$ (17 ± 3.9) | *Zea mays* | Increased germination index | Li et al. (2016) |
| $Fe_2O_3$ (10) | *Solanum lycopersicum* | Increased root and shoot lengths with 50–200 mg $L^{-1}$ solution | Shankramma et al. (2017) |
| Cu-grown carbon nanofibers (95) | *Cicer arietinum* | Increased germination rate, shoot and root lengths, and chlorophyll and protein content | Ashfaq et al. (2017) |
| Nano-γPGA/ CS-$GA_3$ (134 ± 9) | *Phaseolus vulgaris* | Increased leaf area and induced root development (including lateral root formation) | Pereira et al. (2017) |
| $Ag^+$ bentonite (1.5) | *Avena byzantina* | Increase root growth | Tomacheski et al. (2017) |
| ZnO (NR) | *Gossypium hirsutum* | Increased plant growth, biomass, chlorophyll, carotenoids, protein content, superoxide dismutase, and peroxidase | Venkatachalam et al. (2017) |
| ZnO (NR) | *Carthamus tinctorius* | Increased guaiacol peroxidase, polypeptide oxidase, dehydrogenase, and malondialdehyde | Hafizi and Nasr (2018) |
| $TiO_2$ (28.78) | *Vicia faba* | Increased shoot length, leaf area, and root dry weight | Latef et al. (2018) |

*γPGA* poly(γ-glutamic acid), *CS* chitosan, *NR* not reported.

## *3.1 Effects of Engineered Nanomaterials on Common Bean (***Phaseolus vulgaris** *L.)*

### 3.1.1 Experimental Site

This study was carried out in a greenhouse at the Programa de Sustentabilidad de los Recursos Naturales y Energía del Cinvestav-Saltillo, located in Saltillo, Coahuila, Mexico. According to the Köppen climate classification, this area has a semiarid hot climate (BSh). According to the United Nations Food and Agriculture Organization and the United Nations Educational, Scientific, and Cultural Organization (FAO/UNESCO) soil classification system, the soil is a haplic xerosol.

### 3.1.2 Biological Materials

Common bean seeds were donated by INIFAP-Celaya, Mexico. All seeds were kept in the dark at 4 °C until use.

### 3.1.3 Nanomaterials

Nanoparticles of magnetite, ferrihydrite, and hematite were manufactured, while nanoparticles of zinc oxide and titanium dioxide were purchased from Materiales Nanoestructurados SA de CV (San Luis Potosí, Mexico). The crystallographic system is cubic for magnetite, tetragonal for zinc oxide and hexagonal for ferrihydrite, hematite, and titanium dioxide. X-ray diffraction was conducted to verify the pure phase samples, and the magnetic properties of the samples were measured using a MicroMag™ 2900 Alternating Gradient Magnetometer.

### 3.1.4 Cultivation of Plants in the Greenhouse

The full experimental setup was repeated three times. The first experiment was carried out from January to May 2013, the second one from February to June 2013, and the third one from March to July 2013. Sixty subsamples of 3500 g of soil [i.e., five kinds of nanoparticle (nano-$Fe_3O_4$, nano-$FeOOH \cdot xH_2O$, nano-$\alpha$-$Fe_2O_3$, nano-ZnO, and nano-$TiO_2$) in triplicate × four concentrations] were added to square plastic pots whose length × width × height were 17 × 15 × 17 cm. Five treatments (nanoparticles) at four concentrations (0, 1, 3, and 6 g $L^{-1}$) were applied to the soil during irrigation, so we sprayed each plastic pot with 500 mL of a 0, 1, 3, or 6-g $L^{-1}$ nanoparticle suspension throughout the experiment. Three seeds of common bean were planted in 180 plastic pots [i.e., five nanoparticles in triplicate × four concentrations in three experiments]. The seeds were placed at a 2-cm depth in each plastic pot. Five days after planting, the seedlings were thinned to one plant per plastic pot. The plastic pots were placed in the greenhouse for 120 days. A plastic container was placed under each plastic pot to collect drained liquid. However, the irrigation was well controlled, so no leaching was observed. Thirty, 60, and 120 days after sowing, three plastic pots were selected at random from each treatment and each concentration. The entire soil column was removed from the plastic pot, and samples were taken from the 0- to 7.5-cm depth and from the 7.5- to 15-cm depth, with care so as not to damage the root structure. The roots were separated from the shoots, and the root and shoot length were measured. The roots and shoots were dried at 70 °C, weighed, and analyzed for Ti, Fe, Zn, and total N. The soils from the 0- to 7.5-cm and 7.5- to 15-cm depths were analyzed for pH, electrical conductivity (EC), Ti, Fe, and Zn. The amount of chlorophyll was quantified every 2 days after sowing, beginning on day 15. The temperature and moisture content inside the greenhouse during the experiment were 24 °C and 35–45%, respectively.

### 3.1.5 Chemical Analyses

The pH was measured in 1:2.5 soil or wastewater sludge/$H_2O$ suspension, using a 716 DMS Titrino pH meter (Metrohm Ltd., Herisau, Switzerland) fitted with a glass electrode. The EC was determined in a 1:5 soil/$H_2O$ suspension. The organic C in the soil was measured using a TOC-VCSH total organic carbon analyzer (Shimadzu, Columbia, MD, USA). The inorganic C was determined by adding 5 mL of 1-M hydrogen chloride (HCl) solution to 1 g of air-dried soil and trapping the evolved $CO_2$ in 20 mL of 1-M NaOH. The total N in the soil, root, and shoot was measured by the Kjeldahl method using concentrated $H_2SO_4$, $K_2SO_4$, and $CuSO_4$ to digest the sample. The soil particle size distribution was defined by the hydrometer method. The water-holding capacity (WHC) was measured in 6.5 kg of soil placed in a polyvinyl chloride (PVC) tube (length 50 cm, diameter 16 cm), water saturated, stoppered with a PVC ring, and left to stand overnight to drain freely (WHC = [(water-saturated soil − soil dried at 105 °C)/soil dried at 105 °C] × 1000). The amount of chlorophyll was measured with a Minolta SPAD-502 chlorophyll meter. Fe, Ti, and Zn were determined by inductively coupled plasma mass spectrometry (ICP–MS).

### 3.1.6 Statistical Analyses

The data were subjected to an analysis of variance (ANOVA) and means were compared with the Tukey test, using Statistical Analysis System (SAS) software version 8.0 for Windows. Soil and plant characteristics were subjected to one-way ANOVA using a general linear model procedure (PROC GLM) to test for significant differences ($p < 0.05$) between treatments. The methodology used for the principal component analysis (PCA) has previously been described by Fernandez-Luqueno et al. (2016) and Medina-Pérez et al. (2018). All analyses were performed using the SAS statistical package. All data presented are the means of three replicates in soil from three different plots, and the whole experiment was repeated three times ($n = 27$) with sampling after 30, 60, and 120 days.

### 3.1.7 Results and Discussion

None of the five kinds of nanoparticle used in this experiment (magnetite, ferrihydrite, hematite, zinc oxide, and titanium dioxide) significantly modified the chlorophyll content of common bean plants, as evidenced by the Soil Plant Analysis Development (SPAD) unit values (see Fig. 9.2). However, the nanoparticles of magnetite, ferrihydrite, hematite, zinc oxide, and titanium dioxide significantly modified at least one plant characteristic or one yield component of common bean. The nanoparticles containing Fe (magnetite, ferrihydrite, and hematite) were those that significantly affected more crop characteristics such as the total N in the roots or shoots, number of pods, dry weight of pods, number of seeds, and yield of common bean. These findings are an important factor to take into account with regard to the applicability of nanoparticles for long-term use in crops, but selection of the most

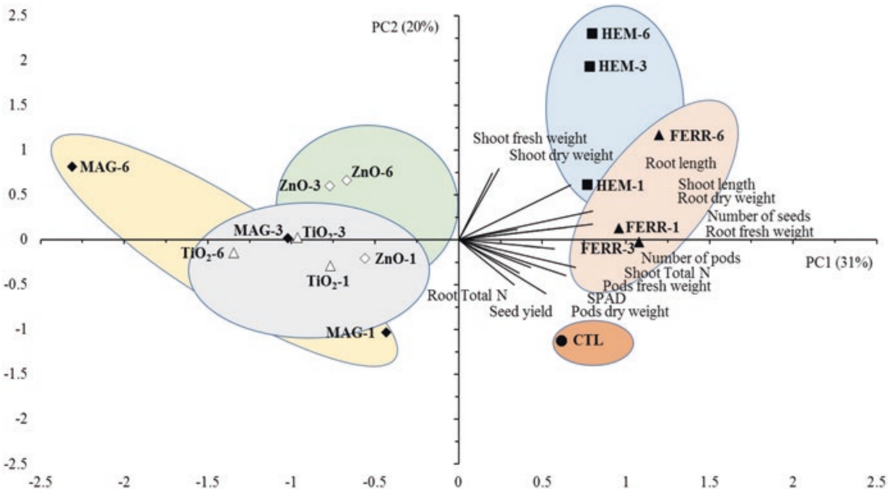


**Fig. 9.2** Principal component (PC) analysis of characteristics of bean plants (*Phaseolus vulgaris* L.) cultivated in agricultural soil irrigated with 500 mL of a 0, 1, 3, or 6-g $L^{-1}$ nanoparticle suspension. Nanoparticles of $Fe_3O_4$, $FeOOH·xH_2O$, α-$Fe_2O_3$, ZnO, and $TiO_2$ were used. The data are the mean values from three square plastic pots with 3.5 kg of dry soil in each one, with three different soils and three experiments (i.e., $n = 27$). Each whole experiment lasted for 120 days. The first two factors explained 51% of the variation. *CTL* control, *FERR-1* 500 mL of a 1-g $FeOOH·xH_2O$ nanoparticle suspension, *FERR-3* 500 mL of a 3-g $FeOOH·xH_2O$ nanoparticle suspension, *FERR-6* 500 mL of a 6-g $FeOOH·xH_2O$ nanoparticle suspension, *HEM-1* 500 mL of a 1-g α-$Fe_2O_3$ nanoparticle suspension, *HEM-3* 500 mL of a 3-g α-$Fe_2O_3$ nanoparticle suspension, *HEM-6* 500 mL of a 6-g α-$Fe_2O_3$ nanoparticle suspension, *MAG-1* 500 mL of a 1-g $Fe_3O_4$ nanoparticle suspension, *MAG-3* 500 mL of a 3-g $Fe_3O_4$ nanoparticle suspension, *MAG-6* 500 mL of a 6-g $Fe_3O_4$ nanoparticle suspension, *SPAD* Soil Plant Analysis Development, *$TiO_2$-1* 500 mL of a 1-g $TiO_2$ nanoparticle suspension, *$TiO_2$-3* 500 mL of a 3-g $TiO_2$ nanoparticle suspension, *$TiO_2$-6* 500 mL of a 6-g $TiO_2$ nanoparticle suspension, *ZnO-1* 500 mL of a 1-g ZnO nanoparticle suspension, *ZnO-3* 500 mL of a 3-g ZnO nanoparticle suspension, *ZnO-6* 500 mL of a 6-g ZnO nanoparticle suspension

appropriate nanoparticles at the most appropriate concentration is important for realization of greater benefits and agrosustainability. Additionally, there is a need to generate more data on chronic effects of long-term and concentrated exposure of plants to nanoparticles, as this is important for better understanding of the potential hazards or risks of these nanoparticles. More studies are also needed to identify the greatest potential of nanoparticles in the rural sector and in the agro-food industry worldwide.

