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# Phytotoxicity of Nanoparticles

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*Editors*
Mohammad Faisal
Department of Botany and Microbiology,
College of Science
King Saud University
Riyadh, Saudi Arabia

Quaiser Saquib
Department of Zoology,
College of Science
King Saud University
Riyadh, Saudi Arabia

Abdulrahman A. Alatar
Department of Botany and Microbiology,
College of Science
King Saud University
Riyadh, Saudi Arabia

Abdulaziz A. Al-Khedhairy
Department of Zoology,
College of Science
King Saud University
Riyadh, Saudi Arabia

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# Preface

In recent years, nanotechnology has exhibited exponential growth in various sectors to accomplish market commodities with higher prospective applications. The small size particles (nanomaterials) are rapidly being used in manufacturing of products of our daily life such as biosensors, cosmetics, food packaging, imaging, medicines, drug delivery, and aerospace engineering, etc., and these products are coming in the global market approximately at the rate of 3–4 per week. In spite of manifold benefits of the power of nanomaterials, there are open questions about how the small size materials affect the environment and human health, while very few reports are available on the hazards of nanoparticles. Compared to the bulk counterpart, the small size and large specific surface area of nanoparticles endow them with high chemical reactivity and intrinsic toxicity. Such unique physicochemical properties of nanoparticles draw global attention of scientists and environmental watchdogs to study potential risks and adverse effects of nanomaterials in the environment. Nanoparticle toxicity has pronounced effects and consequences not only for plants but also for the ecosystem in which the plants form an integral component. Plants growing in nanomaterial-polluted sites exhibit altered metabolism, growth reduction, lower biomass production, and nanoparticle accumulation, and these functions are of serious human health concern. Edible plants with excessive amounts of accumulated toxic nanoparticles are harmful not only to humans but also to the animals when used as animal feed. Nanoparticles adhere to plant roots and exert physical or chemical toxicity and subsequently cell death in plants. On the other hand, plants developed various defense mechanisms to counteract nanoparticle-induced toxicity. Only detailed study of these processes and mechanisms would allow researcher and student to understand the complex plant–nano interactions. However, there are several unresolved issues and challenges regarding the interaction and biological effects of nanoparticles. Therefore, the book was aimed to provide relevant state-of-the-art findings on nanoparticle toxicity, its uptake, translocation, and mechanism of interactions with plants at the cellular and molecular level. Being involved in this area we comprehend that information on the nanoparticle toxicity and their mechanism of interaction with plants is still obscure, and there is no single book available on this aspect.

The intended volume comprised several chapters on relevant topics contributed by experts working in the field of nanophytotoxicity so as to make available a comprehensive treatise designed to provide an in-depth analysis of the subject in question? The book is a compilation of 18 chapters having relevant text, tables, and illustration describing the experimental work on nanomaterial-induced toxicity in plants and current trends reported and some general conclusions also drawn by the contributors. All the chapters have been organized in a way to provide crisp information on phytotoxicity of different types of nanoparticles. Special attention has been given to explore the uptake and mechanism of nanoparticle-induced toxicity and cell death in plants.

The book has been designed to serve as reference for scientist, researchers, and students in the fields of nanotoxicology, environmental toxicology, phytotoxicology, plant biology, plant physiology, plant biochemistry and plant molecular biology and who have interest in nanomaterial toxicity.

We are extremely thankful to all the contributors who wholeheartedly welcomed our invitation and agreed to contribute chapters to embellish toxicological information on nanoparticles (NPs), thus helping in this endeavor.

Riyadh, Saudi Arabia
March 2018

Mohammad Faisal
Quaiser Saquib
Abdulrahman A. Alatar
Abdulaziz A. Al-Khedhairy

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# Editors and Contributors

## About the Editors

**Mohammad Faisal** has over 10 years of research experience in plant biotechnology and is currently working as Associate Professor in the Department of Botany and Microbiology, King Saud University, Riyadh, Saudi Arabia. He has been the recipient of Plant Biotechnologist Award—2017 by SESR, India, and Scientist of the Year Award—2015 by NESA and several National and International fellowships. He holds membership of several academic bodies/societies and Fellow of the SESR. He has published over 67 research articles, 3 book chapters, and 3 books. He is in the editorial board of several journals.

**Quaiser Saquib** is currently working as an Assistant Professor and Coordinator in Al-Jeraisy Chair for DNA Research, Zoology Department, College of Science, King Saud University, Riyadh, Saudi Arabia. He has been conferred with *Scientist of the Year Award—2016 by NESA*, *India*, and Young Scientist Award 2008 by EMSI, India. Dr. Saquib published 46 research articles, 2 books, and 2 book chapters.