### 3.2 *Effects of Engineered Nanomaterials on Maize (Zea mays L.)*

The experimental site, biological materials, nanomaterials, procedures for cultivation of plants in the greenhouse, chemical analyses, and statistical analyses were similar to those described in Sect. 3.1.

#### 3.2.1 Results and Discussion

Magnetite, ferrihydrite, and hematite significantly modified the chlorophyll content of maize plants, as evidenced by the SPAD unit values, while zinc oxide and titanium dioxide did not significantly modify any plant characteristic or yield component at the physiological maturity of the crop (see Fig. 9.3). The nanoparticles containing Fe (magnetite, ferrihydrite, and hematite) were those that significantly increased crop characteristics such as the total N in the roots or shoots, but not the yield of maize.

## 4 Effects of Engineered Nanomaterials on Earthworms

Earthworms live in almost all kinds of soil worldwide and may represent 60–80% of the total soil biomass. Earthworms play a key role in soil ecosystems because they contribute to pedogenesis, water regulation, nutrient cycling, aeration, removal of contaminants, and soil structure formation. Although earthworms accelerate the removal of organic and inorganic pollutants from soils, their activity may be inhibited when excessive amounts of pollutants are discarded in their habitat.

Despite the large amount of research into the potential applications of nanotechnology conducted in recent years, relatively little has been done to assess the potential risks of nanoparticles for earthworms. Stewart et al. (2013) stated that chemical modification of cadmium selenide QDs protected *Eisenia andrei* and reduced the bioaccumulation of nanoparticles by earthworms. Other experiments on the nanotoxicity of nanoparticles to *E. andrei* were carried out by Romero-Freire et al. (2017). They reported that survival, weight change, and reproduction were affected

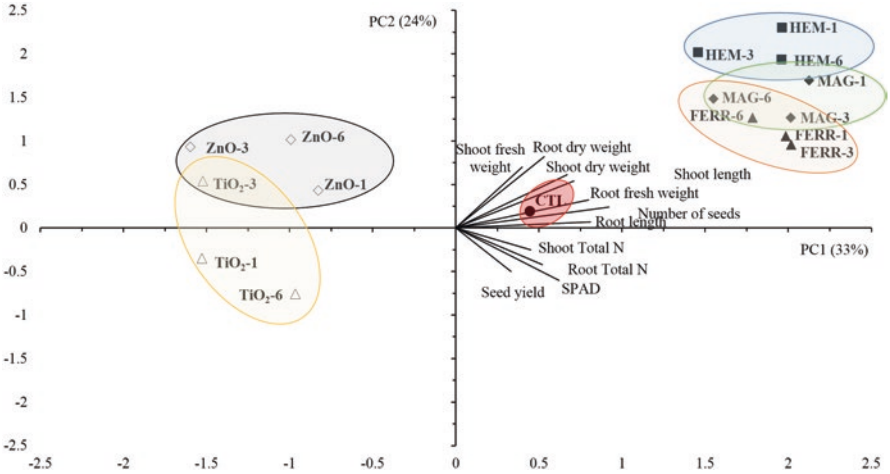


**Fig. 9.3** Principal component (PC) analysis of characteristics of maize (*Zea mays* L.) cultivated in agricultural soil irrigated with 500 mL of a 0, 1, 3, or 6-g $L^{-1}$ nanoparticle suspension. Nanoparticles of $Fe_3O_4$, FeOOH·$x$$H_2O$, α-$Fe_2O_3$, ZnO, and $TiO_2$ were used. The data are the mean values from three square plastic pots with 3.5 kg of dry soil in each one, with three different soils and three experiments (i.e., $n = 27$). Each whole experiment lasted for 120 days. *CTL* control, *FERR-1* 500 mL of a 1-g FeOOH·$x$$H_2O$ nanoparticle suspension, *FERR-3* 500 mL of a 3-g FeOOH·$x$$H_2O$ nanoparticle suspension, *FERR-6* 500 mL of a 6-g FeOOH·$x$$H_2O$ nanoparticle suspension, *HEM-1* 500 mL of a 1-g α-$Fe_2O_3$ nanoparticle suspension, *HEM-3* 500 mL of a 3-g α-$Fe_2O_3$ nanoparticle suspension, *HEM-6* 500 mL of a 6-g α-$Fe_2O_3$ nanoparticle suspension, *MAG-1* 500 mL of a 1-g $Fe_3O_4$ nanoparticle suspension, *MAG-3* 500 mL of a 3-g $Fe_3O_4$ nanoparticle suspension, *MAG-6* 500 mL of a 6-g $Fe_3O_4$ nanoparticle suspension, *SPAD* Soil Plant Analysis Development, *$TiO_2$-1* 500 mL of a 1-g $TiO_2$ nanoparticle suspension, *$TiO_2$-3* 500 mL of a 3-g $TiO_2$ nanoparticle suspension, *$TiO_2$-6* 500 mL of a 6-g $TiO_2$ nanoparticle suspension, *ZnO-1* 500 mL of a 1-g ZnO nanoparticle suspension, *ZnO-3* 500 mL of a 3-g ZnO nanoparticle suspension, *ZnO-6* 500 mL of a 6-g ZnO nanoparticle suspension

by both Zn-NP and $ZnCl_2$, but they could not explain the differences in earthworm toxicity. Similar studies were done by Swiatek et al. (2017) to evaluate the effects of Zn-NP or $ZnCl_2$ on reproduction of *E. andrei*, but zinc was efficiently regulated by the earthworms in all treatments.

*Enchytraeus crypticus* has been also studied to determinate the toxicity of ZnO-NP to annelids (Hrda et al. 2016). It was found that toxicity was clearly dependent on the size of the ZnO-NP agglomerates and the technique used for exposure medium preparation, but it was not correlated with the ZnO-NP concentration. The survival and composition of the gut microflora of *Eisenia fetida* grown in soil polluted with Zn-NP have been also analyzed (Yausheva et al. 2016). It was reported that Zn-NP decreased the diversity of bacteria belonging to the taxon Firmicutes and increased the proportion of Proteobacteria. Other authors have found evidence regarding ENM toxicity to earthworms in soils (Table 9.3).

**Table 9.3** Effects of different engineered nanoparticles (ENPs) on earthworm species

| Types and sizes (nm) of ENP | Species | Effects | Reference |
|---|---|---|---|
| $TiSiO_4$ (<50) | *Eisenia andrei* and *Folsomia candida* | No effect on either species | Bouguerra et al. (2017) |
| $MoO_3$ (92 ± 0.3) | *Eisenia fetida* | Mortality and decreased weight | Lebedev et al. (2016) |
| C-nZVI (NR) | *Eisenia fetida* | No effect | Yirsaw et al. (2016) |
| $AgNO_3$ (NR) | *Allolobophora chlorotica* | Mortality | Brami et al. (2017) |
| Ag-NP (30 ± 2) and $AgNO_3$ (34 ± 3) | *Eisenia andrei* | Reduced number of juveniles; cocoons not viable (not hatched) | Jesmer et al. (2017) |
| ZnO and $ZnCl_2$ (20–40 nm) | *Eisenia andrei* | Effects on survival, weight, and reproduction | Romero-Freire et al. (2017) |

*Ag-NP* silver nanoparticles, *C-nZVI* coated nanoscale zero-valent iron, *NR* not reported

## *4.1 Effects of Nanoparticles of Hematite, Zinc Oxide, and Titanium Dioxide on* Eisenia fetida

The experimental site and nanomaterials used in this experiment were similar to those described in Sects. 3.1 and 3.2.

### 4.1.1 Soil Preparation

The soil was taken to the laboratory and passed separately through a 5-mm sieve, adjusted to 40% WHC by addition of distilled water ($H_2O$), and conditioned at 22 ± 2 °C for 10 days in drums containing a beaker with 1000 mL of 1-M sodium hydroxide (NaOH) solution to trap the evolved $CO_2$, and a beaker with 1000 mL of distilled $H_2O$ to avoid desiccation of the soil. After this process, the soil was tyndallized.

### 4.1.2 Vermicompost Preparation

The vermicompost used to feed the earthworms was obtained from the worm culture maintained at our facility for 2 months, which was kept on precomposted organic material bedding. Thereafter, the material obtained was tyndallized to remove any organisms that could be harmful to the earthworms.

### 4.1.3 *Eisenia fetida* Culture

All earthworms used in the present study came from a culture of *E. fetida* maintained at our facility. The culture is kept on bedding of precomposted organic kitchen waste.

### 4.1.4 Experimental Setup

One hundred and sixty-eight subsamples of 200 g of dry soil [i.e., 14 treatments in triplicate × four destructive sample dates (0, 20, 40, and 60 days after the onset of the experiment)] were added to 900-mL amber glass jars (length 18 cm, diameter 10 cm). $\alpha$-$Fe_2O_3$-NP, ZnO-NP, or $TiO_2$-NP were applied to the soil at three increasing concentrations (0.0, 0.15, and 0.3 g $kg^{-1}$ of dry soil), so six chemical suspensions of nanoparticles were prepared (three nanoparticle types × two concentrations) in distilled water, and they were sonicated for 30 min before use; after the sonication the nanoparticle suspensions were added to the earthworm food (vermicompost or Quaker® oats), and after the food was added it was completely mixed with the soil. The experiment was carried out under plant growth chamber conditions; the average temperature was 22 ± 2 °C, and the photoperiod was 12 h light and 12 h dark. In a completely randomized design, each experimental unit was prepared, incubated, and sampled independently. Ten *E. fetida* earthworms were used in each experimental unit of this research. At the onset of the experiment, 35 g of dry vermicompost was added to each amber glass jar to feed the earthworms. Additionally, 30 and 50 days after the onset of the experiment, 35 g of tyndallized Quaker® oats was added to feed the earthworms. Fourteen treatments were applied to the soil. The aerobic incubation experiment lasted for 60 days, in which four destructive and random samplings were performed on days 0, 20, 40, and 60. On each sampling day, adult earthworms, cocoons, and juveniles were hand sorted and counted.

### 4.1.5 Chemical Characterization of Soil, Vermicompost, and Biochemical Analyses

The methodologies used for chemical analysis of the soil, vermicompost, and earthworms were similar to those described in Sects. 3.1 and 3.2.

### 4.1.6 Data Analysis and Statistical Methods

The methodologies used for statistical analysis were similar to those described in Sects. 3.1 and 3.2. All data presented are the means of three replicates × four destructive sample dates (0, 20, 40, and 60 days after the onset of the experiment) × two consecutive experiments carried out in a plant growth chamber (i.e., $n = 24$).

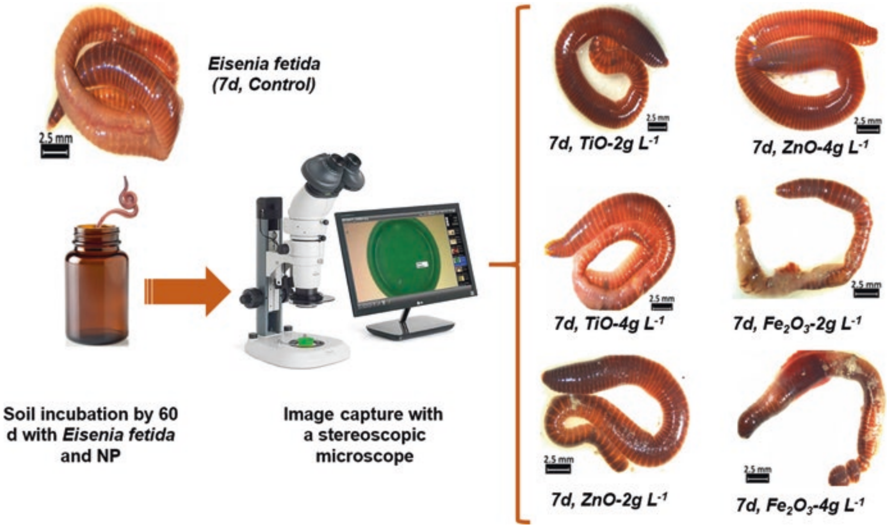


**Fig. 9.4** Physical damage in the body of *Eisenia fetida* at 7 days after treatment with nanoparticles (NP)

### 4.1.7 Results and Discussion

Physical damage was detected in earthworms exposed to increasing doses of $Fe_2O_3$-NP. The main detected types of damage were inflammation and explosion in certain areas of the earthworm's body at 14 days after the onset of the experiment (Fig. 9.4). Seven days after the onset of the experiment, earthworms treated with $Fe_2O_3$-NP died.

Hu et al. (2010) evaluated the toxicity of nanoparticles of $TiO_2$ and ZnO to the earthworm *E. fetida* in soil. Artificial soil systems containing distilled water and 0.1, 0.5, 1.0, or 5.0 g $kg^{-1}$ of nanoparticles were prepared, and earthworms were exposed for 7 days. It was found that Ti and Zn were bioaccumulated and that mitochondria were damaged at the highest dose in soil (5.0 g $kg^{-1}$). The activity of cellulase was significantly inhibited when organisms were exposed to 5.0 g $kg^{-1}$ of ZnO nanoparticles. This study demonstrated that both $TiO_2$-NP and ZnO-NP exert harmful effects on *E. fetida* when their levels are higher than 1.0 g $kg^{-1}$ in soil, and the toxicity of ZnO-NP was greater than that of $TiO_2$-NP.

## 5 Effects of Engineered Nanomaterials on Microorganisms

The broad variety of applications of ENMs has led to their unusual and widespread distribution in several environmental sectors, with different effects on living organisms. ENMs applied for in situ remediation of water or soil inevitably interact with various microbes at the remediation sites directly or indirectly (Xie et al. 2017;

Lefevre et al. 2016). Studies that refer to microbial communities are central not only in soil sciences but also in all related disciplines. This last statement requires knowledge of which microorganisms are responsible for specific processes. According to Blagodatskaya and Kuzyakov (2013), microbial communities in soils consist of an extensive range of organisms in four physiological states: (1) active; (2) potentially active; (3) dormant; and (4) dead.

To date, over 80,000 species of fungi have been described that live in soil, but many more remain undiscovered, considering that the total fungal diversity is estimated at 1.5 million species (Hawksworth 1991). It is well known that 1 g of soil may contain approximately one million individual fungi, while the fungal biomass may amount to 2.5–5 t $ha^{-1}$.

In agricultural soils, most of the biological activity occurs in the top 20 cm (the plow layer), while in noncultivated soils, most of the biological activity occurs in the top 5 cm of soil. Diversity of soil organisms is essential for the maintenance of productive soils because soil organisms are responsible for a range of ecological functions and ecosystem services. Therefore, excessive reduction of species with critical features might result in severe effects, including long-term degradation of soils, changes in the landscape, decreasing soil resilience, and loss of agricultural productivity. It has to be remembered that soil health, soil quality, and soil resilience are all fundamental to sustain the productivity and viability of agricultural systems throughout the world.

Microbial communities play a significant and relevant role regarding greenhouse gas (GHG) emissions worldwide. GHG emissions result from complex interactions between abiotic drivers and multiple microbial metabolic processes. Mechanisms controlling $CO_2$, $CH_4$, and $N_2O$ production have been well characterized in both oxisol and permafrost (i.e., in all types of soil worldwide).

In the last decade, several publications have reported fragments of information about the interaction, detection, uptake, and translocation of ENMs in microorganisms, and several papers have described negative effects of ENMs on microbial communities (Table 9.4).

## *5.1 Microbial Communities in a Soil Amended with Engineered Nanomaterials*

The experimental site, nanomaterials, chemical analyses, and statistical analyses were similar to those described in Sect. 3.1.

## *5.2 Experimental Setup and Treatments*

The soil was taken to the greenhouse, sieved (<5 mm), air dried, and characterized. One week before the onset of the experiment, the soil was divided into two equal parts and adjusted to field capacity by addition of distilled water ($H_2O$). Half of the

**Table 9.4** Negative effect of different engineered nanoparticles (ENPs) on soil microorganisms

| Types and sizes (nm) of ENP | Species | Effects | Reference |
|---|---|---|---|
| Ag (1–10) | *Acidobacteriaceae bacterium* Ellin5095 (AY234512.1), *Acidobacteriaceae bacterium* Ellin311 (AF498693.1), *Acidobacteriaceae bacterium* Ellin310 (AF498692.1), and other species | Decreased microbial community | Carbone et al. (2014) |
| ZnO (17) | *Acinetobacter baumanni*, *Escherichia coli*, *Klebsiella pneumonia*, *Proteus mirabilis*, *Pseudomonas aeruginosa*, *Salmonella typhi*, and other microorganisms | Ultrastructural changes | Aal et al. (2015) |
| $TiO_2$ (15) and $CeO_2$ (10) | *Azotobacter* | Reduced abundance of functional bacteria and enzymatic activity | Chai et al. (2015) |
| Ag (20) | Different microorganisms in *Zea mays* rhizosphere | Effects on community composition | Sillen et al. (2015) |
| $Fe_3O_4$ (NR) | AMF in *Zea mays* rhizosphere | Decreased soil bacterial abundance and community composition shifted | Cao et al. (2016) |
| Ag (50) | *Nitrosomonas europea* | Damaged cell wall of *N. europea*, disintegrated nucleoids, and condensed next to cell membrane | Wang et al. (2017) |

*AMF* arbuscular mycorrhizal fungi, *NR* not reported

soil was adjusted to 40% WHC (considered the conditioned soil samples) and pre-incubated for 7 days in drums containing a beaker with 1000 mL of 1-M NaOH solution to trap the evolved $CO_2$, and a beaker with 500 mL of distilled $H_2O$ to avoid desiccation of the soil. The drums were opened every day to avoid anaerobic conditions. Thereafter, 20 g of soil was amended with ENMs (nano-$Fe_3O_4$, nano-ZnO, or nano-$TiO_2$) at 0, 1, 3, and 6 g $kg^{-1}$ of dry soil. After 0, 30, 60, and 90 days, three soil subsamples were selected at random from each treatment and plot ($n = 9$) and the number of viable soil microorganisms (i.e., heterotrophic bacteria, fungi, and actinomycetes) was determined as colony-forming units (CFUs).

The numbers of heterotrophic bacteria and actinomycetes were determined by culturing in a mineral salt medium, while fungi were counted using the Martin medium. Culture media were prepared in sterile conditions, autoclaved, and poured into the petri dish bottom. We used the standard plate count technique to determine the number of microorganisms. Bacteria and actinomycetes were counted in $10^{-3}$, $10^{-4}$, $10^{-5}$, and $10^{-6}$ dilutions, while fungi microorganisms were counted in $10^{-3}$, $10^{-4}$, and $10^{-5}$ dilutions.

### 5.3 Results and Discussion

The CFUs of bacteria and actinomycetes decreased significantly, modified by ENMs (Fig. 9.5a, b). However, ZnO-NP increased the CFU of fungi. Asadishad et al. (2018) stated that $TiO_2$-NP slightly decreased enzyme activity in agricultural soil. However, they also found that Illumina MiSeq sequencing of microbial communities indicated a shift in soil microbial community composition upon exposure to high doses of metal ions or Ag-NP, and a negligible shift in the presence of $TiO_2$-NP. In another study, ZnO-NP demonstrated adverse effects on C transformations (but not on N transformations) and adverse effects on dehydrogenase and phosphatase activities in natural soil (Garcia-Gomez et al. 2015).

Liu et al. (2018) studied the impact of wastewater effluent (WE) containing aged nanoparticles. They established a soil microecosystem including a microbiome, four *Arabidopsis thaliana* plants, and three *E. fetida* earthworms, for a duration of 95 days. Although the microbial biomass, carbon, and nitrogen were not significantly reduced, the population distribution of the microbial communities was shifted in WE-irrigated soil compared with the control soil. The abundance of cyanobacteria (cyanophyta) was increased by 12.5% in the WE-irrigated soil, manifested mainly by an increase in *Trichodesmium* spp., and the abundance of unknown archaea was increased from 26.7% in the control soil to 40.5% in the WE-irrigated soil (Liu et al. 2018).

Enough evidence has been found that ENMs significantly modify microbial communities in soils and also change some parameters of other soil organisms such

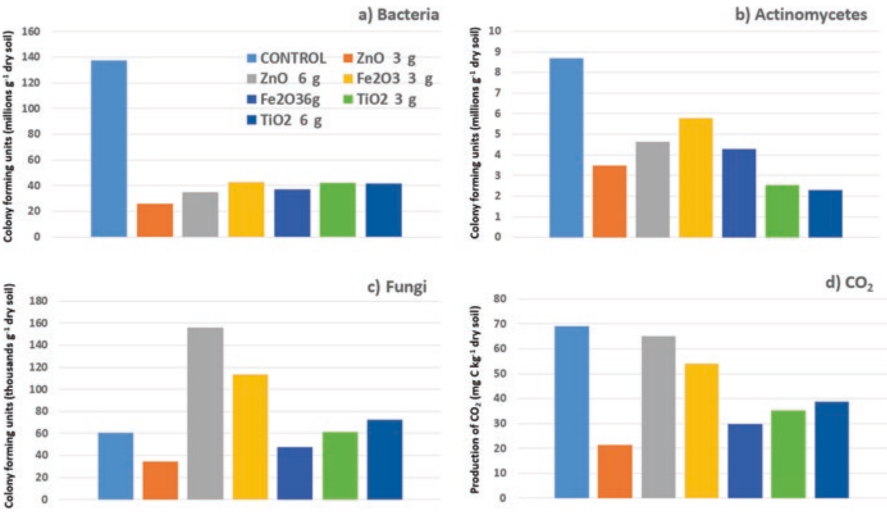


**Fig. 9.5** Colony-forming units of soil microorganisms and production of $CO_2$. (**a**) Bacteria. (**b**) Actinomycetes. (**c**) Fungi. (**d**) Production of $CO_2$. The data were pooled for four sampling dates in triplicate × three soil sites (i.e., $n = 36$)

as plants or earthworms. Therefore, regulations regarding the use of ENMs and their spread in the environment must be implemented to avoid damage to ecological or human health.

## 6 Conclusion

Overall, the available knowledge indicates an urgent need to synthesize environmentally sustainable ENMs. In addition, it is suggested that precise and standardized tests should be utilized to assay the long-term effects of acute and chronic exposure to different nanoparticles existing in food systems before mass production and utilization of nanoparticles in the food industry or in emerging technologies, in order to avoid the spread of unregulated or untested ENMs.

Some nanoparticles could have harmless applications. For instance, an evaluation of studies of biologically active nanoparticles provides guidance for the synthesis of nanoparticles with the goal of developing new antibiotics/antifungals to combat microbial resistance. However, the current information leaves no doubt that there are still many aspects in need of additional investigations for us to fully understand the effects of ENMs in organisms. In plants and other organisms of agronomic interest, little is known about the transgenerational effects of ENM exposure and the changes at the agronomical and physiological levels.

Since ENMs have been found in edible tissues, it is expected that they will be present in the food chain; thus, studies on their trophic transfer are required. Overall, nanoscience and nanotechnology require transdisciplinary work by scientists from different areas to study the potential toxicity of ENMs prior to their use or spread in ecosystems.