**Abdulrahman Alatar** is working as Professor in the Department of Botany and Microbiology, King Saud University, Riyadh, Saudi Arabia. He is also serving as consultant for human resource and management in the Ministry of Higher Education, Saudi Arabia. He has been the PI and Co-I of various projects and supervised 3 Ph.D. and 7 M.Sc. students. He has published more than 65 scientific articles and 2 books, and his work has been cited in various leading journals.

**Abdulaziz A. Al-Khedhairy** is currently serving as Director of Twasol Research Excellence Program and Al-Jeraisy Chair for DNA Research in King Saud University, Riyadh, Saudi Arabia. He has published 160 research articles, 9 book chapters, 2 books, and one US patent. As a PI and CO-I, he has successfully supervised several projects funded by KACST, KSA.

## List of Contributors

**Neama Abdalla** Plant Biotechnology Department, Genetic Engineering Division, National Research Center, Giza, Egypt

**Eslam M. Abdel-Salam** Department of Botany and Microbiology, College of Sciences, King Saud University, Riyadh, Saudi Arabia

**Bilal Ahmed** Faculty of Agricultural Sciences, Department of Agricultural Microbiology, Aligarh Muslim University, Aligarh, Uttar Pradesh, India

**Abdulrahman A. Alatar** Department of Botany and Microbiology, College of Sciences, King Saud University, Riyadh, Saudi Arabia

**Fatemeh Aliyari** Department of Forestry, Shahrkord University, Shahrkord, Iran

**Abdulaziz A. Al-Khedhairy** Zoology Department, College of Science, King Saud University, Riyadh, Saudi Arabia

**Tarek Alshaal** Soil and Water Department, Faculty of Agriculture, Kafrelsheikh University, Kafr El-Sheikh, Egypt

**M. Al-Shaeri** Faculty of Science, Department of Biological Sciences, King Abdulaziz University, Jeddah, Saudi Arabia

**Peyman Ashkavand** Department of Forestry, Tarbiat Modares University, Tehran, Iran

**Monika Asztemborska** Faculty of Biology, Isotope Laboratory, University of Warsaw, Warsaw, Poland

**Cristina Buzea** IIPB Medicine Corporation, Owen Sound, ON, Canada

**Giampiero Cai** Dipartimento Scienze della Vita, Università di Siena, Siena, Italy

**Jinyu Chu** The High School Affiliated to Beijing Normal University, Beijing, China

**Raghunandan Deshpande** H.K.E.S's Matoshree Taradevi Rampure Institute of Pharmaceutical Sciences, Gulbarga, Karnataka, India

**Éva Domokos-Szabolcsy** Agricultural Botany, Plant Physiology and Biotechnology Department, Debrecen University, Debrecen, Hungary

**Nevien Elhawat** Faculty of Home Economics, Biological and Environmental Science Department, Al-Azhar University, Cairo, Egypt

**Eman El-Nahrawy** Agricultural Microbiology Department of Soil, Water and Environment Research Institute (SWERI), Sakha Agricultural Research Station, Agriculture Research Center (ARC), Kafr El-Sheikh, Egypt

**Sahar El-Nahrawy** Agricultural Microbiology Department of Soil, Water and Environment Research Institute (SWERI), Sakha Agricultural Research Station, Agriculture Research Center (ARC), Kafr El-Sheikh, Egypt

**Hassan El-Ramady** Faculty of Home Economics, Biological and Environmental Science Department, Al-Azhar University, Cairo, Egypt

**Tamer Elsakhawy** Agricultural Microbiology Department of Soil, Water and Environment Research Institute (SWERI), Sakha Agricultural Research Station, Agriculture Research Center (ARC), Kafr El-Sheikh, Egypt

**Mohammad Faisal** Department of Botany and Microbiology, College of Sciences, King Saud University, Riyadh, Saudi Arabia

**Sheng Feng** Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, China

Hebei Provincial Key Lab of Green Chemical Technology & High Efficient Energy Saving, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin, China

**Fernanda Fidalgo** Faculty of Sciences, GreenUPorto, Department of Biology, University of Porto, Porto, Portugal

**Azza Ghazi** Agricultural Microbiology Department of Soil, Water and Environment Research Institute (SWERI), Sakha Agricultural Research Station, Agriculture Research Center (ARC), Kafr El-Sheikh, Egypt

**Mar Gil-Díaz** IMIDRA, Finca “El Encín”, Alcalá de Henares, Madrid, Spain

**Gea Guerriero** Environmental Research and Innovation, Luxembourg Institute of Science and Technology, Esch-sur-Alzette, Luxembourg

**Eman Hamad** Agricultural Microbiology Department of Soil, Water and Environment Research Institute (SWERI), Sakha Agricultural Research Station, Agriculture Research Center (ARC), Kafr El-Sheikh, Egypt