**Acknowledgements** This research was funded by Ciencia Básica SEP-CONACYT project numbers 151881 and 287225, the Sustainability of Natural Resources and Energy Programs (Cinvestav-Saltillo), and Cinvestav-Zacatenco. G.M.-P., H.P.-H., G.S.-H., and A.Z.-C. received grant-aided support from Becas CONACYT. F.F.-L., R.G.C.-M., F.L.-V., E.V.-N., and S.L.-S. received grant-aided support from Sistema Nacional de Investigadores (SNI), Mexico.

**Competing interests** The authors declare that they have not competing interests.

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# Chapter 10
# Engineered Nanoparticles: Are They an Inestimable Achievement or a Health and Environmental Concern?

**Sein León-Silva, Fabián Fernández-Luqueño, and Fernando López-Valdez**

**Abstract** Inorganic particles often exhibit novel and outstanding properties as their size approaches nanosize dimensions. The synthesis of these nanoengineered materials with specific composition, architecture, and functionality, and their uses in diverse fields, are changing paradigms. In this chapter we highlight the application of a lot of nanoparticles in biology, medicine, and biomedical engineering, and some concerns regarding human and environmental health are also discussed. There are two approaches to nanoparticle development and application for health care purposes: the bottom-up (science-driven) approach and the top-down (regulation-driven) approach, but neither of these has been able to demonstrate health care benefits without toxicological side effects. Consequently, nanoparticle toxicity has to be assessed, and the standardization of techniques should be set by scientists and decision makers worldwide. Cutting-edge knowledge regarding the interactions between nanoparticles and human health has to move forward, but environmental quality and social welfare must also be ensured.

**Keywords** Biocompatibility and toxicity · Current challenge · Drug delivery · Environment pollution · Human disease · Modern medicine · Molecular diagnostics · Sustainable development

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F. López-Valdez, F. Fernández-Luqueño (eds.), *Agricultural Nanobiotechnology*, https://doi.org/10.1007/978-3-319-96719-6_10

## 1 Introduction

Engineered nanoparticles are intentionally designed with at least one dimension ranging from 1 to 100 nm, and they are produced to be applied in several fields such as environmental remediation, materials science, catalysis, electronic devices, cosmetics, pharmaceuticals, biomedicine, energy, and food production (Angeli et al. 2008; Logothetidis 2012; Nie et al. 2007; Qu et al. 2013; Rashidi and Khosravi-Darani 2011; Shi et al. 2010; Smith et al. 2013; Song and Kim 2009; Sozer and Kokini 2009). Among the various existing nanomaterials, inorganic nanoparticles are especially important for current developments because they exhibits novel properties as their size approaches the nanometer scale (1 nm = $10^{-9}$ m), such as superconductivity (Iijima 2002; Shi et al. 2012), superparamagnetism (Vatta et al. 2006), ultrahardness (Lamni et al. 2005), thermal resistance (Miyake et al. 2013), optical performance (Kelly et al. 2003), anticorrosive properties (Hamdy and Butt 2007), photocatalytic properties (Evanoff and Chumanov 2005; Tong et al. 2012), and antibacterial properties (Chen and Chiang 2008), which are some of the most commonly used properties.

Inorganic nanoparticles can be easily synthesized, characterized, and industrially produced; they can also be quickly integrated into several applications (Baker et al. 2005; Evanoff and Chumanov 2005; Gehrke et al. 2015; Hwang et al. 2000; Piccinno et al. 2012). This is possible by controlling the shape, size, and structure of their inorganic core, and selectively linking active molecules to the nanoparticle surface, allowing them to interact with different biological materials or environmental systems.

In this context, because of the various properties and effects of inorganic nanoparticles on the materials' surface, human and environmental organisms can easily be exposed to them through respiration, ingestion, or the dermal route (Reidy et al. 2013; Tinkle et al. 2003), with potential side effects and various implications for health and safety. Actually, many investigations have studied the toxicity of inorganic nanoparticles in cell lines and animal models; nevertheless, their conclusions have often been contradictory, with results depending on controlled conditions (Alt et al. 2004; Braydich-Stolle et al. 2005; Hussain et al. 2005; Kathiresan et al. 2009). Therefore, there is a lack of comprehensive regulation and no assessment framework to manage the complete life cycle of nanomaterials, from their manufacture to their distribution, storage, exposure/dosage, and final disposal (Fig. 10.1). To address this concern, appropriate in vivo toxicological studies should be performed to identify, evaluate, and regulate human and environmental exposure limits and disposal before use of nanoparticles is scaled up into commercial products (Liu and Jiang 2015). Additionally, in a complex system, biological interactions such as immune responses, absorption, and agglomeration—as well as physicochemical properties such as particle size, shape, surface charge, concentration, stability, surface chemistry, and storage time (León-Silva et al. 2016)—must be considered for understanding of the complete toxicity mechanisms and determination of ecotoxicological potential.

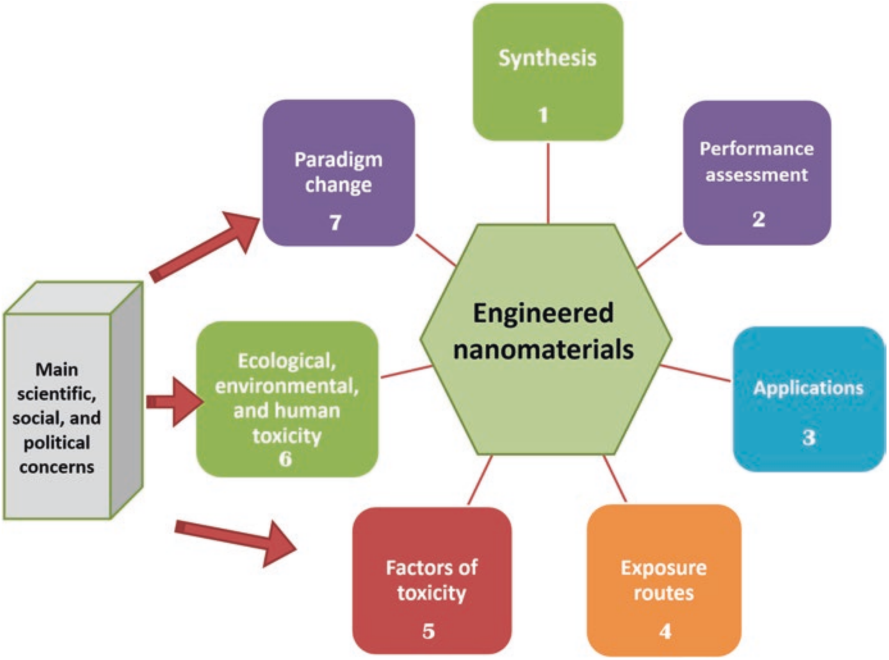


**Fig. 10.1** Production and uses of engineered nanoparticles, and the main concerns regarding them

## 2 Nanoparticles in Biology, Medicine, and Biomedical Engineering

Within the diverse application areas of nanotechnology, biological sciences (including biomedical engineering and medicine) have benefited considerably from the introduction of nanomaterials in the preventive branch of medicine and in prevention of biological complications. Nanotechnology has become a powerful tool for treatment and diagnosis applications (Angeli et al. 2008; Shenava et al. 2015; Shi et al. 2010). With the addition of the unique properties of inorganic nanoparticles to cells, diseases may be managed or cured at the appearance of the first symptoms. In other words, diagnosis of illness could become more precise and accurate, avoiding severe complications (Marchesan and Prato 2013). Additionally, nanomaterials are helpful in the transport of medicines to specific parts of the body, making possible the alteration of damaged cells and transformation of genes, to improve the function of specific cells (Panyam and Labhasetwar 2003).

Certain subdisciplines of nanomedicine such as ethics, drug delivery, and genetics (Fig. 10.2) need to define the current "state of the art" so that we can advance toward cutting-edge knowledge. However, areas such as toxicology, the legal framework, and sustainable development have to be taken into account.

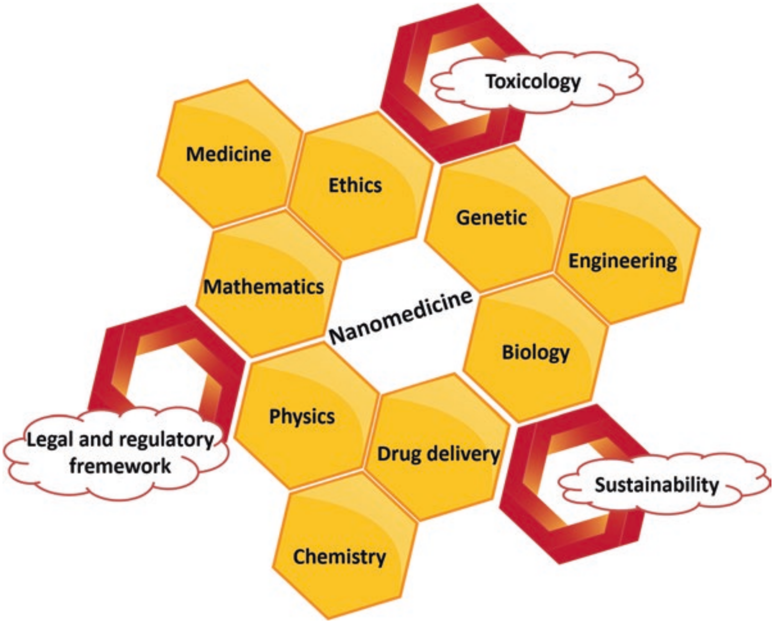


**Fig. 10.2** Nanomedicine and its subdisciplines. The *red hexagons* highlight three strongly related areas that are seldom taken into account

Despite their different material properties, it has been found that mixing of some elements with nanoparticles increases their biological effects. Inorganic materials with cores composed of noble and magnetic metals (e.g., Au, Ag, Pt, and Pd), including their alloys and oxides (e.g., $Fe_3O_4$, Co, $CoFe_2O_4$, FePt, and CoPt), as well as semiconductors (e.g., CdSe, CdS, ZnS, $TiO_2$, PbS, InP, and Si) and compound nanostructures, have shown vast potential for application in many different areas of biomedicine such as gene therapy, drug delivery, tracking agents, regeneration of cells, diabetes and cancer healing, hyperthermia treatments, labeling, magnetic resonance imaging (MRI), and transmission electron microscopy (TEM) imaging (Bai et al. 2007; Chen and Schluesener 2008; Gong et al. 2007; Hwang et al. 2000; Krzyzewska et al. 2016; Nie et al. 2007; Sotiriou et al. 2011; Sperling et al. 2008).

As a result of the increasing functionality of inorganic nanomaterials, more than 1000 research articles have been published in the Web of Science within the last 5 years (https://apps.webofknowledge.com.access.biblioteca.cinvestav.mx), using a wide variety of nanoparticles, particularly silver, gold, palladium, platinum, silica, quantum dots, iron oxide, zinc oxide, and metal fluorides (Dastjerdi and Montazer 2010; Ladj et al. 2013; Sekhon and Kamboj 2010) (Table 10.1). For example, silver nanoparticles are commonly used to provide enhanced opportunities for drug delivery (Panyam and Labhasetwar 2003). Also, nanocrystalline quantum dots are used for applications in biomedical imaging and electro-optical devices (Bera et al. 2010). Additionally, gold nanoparticles are used for bioseparation, cancer therapy,

**Table 10.1** Principal properties of inorganic nanoparticles and their applications in biomedicine

| Type of nanoparticle | Property | Application |
|---|---|---|
| Iron oxide (FeO), cobalt (Co), nickel (Ni) | Superparamagnetic | – Sensor and diagnosis<br>– Drug delivery<br>– Photothermal therapy<br>– Magnetic resonance imaging (MRI) contrast agents |
| Gold (Au), silver (Ag), palladium (Pd), platinum (Pt) | Antimicrobial | – Optical imaging<br>– Photothermal therapy<br>– Antimicrobial coatings<br>– Drug delivery<br>– Biochemical sensing<br>– Cancer treatment |
| Silicon dioxide ($SiO_2$), quantum dots (QD), zinc oxide (ZnO), silica oxide ($SiO_2$) | Fluorescence | – Energy transfer for sensing and diagnosis<br>– High-resolution imaging |
| Zinc oxide (ZnO), quantum dots (QD), titanium dioxide ($TiO_2$) | Semiconductor | – Biosensor<br>– Photobleaching stability<br>– Imaging devices<br>– Detectors |

gene delivery, and immunoassay diagnostics (Ghosh et al. 2008; Saha et al. 2012; Sperling et al. 2008). According to Bobo et al. (2016), some key examples of nanomedicines (listed by material category) are polymeric nanoparticles, polymeric micelles, liposomal nanoparticles, protein nanoparticles, inorganic nanoparticles, and crystalline nanoparticles. In this chapter we discuss inorganic nanoparticles such as Ag-NP, Au-NP, Pd-NP, and Pt-NP.

## *2.1 Silver*

Since ancient times, silver has been used against infections and to prevent food spoilage (Suman et al. 2013). Silver nanoparticles (Ag-NP) can be synthesized by several routes and methods to obtain certain characteristics in terms of size, shape, and agglomeration (Panacek et al. 2006). By these processes, Ag-NP acquire unique electrical, optical, thermal, and antifungal properties, which are incorporated into products ranging from photovoltaics to electronics, medical devices, and chemical sensors (Abou El-Nour et al. 2010; Marambio-Jones and Hoek 2010; Nasrollahzadeh et al. 2014). In the biomedical area, Ag-NP are incorporated into a large number of consumer products that take advantage of the antibacterial effects of silver for therapeutic purposes (Prabhu and Poulose 2012; Shenava et al. 2015). The antibacterial mechanism of silver metal ions works by destroying the cell membrane and bonding the –SH group of the cellular enzymes, then as a consequence of the critical enzymatic decrease, the metabolism changes, inhibiting cell growth until the bacterium dies (Marambio-Jones and Hoek 2010; Prabhu and Poulose 2012).

The purposes of using Ag-NP in the medical and biomedical fields are to prevent bacterial infections and reduce inflammation. They are used as a coating for, or integrated into, contraceptive devices, female hygiene products, bone cement, wound dressings, surgical instruments, dental fillings, catheters, sutures, prostheses, and bandages (Furno et al. 2004; Silver et al. 2006). Additionally, Ag-NP are used in the treatment of diseases that requires specific drug delivery. Biosensing is another field of Ag-NP application; because of their plasmonic properties, they can detect several disorders and illnesses in the human body, such as cancer (Syed et al. 2013). Moreover, Ag-NP are harnessed in bioimaging for monitoring of dynamic reactions (Sekhon and Kamboj 2010). Also, Ag-NP are impregnated into different surgical instruments, such as dental instruments, or composites. For example, Ahn et al. (2009) used Ag-NP in orthodontic adhesives to increase their strength and resistance, and Furno et al. (2004) and Roe et al. (2008) developed polyurethane catheters with antibacterial coating to prevent infections. Moreover, Alt et al. (2004), Chaloupka et al. (2010), Durán et al. (2007), Li et al. (2006a), and Grunkemeier et al. (2006) integrated Ag-NP into surgical masks, cardiovascular heart valves, bone cements, and dressings for use in artificial prostheses and treatment of wounds, burns, and ulcers for prevention and treatment of bacterial infections.

## *2.2 Gold*

Gold nanoparticles (Au-NP) possess unique optoelectronic properties, high dispersibility, size uniformity, and catalytic properties, which have been utilized in photovoltaics, therapeutics, drug and gene delivery, sensory probes, biosensing, electrical conductors, and catalysis applications, among others (Ghosh et al. 2008; Panyala et al. 2009; Sperling et al. 2008). Additionally, the versatility of the properties of Au-NP enhances the possibility of their use in medical applications such as cancer treatment; through control of the size, shape, and surface of the particles, they can bind cysteine–lysine proteins, causing an antiangiogenic effect, which avoids tumor growth of cancer cells (Huang and El-Sayed 2010; Panyala et al. 2009).

Furthermore, the large surface area of Au-NP allows the possibility for them to be coated with therapeutic agents or antifouling polymers to serve as drug carriers to specific cells (Ghosh et al. 2008). Moreover, gold nanorods and nanoshells have the potential to enhance the contrast of blood vessels, mainly for use in MRI. Also, they can be heated by light, enabling them to eliminate targeted tumors; this process is called photodynamic or hyperthermia therapy (Huang and El-Sayed 2010). Other Au-NP applications in this field include diagnosis of heart diseases through detection of biomarkers and infectious agents (Mieszawska et al. 2013; Panyala et al. 2009). Also, they are used in a variety of sensors for detection of food spoilage or as substrates for chemical bonds (Sperling et al. 2008). Finally, Au-NP can produce dark field array colors, usually employed for biological imaging and probes in TEM (Wang and Ma 2009).

## 2.3 Palladium

Palladium nanoparticles (Pd-NP) are characterized by their catalytic and optical properties, which enable them to be used as a photothermal agent and drug activator. Serious drawbacks of this material are its high cost and its allergenicity in contact with skin, which restrict its application (Larese Filon et al. 2016). Nevertheless, in medicine, Pd-NP are used in dental appliances, as an antibacterial agent, and for cancer and microbial therapy (Adams et al. 2014). Because of their high photothermal efficiency, size, biocompatibility, and numerous applications in combined therapies, Pd-NP have become an attractive alternative for noninvasive cancer treatment. Also, Pd-NP-coated needles are used for treatment of prostate cancer and in choroidal melanoma brachytherapy (Blasko et al. 2000; Dumas and Couvreur 2015; Finger et al. 2002; Saldan et al. 2015).

Additionally, Pd-NP hold promise for use in biosensors; for example, Baccar et al. (2013) developed a chronoamperometric nonenzymatic sensor using various sizes of Pd-NP to detect hydrogen peroxide ($H_2O_2$) in milk. Also, Kowalska et al. (2013) developed a hydrogen sensor using Pd-NP; this makes use of the selective absorption of hydrogen, which forms palladium hydride. These Pd hydrides possess greater electrical resistance than other metals, allowing design of thick-film hydrogen sensors with increasing electrical resistance. Finally, Pd-NP are used to control water pollutants and emissions, such as emissions of halogenated compounds, and they are also used in the production of fuel cells (Long et al. 2013; Mackenzie et al. 2006).

## 2.4 Platinum

Platinum nanoparticles (Pt-NP) are another type of inorganic nanomaterial, which displays excellent catalytic properties and antioxidant properties. In the biomedical field, Pt-NP are commonly used in consumer products such as cosmetics and supplements (Shibuya et al. 2014). Also, Pt-NP have been shown to have therapeutic efficacy against solid tumors and are used in electrochemical sensors and biosensors (Luo et al. 2006). However, the duration of their clinical use is limited by their side effects such as systemic toxicity and drug resistance (Wang 2010; Zalba and Garrido 2013). In biological and chemical applications, Pt-NP are studied for their capacity to encourage the oxygen reduction reaction, producing water, which is used to oxygenate cells. In other experiments, Pt-NP have been coupled with Au-NP to produce devices capable of following chemical reactions such as oxidation of carbon monoxide (Newton et al. 2015).

Apart from the positive effects of nanoparticles, recent investigations have been performed to control and take advantage of their negative impacts; for example, platinum ions are used as a reservoir to induce DNA damage in cancer cells (Wang 2010). Additionally, Gehrke et al. (2011) evaluated Pt-NP in a human colon carcinoma cell line (HT29) in vitro, concluding that the small size of Pt-NP caused a harmful effect on DNA while cellular glutathione was decreased. Furthermore, Porcel et al. (2010) suggested that the combination of ion radiation with Pt-NP should improve cancer therapy protocols.

## *2.5 Iron Oxide*

Iron oxide nanoparticles (FeO-NP) are one of the most popular and safe nanomaterials used in medicine (Ling and Hyeon 2013). They usually take the form of magnetite ($Fe_3O_4$) or maghemite ($\gamma$-$Fe_2O_3$) particles, ranging from 1 to 100 nanometers in size. Recent investigations have focused on control of their size, crystalline structure, uniformity, and surface properties. In biomedicine, FeO-NP are commonly used for in vitro and in vivo diagnostic applications, as well as in hyperthermia, drug delivery, biosensing, and biomedical imaging (Mohapatra and Anand 2010). These uses are possible because of their superparamagnetic properties and biocompatibility, which provide additional stability, allowing separation and purification of biomolecules (e.g., antibodies, proteins, and antigens) and detection of protein and nucleic acids (Ladj et al. 2013; Tuçek et al. 2014). The common use of these nanoparticles in biomedicine is made possible through a chemical modification of their surface chemistry, polymer adsorption, or incorporation into colloidal particles via an encapsulation process. Iron oxides are used as support to capture specific targets such as bacteria or viruses in a microsystem, then, with use of an external magnetic field, they can be separated from the biomolecules simple and quickly, instead of through a conventional filtration and centrifugation process, reducing the time and cost considerably (Rahman and Elaissari 2010).

As a result of these magnetic characteristics, several applications of FeO-NP have been reported. Na et al. (2009) used iron oxide nanoparticles as MRI contrast agents because of their ability to shorten relaxation times in the liver, spleen, and bone marrow. Additionally, Kayal and Ramanujan (2010) coated a magnetite ($Fe_3O_4$) nanoparticle with polyvinyl alcohol (PVA) to serve as a drug carrier of doxorubicin (DOX), concluding that iron nanoparticles could be a viable option for drug delivery. Moreover, Wahajuddin and Arora (2012), reported the use of maghemite and magnetite as gene carriers for gene therapy in cancer treatments. Finally, Stanley et al. (2012) employed iron oxide nanoparticles as a platform for adjuvants in the activation of cell production.

## *2.6 Zinc Oxide*

Zinc oxide nanoparticles (ZnO-NP) exhibit unique semiconducting, optical, and piezoelectric properties, which are useful in several industrial applications. ZnO nanomaterials have low toxicity and biodegradability; in this context, Schilling et al. (2010) inferred that there was no conclusive evidence that ZnO-NP pose a phototoxicity or genotoxicity risk to humans. On the contrary, the authors considered that this nanomaterial protected human skin by absorbing ultraviolet (UV) radiation, preventing harmful effects and providing protection against DNA damage. Additionally, ZnO-NP are considered a promising material in cancer treatment and food additives (Wang et al. 2007). In the biological field, they are commonly used in bioimaging probes, degradation of organic compounds, antimicrobial agents, and drug carriers (Padmavathy and Vijayaraghavan 2008). Moreover, in the food industry ZnO-NP have extensive applications because of their antibacterial action against pathogens, improving the effectiveness of food packaging and thereby encouraging their use and development in food nanotechnology (Espitia et al. 2012).

Several features and attractive characteristics of ZnO-NP have made them a promising candidate among metal oxides to be utilized as a successful tool against multidrug-resistant microorganisms and a viable substitute for antibiotics. Finally, ZnO-NP-specific properties have been developed to extend their applications in several fields, particularly in biomedicine and catalysis (Sirelkhatim et al. 2015).