**Changwei Hu** College of Biological Chemical Science and Engineering, Jiaxing University, Jiaxing, P.R. China

**Qingguo Huang** Department of Crop and Soil Sciences, University of Georgia, Griffin, GA, USA

**Mohammad Saghir Khan** Faculty of Agricultural Sciences, Department of Agricultural Microbiology, Aligarh Muslim University, Aligarh, Uttar Pradesh, India

**Kanuparthi Prasanna Laxmi** Biology and Biotechnology Division, Indian Institute of Chemical Technology, Hyderabad, Telangana, India

**Giuseppe Lazzara** Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Palermo, Italy

**M. Carmen Lobo** IMIDRA, Finca “El Encín”, Alcalá de Henares, Madrid, Spain

**Yuhui Ma** Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, China

**Marina Massaro** Dipartimento STEBICEF, Sez. Chimica, Università degli Studi di Palermo, Palermo, Italy

**Pragati Misra** Department of Molecular and Cellular Engineering, Jacob School of Biotechnology and Bioengineering, Sam Higginbottom Institute of Agriculture, Technology and Sciences, Allahabad, Uttar Pradesh, India

**Javed Musarrat** Faculty of Agricultural Sciences, Department of Agricultural Microbiology, Aligarh Muslim University, Aligarh, Uttar Pradesh, India

Baba Ghulam Shah Badshah University, Rajouri, Jammu and Kashmir, India

**Remya Nair** Nano Research Facility, One Brookings Drive, Washington University, St. Louis, MO, USA

**Narendhran Sadasivam** Department of Biotechnology, Sri Ramakrishna College of Arts and Science College – Autonomous (Formerly SNR Sons College), Coimbatore, India

**Günter Neumann** Institute of Crop Science (340h), Hohenheim University, Stuttgart, Germany

**Alaa El-Dein Omara** Agricultural Microbiology Department of Soil, Water and Environment Research Institute (SWERI), Sakha Agricultural Research Station, Agriculture Research Center (ARC), Kafr El-Sheikh, Egypt

**Ivan Pacheco** Department of Pathology, Grey Bruce Health Services, Owen Sound, ON, Canada

Department of Pathology and Laboratory Medicine, Schülich School of Medicine and Dentistry, Western University, London, ON, Canada

**Asra Parveen** H.K.E.S’s Matoshree Taradevi Rampure Institute of Pharmaceutical Sciences, Gulbarga, Karnataka, India

**Ruth Pereira** Faculty of Sciences, GreenUPorto, Department of Biology, University of Porto, Porto, Portugal

**Ahmad A. Qahtan** Department of Botany and Microbiology, College of Sciences, King Saud University, Riyadh, Saudi Arabia

**Rajiv Periakaruppan** Department of Biotechnology, School of Life Sciences, Karpagam Academy of Higher Education, Coimbatore, Tamil Nadu, India

**Serena Riela** Dipartimento STEBICEF, Sez. Chimica, Università degli Studi di Palermo, Palermo, Italy

**Quaiser Saquib** Zoology Department, College of Science, King Saud University, Riyadh, Saudi Arabia

**Ali Sattarian** Department of Forestry, Gonbad-Kavoos University, Golestan, Iran

**Pradeep Kumar Shukla** Department of Biological Sciences, School of Basic Sciences, Sam Higginbottom Institute of Agriculture, Technology and Sciences, Allahabad, Uttar Pradesh, India

**Rajeshwari Sivaraj** Department of Chemistry, Government Arts College, Udumalpet, Tamil Nadu, India

**Cristiano Soares** Faculty of Sciences, GreenUPorto, Department of Biology, University of Porto, Porto, Portugal

**Gustavo Gabriel Striker** IFEVA-CONICET, Facultad de Agronomía, Universidad de Buenos Aires, Buenos Aires, Argentina

**Masoud Tabari** Department of Forestry, Tarbiat Modares University, Tehran, Iran

**Pathipati Usha Rani** Biology and Biotechnology Division, Indian Institute of Chemical Technology, Hyderabad, Telangana, India

**Filiz Vardar** Science and Arts Faculty, Department of Biology, Marmara University, Istanbul, Turkey

**Fang Yang** Hebei Provincial Key Lab of Green Chemical Technology and High Efficient Energy Saving, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin, China

**Fatma Yanik** Science and Arts Faculty, Department of Biology, Marmara University, Istanbul, Turkey

**Mehrdad Zarafshar** Fars Agricultural and Natural Resources Research and Education Center, AREEO, Shiraz, Fars, Iran

**Olga Zaytseva** Institute of Crop Science (340a), Hohenheim University, Stuttgart, Germany

**Liwen Zhang** Department of Crop and Soil Sciences, University of Georgia, Griffin, GA, USA

**Zhiyong Zhang** Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, China

# Nanoparticle Uptake by Plants: Beneficial or Detrimental?

1

Ivan Pacheco and Cristina Buzea

## 1.1 Introduction

Nanoparticles can be defined as very small particles with size in the nanometer range. They can be as small as 1 nm and as large as hundreds of nm.