## *2.7 Quantum Dots*

Quantum dots (QDs) are semiconductor nanocrystals with three spatial dimensions at the nanometer scale (Bera et al. 2010). Because of their optical properties and distinctive surface, they have been used in detection probes, biomolecule labels, and drug delivery (Rosenthal et al. 2011). QDs can be composed of several materials, including CdSe, CdTe, CdS, ZnS, ZnSe, ZnO, GaP, GaN, GaAs, and InAs. Nevertheless, the most common combination is cadmium–selenium (CdSe). Their photostability and spectral properties enable their use for in vitro and in vivo imaging of a wide variety of cellular processes (Biju et al. 2010; Nida et al. 2008). Furthermore, because of their nanocrystal size (2–10 nm) and semiconductor properties, QDs exhibit nonfluorescent bleaching, which enhances their broader excitation spectra, and they can be used as an alternative to the usual fluorescent molecules (fluorescein and rhodamine) for detection, imaging, and labeling of particles in complex experimental media (Alivisatos et al. 2005; Wu et al. 2003).

In this context, Qi and Gao (2008) applied QDs to cell lines for use as drug carriers. Also, Gui et al. (2014) developed QDs featuring carriers for real-time monitoring of drug release. In both investigations it was concluded that QDs could be a viable tool for fluorescent probes, especially for long-term, multiplexed, and quantitative imaging and detection systems. However, a serious drawback in industrial production of QDs is related to the technique used for their synthesis, which requires controlled conditions and coupling to several surfactants for stabilization and prevention of aggregation, consequently raising the cost of their production (Ladj et al. 2013).

## 2.8 Silica

Silica nanoparticles (Si-NP) are considered the main basis for the development of nanostructures used in bioimaging, biomolecular adsorption, and polymeric materials (Selvan 2010; Tallury et al. 2008). Because of their highly active surfaces, controlled particle size, enhanced water solubility, high colloidal stability, low nonspecific interaction, and biocompatibility, they are used in several medical applications (Zhang et al. 2014a). Biofunctionalization of Si-NP with organic nanostructures such as DNA or antibodies provides controlled release and recognition capabilities for drug delivery, assay labeling, and biosensing applications (He and Shi 2011). Si-NP are also used in the detoxification of lead, cadmium, and mercury in blood, as well as in targeting of cancer cells (Sangvanich et al. 2014). Moreover, Si-NP have been used for drug delivery in biological studies in vitro. For example, Mackowiak et al. (2013) demonstrated that mesoporous Si-NP could be used in hydrophobic anticancer drugs. By use of a magnetic nanocrystal coating, silica can be manipulated and monitored inside living cells to target cancerous cells and induce apoptosis, as well as being useful for imaging and therapeutic applications.

Furthermore, Si-NP are mixed with organic materials to create hybrid systems, which combine the functional organic chemistry with the thermal stability of the inorganic structures. Liu et al. (2014) used poly(methyl methacrylate) with $SiO_2$ as a filler in dental resins. Combination of organic and inorganic materials in biomedical appliances enhances the strength of bone grafts, as well as providing the potential for effective bone regeneration (Wang et al. 2014).

## 2.9 Titanium Oxide

The high strength and fatigue endurance of nanostructured titanium and its alloys make them very attractive for medical applications (Kashef et al. 2011). Titanium oxide ($TiO_2$) plays a major role in the improvement of health care, especially in cancer treatment and medical implants (Elias et al. 2008; Valiev et al. 2008). Principally because of its photocatalytic activity, high stability, broad-spectrum antibiotic properties, and long-lasting nature (Fu et al. 2005), $TiO_2$ shows the capability to eliminate cancer cells. Additionally, it is used for cell imaging, biological analysis, antibacterial activity, protection against UV radiation, drug delivery, dental implants, catheters, medical coatings, and environmental purification (Elias et al. 2008; Gong et al. 2007; Li et al. 2006b; Yeung et al. 2009; Yin et al. 2013).

Titanium has better characteristics than other surgical metals, principally because of the formation of a stable passive layer of $TiO_2$ on its surface. Also, $TiO_2$ is intrinsically biocompatible and exhibits direct bone apposition (Niinomi 2008). Another important characteristic is its low elastic modulus, which results in less stress shielding and associated bone resorption around orthopedic and dental implants

(Mishnaevsky et al. 2014). Furthermore, $TiO_2$ is lighter than other surgical materials, and it is used to produce diverse devices on computed tomography (CT) and MRI. In water remediation it is useful for removal of hazardous substances and disinfection. Finally, in the agricultural field, $TiO_2$ is used to remove residual pesticides and deodorize hydroponic crops (Geetha et al. 2009).

## *2.10 Other Nanoparticles*

### 2.10.1 Cobalt

Cobalt nanoparticles (Co-NP) play a major role in the medical field because of their magnetic properties, with promising applications in imaging as a contrast agent for MRI, drug delivery of cancer therapies, catalysis, optics, microelectronics, and biological sensors (Ogunlusi et al. 2012). Xu et al. (2008) coated graphitic carbon with magnetic Co-NP shells, generating thermal cellular damage to induce cancerous cell death, creating the possibility to apply this therapy to other biological systems for successful tumor treatment in clinical applications. In this context, Rutnakornpituk et al. (2002) used Co-NP in silica spheres as carriers for their application in ophthalmic surgery. Finally, Sathya et al. (2016) investigated the effects of cobalt nanotubes in theranostic applications, concluding that cobalt nanotubes could serve as heat mediators for in vivo hyperthermia and MRI applications.

### 2.10.2 Copper

Copper nanoparticles (Cu-NP) have potentially very useful properties such as superconductivity, electron correlation effects, and spin dynamics. Thus, Cu-NP have diverse applications in several fields, being useful in supercapacitors, solar cell batteries, biosensors, nanofluids, photodetectors, superhydrophobic surfaces, gas sensors, solar energy conversion, and field emission emitters. They are also useful for removal of arsenic and organic pollutants from wastewater (Zhang et al. 2014b). Additionally, Cu-NP can improve fluid viscosity and enhance thermal conductivity (Garg et al. 2008). Furthermore, copper oxide crystal structures exhibit a narrow band gap, which gives them useful photocatalytic and photovoltaic properties, coupled with photoconductive functionality (Shaabani et al. 2014; Zhang et al. 2014a). Cu-NP also have bactericidal properties for use in medical applications against a range of bacterial pathogens, including methicillin [meticillin]–resistant *Staphylococcus aureus* (MRSA) and *Escherichia coli*, with minimum bactericidal concentrations (Ren et al. 2009).

### 2.10.3 Cerium Oxide

Notably, cerium oxide nanoparticles ($CeO_2$-NP) have attracted the attention of researchers because of their antioxidant potential and biocompatibility, showing adequate protection of cells against damage caused by increased formation of reactive oxygen or nitrogen species (Karakoti et al. 2010). The protective effects of $CeO_2$-NP have been used for cardioprotection, reduction of chronic inflammation, wound healing, neuroprotection, cancer treatment, and ocular treatment (Kim and Hyeon 2013). Chigurupati et al. (2013) showed that the antioxidant properties of cerium reduce tumor growth in ovarian cancer treatment. Moreover, Pagliari et al. (2012) showed that cerium nanoparticles represented a promising tool to control oxidative stress in isolated cardiac progenitor cells.

## 3 Concerns Regarding Human and Environmental Health

Recently, there has been increasing interest in nanoscience and nanotechnology worldwide, because of their enormous potential for development of new products and applications with improved performance and new functionalities. It has to be remembered that nanotechnology is an emerging field for production of nanoscale products/devices with more efficient reactivity and larger surface areas than their bulk forms. These unique attributes of nanoparticles offer immense potential for their application in almost all scientific and technological areas. However, while nanoscience and nanotechnology might revolutionize a number of industrial and consumer sectors, there are uncertainties and knowledge gaps regarding the toxicological effects of these emerging sciences (Table 10.2). It has to be stated that although nanoparticle research has been ongoing for more than 30 years, the development of methods and standard protocols required for their safety and efficacy testing for human use is still a work in progress. Additionally, there are still no protocols or regulatory and legal frameworks worldwide for protection of human and environmental health.

Uncontrolled release of nanoparticles or nanomaterials in the environment can harm the abundance and diversity of biotic ecosystem components such as microorganisms, plants, or animals. Additionally, these materials may also affect some abiotic components such as soil moisture, temperature, and nutrient availability. Because these particles have a higher surface area to volume ratio than their bulk forms, nanoparticles are highly reactive and effective in their actions. The attributes of these nanomaterials are very similar to those of their parent chemical species. Thus, active involvement of these materials in various biological, physicochemical, and biochemical processes in the environment may be detrimental to ecological systems. A few metal nanoparticles such as $TiO_2$, ZnO, AgO, CuO, and $Fe_2O_3$ are well known for their toxicity and antimicrobial activities when present in excessive amounts (Fernández-Luqueño et al. 2014; Kumari and Singh 2016; León-Silva et al. 2016).

**Table 10.2** Human health and environmental concerns

| Concern | Novel research | Reference |
|---|---|---|
| Exposure | – Potential routes of exposure have been elucidated, including inhalation, dermal, oral, and parenteral<br>– Additionally, toxicity has been studied at lungs, skin, kidneys, or genitals, in order to determine the nanomaterials dose-response | Stern and McNeil (2008); Van Broekhuizen et al. (2012) |
| Harmful effects | – Different inflammatory and oxidative effects can generate cytotoxicity or genotoxicity potencies in experimental systems<br>– In consequence several studies suggest that cytotoxicity and genotoxicity also depend on size, shape, concentration, stability, superficial charge, and time exposure of the nanoparticles | Asharani et al. (2009); Kim et al. (2009); Krzyzewska et al. (2016) |
| Economic viability | – Purity compounds, low process yields, and hi-tech infrastructure could complicate their large-scale manufacturing<br>– Cost-effective evaluation | Şengül et al. (2008); Tian et al. (2012) |
| Normalization and regulation | – No clear standards for workers and final consumer protection<br>– No international regulation policies or assessments frameworks, in order to standardize the use and production of nanomaterials | Kulinowski and Lippy (2011); Schulte et al. (2014); Renn and Roco (2006) |
| Final disposal | – Elaboration and implementation of recollection protocols after used<br>– Further investigations about the long-term toxicity in human health and environment<br>– A complete evaluation of their life cycle impacts is required | Keller et al. (2013); Miseljic and Olsen (2014) |
| Scientific dissemination | – Communication with society about safety information and the latest toxicological investigations made in nanomaterials is currently scarce, creating barriers in the diffusion, acceptance, and growth of this sector | Helland and Kastenholz (2008) |

In recent years, inorganic nanoparticle use, especially use of magnetic iron oxide materials for imaging, has been a particular focus, and their impacts on human cell and tissue functions pose compelling safety and toxicity concerns (Hofmann-Amtenbrink et al. 2015) (Fig. 10.3). According to Hofmann-Amtenbrink et al. (2015), assessments of the influences of their particle size, morphology, and surface charge, and the resulting interfacial protein adsorption in their interactions with tissues, uptake by lymphatic or blood components, and correlations with toxicity or safety risks have certainly provided no consensus to date; thus, in vitro methods and

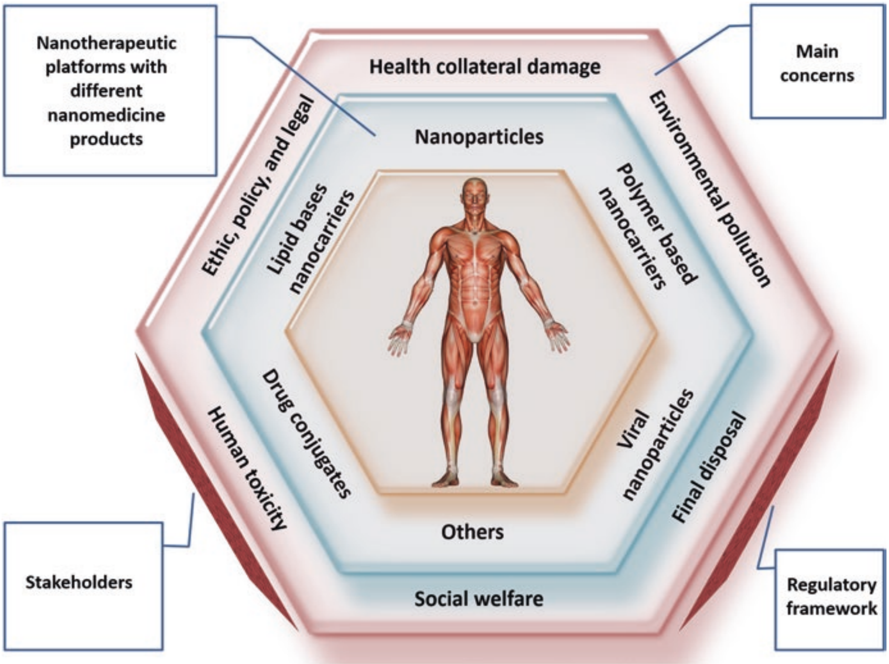


**Fig. 10.3** Nanotherapeutic platforms with different nanomedicinal products and the main concerns regarding use of nanomedicine. Stakeholders are not able to work about that because they have limited knowledge of the problem. Therefore, many countries throughout the world have not implemented suitable regulatory frameworks

preclinical models to produce such correlations for human use currently lack validation and standards. Hence, without accepted approaches for assessing safety, translation of nanomaterials and nanoparticles as marketable biomedical products may prove to be challenging (Hofmann-Amtenbrink et al. 2015; León-Silva et al. 2016).

According to Hofmann-Amtenbrink et al. (2015), the many variations in reported investigations—often with only vague descriptions of materials and preparation, storage, and analytical certification methods—prevent robust scientific comparisons of the diverse published results on seemingly related inorganic particle chemistries. Additionally, industrial standards are lacking for these systems: relevant legal guidelines and important definitions remain vague, but also a lack of legal and regulatory frameworks regarding nanomaterials, nanoparticles, and nanodevices is common worldwide. Nanoparticles offer a wealth of opportunities for developing innovative products with applications in biomedicine, pharmaceuticals, and food processing, among other applications, which may bring important benefits to industry and consumers. However, negative effects caused by exposure, use, and final disposal of products using Ag-NP may include DNA damage, gene perturbation, and metabolic changes, with toxicity varying depending on the size, shape, size distribution, exposure, and concentration in the environment. Therefore, it is important to address the compelling needs for improved and standardized assessments of inorganic nanoparticles and their toxicity in various biomedical uses, for coherence between scientific developments and corresponding health and safety regulations, and for definition of the necessary prerequisites for implementing and enforcing such regulations. These concerns have led to the following three key issues (Hofmann-Amtenbrink et al. 2015):

1. *Nanoparticle properties and characterization methods:* The sizes and shapes of inorganic nanoparticles, their physicochemical properties and, most importantly, their surface and interfacial properties in biological milieu that result in formation of ubiquitous adsorbed protein corona on particle surfaces are proposed as critical parameters to measure. Importantly, these properties should be verified and monitored to correlate and control their interactions with living systems throughout the entire product life cycle.
2. *Toxicity assessment:* Despite global proliferation of engineered nanoparticle research and production, reliable, validated, high-throughput, and standardized methods are still needed for rapid assessment of nanoparticle toxicity in various environmental conditions, human routes of exposure, dosing of cell cultures, and in vivo biological conditions. Correlations of in vitro cell and protein exposure result in in vivo host responses that are often uncertain and unpredictable for use in risk–benefit analysis. Furthermore, to date, there is not current consensus, validation, or standardization of the preclinical in vivo experiments and models necessary to best mimic a given dose–exposure situation for these nanoparticles in formulations appropriate for human use.
3. *Regulation:* Government policies governing nanomaterial production and occupational exposure, environmental release, commercial product stewardship, and human exposure remain a critical part of the entire product life cycle of nanoenabled products. Policy formulation and implementation must enable creation of clear guidelines to govern interactions between nanomaterial researchers, developers, and regulatory bodies to collaboratively facilitate responsible transfer of research results assessing toxicity (if any) to ensure product safety for industrial and medical users. This should be a living, dynamic engagement: research and development in nanotechnologies/nanoparticles for biomedical products are continuously evolving. New details of nanoparticle properties and toxicity, with their associated implications for benefits and risks, are continually mentioned in scientific reports, as well as in consumer digests in the public media. The associated evolving legal aspects surrounding these issues must also be considered and appropriate measures taken to provide both stability via responsibility to industrial developers for their future markets and also safety to the consumer in terms of appropriate use and exposure.

At present, the most significant concerns involve risk assessment, risk management of engineered nanomaterials, risk communication and, of course, fraud (Resnik and Tinkle 2007). As the science and technology of nanomedicine forge ahead, ethics, policy, and the law are struggling to keep up. It is important to proactively address the ethical, social, and regulatory aspects of nanomedicine to minimize its adverse impacts on the environment and public health—and also to avoid a public backlash.

Rapid growth in nanotechnology toward the development of nanomedicinal products holds great promise to improve therapeutic strategies against some common and terminal diseases. According to Bobo et al. (2016), a nanomedicine is a therapeutic or imaging agent that uses a nanoparticle to control the biodistribution, enhance the efficacy, or reduce the toxicity of a drug or biological agent. It has to be recognized that nanomedicinal products represent an opportunity to achieve sophisticated targeting strategies and multifunctionality, but the challenges faced in using nanomedicinal products and translating them from the preclinical level to the clinical setting must also be understood. Bobo et al. (2016) identified 51 nanomedicines approved by the US Food and Drug Administration (FDA) and 77 products in clinical trials. While the FDA-approved materials are heavily weighted toward polymeric, liposomal, and nanocrystal formulations, there is a trend toward development of more complex materials comprising micelles or protein-based nanoparticles, and also the emergence of a variety of inorganic and metallic particles in clinical trials. It has to be taken into account that some nanoparticles used as medicines have been approved by the FDA but subsequently withdrawn from the market (Bobo et al. 2016). However, nanoparticles have gained much interest as a specific and sensitive tool for diagnosis of bacterial, fungal, and viral diseases (Shaalan et al. 2016).

In recent years there has been exponential growth in publications focusing on "cancer + nanoparticles." According to Web of Science®, in 2017 alone, 13,711 manuscripts were published regarding "cancer* + nano*," but only 2995 manuscripts were published regarding "cancer* + nano* + toxic*," i.e., there is enough evidence that nanoparticles may have the ability to heal some diseases, but some doubts have arisen, e.g., nanoparticles may heal some diseases, but won't they cause collateral damage? Also, could people who have been healed by nanomedicine suffer an aftermath? (Fig. 10.3).

According to Hofmann-Amtenbrink et al. (2015), considering the current situation and future needs regarding nanoparticles in medicine, a general picture may be constructed, taking into account the following:

1. Improved methodology and testing tools are needed to characterize nanomaterials from the research stage to marketable versions and throughout the product life cycle, covering the diverse manifestations and impacts of these materials on both human health and on the environment.
2. The assessment of possible risks should be harmonized between the main stakeholders worldwide.
3. Researchers working on nanomaterial-based products for industry and medicine should adopt a common approach to safety and toxicology testing, distinct in certain aspects from traditional testing of new soluble drugs. This is especially important for nanomedicinal products based on inorganic nanoparticles, for which conventional toxicological knowledge is often insufficient in routine pharmaceutical toxicology testing (Hofmann-Amtenbrink et al. 2015). Nanoparticle

assays and their outcomes are not comparable with soluble molecule–based product assessments and must be treated differently.

4. Improvements in regulation of nanomaterials, especially nanoparticles, are necessary to address current ambiguities in industries that avoid use of "nanobranding" in their nanomaterial-containing products if it is not specified as a marketing instrument.
5. Several current nanomedicinal products are based on reinvention or adaptation of formulation strategies for existing poorly soluble or insoluble drugs that show improved performance when encapsulated in lipid vehicles (i.e., liposomes) or protein complexes, or in nanocapsules and organic (polymer) nanoparticles.

In order for us to take advantage of nanotechnology in medical applications, the properties of nanoparticles should be known and their behavior must be identified under various conditions. The success of nanoparticles in healing or reducing the discomforts caused by chronic diseases may be affected by their physicochemical properties, size, shape, and surface chemistry, which can characterize their biodistribution, pharmacokinetics, and biocompatibility (Yadollahpour 2015). In characterization and control of the physicochemical properties of magnetic nanoparticles (MNPs), synthesis and coating processes play a crucial role. Various structural models for MNPs have been proposed, each of which has its own advantages and drawbacks for medical applications in clinical settings. In order for us to propose new MNPs and elucidate their behaviors in a living body, high-tech methods are needed. Considering the recent advances in synthesis of NPs, as well as biotechnological advances, we can expect clinical uses of MNPs in different fields of medicine in the near future.

Nanocomposite scaffolds combining biopolymers and nanosized bioresorbable fillers such as calcium phosphates (CaPs) have great potential in tissue engineering and regenerative medicine (TERM) because of their ability to mimic the structural and mechanical properties of native tissues. Natural polymers are appealing because of their different degradation rates, while CaPs offer the required osteoconductivity and biocompatibility features (Pina et al. 2015). In addition, research efforts in designing an ideal nanocomposite material for repair and regeneration of damaged/diseased tissues have revealed the promise of nanocomposites comprising collagen, gelatin, silk fibroin, chitosan, alginate, hyaluronic acid, gellan gum, derivatives such as natural polymeric matrices, and hydroxyapatite (HAp) and β-tricalcium phosphate (β-TCP, a high-temperature phase of CaPs) as bioactive fillers.

Nanocomposites from natural polymers and CaPs have nanofeatured structures such as a large surface area and enhanced porosity, which are essential for appropriate cellular adhesion, proliferation, and differentiation. Furthermore, they can be functionalized with bioactive molecules and stem cells to enhance tissue healing/regeneration. In vitro cell culturing in three dimensions, using perfusion bioreactor systems, may be also applied to produce mature tissues. Such dynamic systems can provide an optimal environment for convectively transporting nutrients to cells and removing metabolites, with appropriate mechanical stresses to guide cell growth and proliferation, and extracellular matrix production.

However, an entire natural nanocomposite scaffold, mimicking the hierarchical structure and morphology of bone while performing a temporary function, has not yet been developed. Still, silk fibroin and collagen biopolymers combined with CaPs have shown great promise in preclinical studies (Pina et al. 2015). It has to be noted that these scaffolds are still at the stage of research and development, lacking application in clinical surveys. Future developments of this kind of nanocomposite for tissue repair and regeneration, aimed at clinical applications, should be devoted to clear understanding of the nanocomposite–tissue interactions, optimization of their composition and hierarchical structure for long-term service, and the related mechanical strength, especially the fatigue limit under periodic external stress. Furthermore, the use of these nanocomposites for therapeutic effects and drug delivery, combined with differentiated or undifferentiated autologous cells, should be thoroughly investigated (Pina et al. 2015).

Nanoparticles have also been used in imaging technology for vascular pathology, where high specificity and a practically universal target range make antibodies natural candidates for nanoparticle targeting (Annapragada 2015). The key applications of antibody targeting of imaging nanoparticles have been summarized by Annapragada (2015). However, although numerous attempts at antibody targeting of nanoparticles have been made, the fundamental obstacles in the path of this approach include the large size of the antibody molecule (700 kDa), the expense of raising the antibodies, their relative instability, and the potential for immune reactions unless the antibodies are humanized. The large size raises significant problems with accelerated clearance and makes the masking–unmasking approach difficult to practice (Annapragada 2015). Nanoparticle-based imaging technologies for vascular pathologies are at various stages of development, ranging from early investigations to clinical trials, but are not yet at the commercial stage. However, several targeted and untargeted nanoparticle imaging agents are currently in development, and the future is bright for nanoparticle-enabled imaging of vascular pathologies (Annapragada 2015).

According to Bonifacio et al. (2014), nanosized drug delivery systems for herbal drugs could potentially enhance their biological activity and overcome problems associated with plant medicines. However, significant challenges remain for implementation of clinically viable therapies in this field. Trials of novel methods to control the interactions of nanomaterials with biological systems represent some of the current challenges involved in translating these technologies into therapies. Other new challenges in the development of nanotechnology-based drug delivery systems include the feasibility of scaling-up processes to bring innovative therapeutic techniques to the market quickly, the possibility of obtaining multifunctional systems to fulfill several biological and therapeutic requirements, probing the targeting efficiency of nanoparticles, and satisfying international standards for their toxicology and biocompatibility (Bonifacio et al. 2014). It has to be noted that nanotechnology-based drug delivery systems have been well studied and documented in recent years. Reviews regarding this topic have been published by Calixto et al. (2016), da Silva et al. (2016), Fonseca-Santos et al. (2015), and Gidwani and Vyas (2015), among others.

According to the above, there are strong scientific teams working very hard worldwide to determine the appropriate uses of nanoparticles in medicine and related knowledge areas. However, the toxicological potential of nanoparticles has scarcely been studied. To take advantage of nanotechnology in medical applications, the properties of nanoparticles must be well known and their behavior must be identified under various conditions. Also, it has to be noted that new treatments based on nanoparticles or other nanotechnological developments must be validated and backed by internationally recognized organizations. Unfortunately, regulatory frameworks regarding nanotechnology are lacking in many countries.

## 4 Current Challenges

It is widely acknowledged that nanotechnologies will contribute to shaping future growth and our lives. However, because of their peculiar features, there are some concerns that the innovation generated by these technologies may be linked to risks and societal implications that could challenge their use. The need for research and innovation in response to these issues is unavoidable to fulfill the expectations raised by these technologies (Mantovani et al. 2016). The key to the fulfillment of these expectations is the Responsible Research and Innovation (RRI) approach of the European Commission, i.e., the development of products, processes, and services that are safe and respectful of the fundamental ethical and social needs and expectations. According to Mantovani et al. (2016), the European Commission has made RRI a cornerstone of Horizon 2020 to support European research in the years 2014–2020. The Horizon 2020 Specific Programme describes the aim of Part V—“Science with and for Society” (SWAFS)—as follows: “The aim is to build effective cooperation between science and society, to recruit new talent for science and to pair scientific excellence with social awareness and responsibility.” Figure 10.4 shows some human values and technological or scientific considerations that should be taken into account to build nanoparticles without unwanted effects. Taking into account the aim stated by Horizon 2020, scientists should work in nanomedicine considering not only the health benefits but also bearing in mind the ethical, social, economic, and environmental concerns, i.e., scientists should go to the cutting edge to solve problems and to shape a sustainable future, but never with money and the fame as the only interests.

A little-studied topic is the nanotoxicology of nanoparticles and their final disposal, as well as remediation techniques when nanoparticles are released into the environment. Application of physicochemical processes for removal of these nanoparticles from soil and water may not be feasible due to lack of cost-effectiveness and eco-friendly nature of the process. There is the need for the development of eco-friendly and sustainable bioremediation technology that is cost-effective, eco-friendly, and target specific. Successful phytoremediation technology and recovery of nanoparticles from water and soil are still remote dreams. There are urgent needs

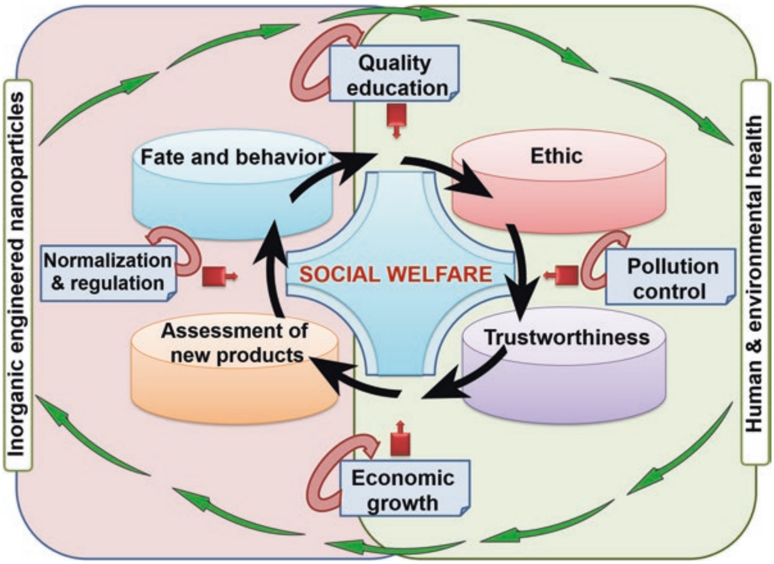


**Fig. 10.4** Human values and technological or scientific considerations that should be taken into account to build nanoparticles without unwanted effects. These criteria should be considered before nanoparticles are marketed

not only for assessment of the ecological risk and consequences caused by nanoparticles but also for thorough understanding of their environmental fate.

In addition, there are specific challenges for some scientific teams. According to Vizirianakis et al. (2016), the existing tumor heterogeneity and the complexity of cancer cell biology critically demand powerful translational tools to support interdisciplinary efforts aiming to advance personalized cancer medicine decisions in drug development and clinical practice. In this sense, science has to lead with development of physiologically based pharmacokinetic (PBPK) models to predict the effects of drugs in the body and facilitate the clinical translation of genomic knowledge and implementation of in vivo pharmacology experience with pharmacogenomics. This would unequivocally empower the scientific capacity to make personalized drug dosage scheme decisions for drugs, including molecularly targeted agents and innovative nanoformulations, i.e., to establish pharmacotyping in prescribing. In this way, the applicability of PBPK models to guide individualized cancer therapeutic decisions of broad clinical utility in nanomedicine in real time and at a low cost should be developed (Vizirianakis et al. 2016). The necessity for combined efforts within the scientific borders of genomics, medicine, and nanotechnology to ensure significant benefits and productivity in nanomedicine and personalized medicine interventions must be noted. It has to be stated that there are also other challenges regarding nanomaterials which, after they are used, will be released into the environment (Table 10.3).

**Table 10.3** Main challenges that nanomaterials most face currently and their potential applications

| Challenge | Actual situation | Recent developments | References |
|---|---|---|---|
| Sustainable energies | – Energy demand is forecast to increase by 50% for 2025<br>– 60% of energy depends on fossil fuels<br>– More than 1.6 billion people have no access to electricity | – Development of more efficient fuel cells with solid oxide nanostructures electrodes<br>– Enhance hydrogen storage capacity using carbon nanotubes<br>– High-efficiency photovoltaic solar cell with mesoporous oxides | Jiang (2012); Conserve Energy Future (2017); Schlapbach and Züttel (2001); Lee et al. (2012) |
| Provide potable water | – About 1.1 billion people do not have access to safe water<br>– More than 2.4 billion humans lack sanitation facilities<br>– 80% of developing world diseases are waterborne with an estimate of 3.4 million deaths | – Disinfection and microbial control using AgNP, carbon nanotubes, and $TiO_2$<br>– Detection and adsorption of recalcitrant contaminants with metal oxide nanoparticles | Qu et al. (2013); Gehrke et al. (2015) |
| Enhance human health | – 30% of worldwide deaths are due to HIV/AIDS, Ebola, and Avian Flu<br>– Approximately cancer kills over 500,000 people and 1.5 million are diagnosed annually in the United States | – Prompt diagnostics, biosensoring, bioimaging, and drug delivery are some examples of the use of AgNP, AuNP, and $TiO_2$ for medical applications<br>– AgNP are used for cancer treatment taking advantage of their potential to modify DNA | Marambio-Jones and Hoek (2010); Furno et al. (2004); Silver et al. (2006) |
| Preservation and improvement of the environment | – There are more than 500 million cars in the world and by 2030 the number will rise to one billion<br>– $CO_2$ concentrations have increased the greenhouse effect | – Strong, lightweight polymers are used for automobiles to reduce fuel consumption<br>– Nanoscale zeolites, metal oxides, carbon nanotubes, and enzymes are used for in situ remediation<br>– Reduction of greenhouse gases emission | Paul and Robeson (2008); Karn et al. (2011); Samimi and Zarinabadi (2012) |

The current challenges regarding nanoparticles in medicine have a wide scope, but the main difficulties relate to current concerns regarding (1) the stage of research and development of nanomedicine; (2) environmental pollution; (3) the lack of real applications; (4) the ethical, social, and regulatory aspects; (5) translation of these technologies into therapies; and (6) recovery of nanoparticles from water and soil after treatment.

## 5 Conclusion

In order for us to take advantage of nanotechnology in medical applications, the properties of nanoparticles must be understood and their behavior must be identified in various conditions in accordance with international regulatory frameworks. The success of nanoparticles to heal or reduce the discomforts caused by chronic diseases may be affected by their physicochemical properties, size, shape, and surface chemistry, which can characterize their biodistribution and pharmacokinetics, as well as their biocompatibility. Moreover, it has to be noted that nanocomposite scaffolds are still at the research and development stage, lacking application in clinical surveys. Trials of novel methods to control the interactions of nanomaterials with biological systems represent some of the current challenges involved in translating these technologies into therapies.

Additionally, there is potential for growth in the use and study of clinical nanoparticles, which will continue to be a productive and challenging field for academics, industry, clinicians, and regulators. As the science and technology of nanomedicine forge ahead, ethics, policy, and the law are struggling to keep up. It is important to proactively address the ethical, social, and regulatory aspects of nanomedicine to minimize its adverse impacts on the environment and public health—and also to avoid a public backlash.

Removal of accidentally or unintentionally released nanoparticles from the environment is crucial for maintaining sustainable ecosystem function. However, successful remediation technology for recovery of nanoparticles from water and soil is still a remote dream.

The discussion regarding the possibilities for transdisciplinary collaboration between medical science, environmental science, social science, and humanities needs to go on and make such collaboration a reality. Nanomedicine entails strong challenges that can only be addressed by transdisciplinary scientific teamwork. No area of knowledge in isolation can provide adequate solutions to the long list of diseases and discomforts that people suffer worldwide.

**Acknowledgments** This research was founded by 'Ciencia Básica SEP-CONACyT' projects 151881 and 287225, the Sustainability of Natural Resources and Energy Programs (Cinvestav-Saltillo), and Cinvestav Zacatenco. L-S S received grantaided support from 'Becas Conacyt'. F-L F and L-V F received grant-aided support from 'Sistema Nacional de Investigadores (SNI)', México.

**Competing Interests** The authors declare that they have not competing interests.

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F. López-Valdez, F. Fernández-Luqueño (eds.), *Agricultural Nanobiotechnology*, https://doi.org/10.1007/978-3-319-96719-6