Due to their small size, nanoparticles can be internalized by plants, animals, and humans. Further, they can enter cells and organelles and affect cellular processes. Nanoparticles with selected compositions had shown some beneficial effects in selected plants, and, as a result, some scientists are promoting their use in agriculture. However, nanoparticles are phytotoxic for many other plants. In addition, nanoparticles are toxic to humans and animals, being associated to a multitude of diseases, ranging from respiratory and cardiovascular to neurological diseases. As a result of their toxicity, it is necessary to environmentally monitor man-made nanoparticles and to pass regulations and laws regarding the use and safe handling of nanoparticles.

What makes nanoparticles different from larger particles of the same material are surface and quantum effects (Buzea and Pacheco 2017). A material in nanoform exhibits different physical, chemical, and mechanical properties than the material in bulk form. Decreasing the size of a nanoparticle, the ratio between the atoms on its surface compared to those in its interior increases, leading to a smooth scaling of its physical and chemical properties. As a result, nanoparticles will have higher surface/volume ratio, increased chemical reactivity, and reduced melting point. Due to the

I. Pacheco
Department of Pathology, Grey Bruce Health Services, Owen Sound, ON, Canada

Department of Pathology and Laboratory Medicine, Schülich School of Medicine and Dentistry, Western University, London, ON, Canada
e-mail: ipacheco@gbhs.on.ca

C. Buzea (✉)
IIPB Medicine Corporation, Owen Sound, ON, Canada
e-mail: cristinabuzea@mdcorporation.ca



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small size of a nanoparticle, its electrons become confined and will have a quantized energy spectrum, resulting in quantum size effects. An example of quantum size effect is the appearance of magnetic moments. For example, there are nanoparticles of materials nonmagnetic in bulk that, when in nanoform, develop magnetic moments. Among these are gold, platinum, and palladium.

Nanoparticles can have various sizes, morphologies, and crystallinities, as illustrated in Fig. 1.1. They can have a short aspect ratio, with spherical or cubic morphologies, or a long aspect ratio, in the form of tubes or long whiskers (Soto et al. 2005; Murr and Soto 2004; Rui et al. 2015; Qiu et al. 2010).

Nanotoxicology is a branch of toxicology that studies the toxicity of nanoparticles in humans and animals. It encompasses in vitro studies performed on animal and human cell lines, in vivo experiments on animals and humans, epidemiological data related to particle pollution, and occupational exposure studies of workers involved in handling nanoparticles (welding, mining, etc.).

Nanoparticles are being increasingly used in applications, including agriculture. However, many types of nanoparticles are proved to be toxic, despite the fact that the same material in bulk form is harmless. It is impossible to predict the toxicity degree of a nanoparticle type without experimental data. As most of the nanotoxicity studies are published in very specialized journals, the dissemination of information on nanoparticle toxicity is not readily available for the scientists that are starting to use these nanoparticles in applications, including agrichemicals.

The researchers working in their application in agriculture, being unaware of nanoparticle toxicity, are likely to suffer health effects in the coming years due to incorrect handling and inadvertently exposure to nanoparticles. Due to their small size, nanoparticles can easily become airborne and be inhaled and ingested and enter in contact with the skin. Secondly, the use of agricultural nanoparticles poses a risk for the population and ecosystem.

Having remembered asbestos and the severe health effects due to its use in construction, we would like to prevent a similar situation from happening. However, nanoparticles use in agriculture might pose a higher environmental and toxic threat than asbestos. Asbestos use was limited mainly to the construction industry, being confined to buildings, and is now relatively easy to remove. Nanoparticles used in agriculture will not be confined to a specific place; they will enter the atmosphere and become respirable particles, pollute the water, and lead to devastating consequences for humans and other life species.

This chapter will focus on evaluating the beneficial and detrimental effects of nanoparticles on plants together with their toxicity in humans and animals. Weighting the pros and cons will allow the reader to form an idea whether or not nanoparticles should be used in agriculture. We show research regarding nanoparticle uptake and accumulation in plants, together with phytotoxicity studies. We also show selected beneficial effects in some plants. Following are subchapters dedicated to toxic effects of nanoparticles in humans and animals together with comparative toxicity for various compositions. After reading this chapter, the reader should be informed on the pros and cons of using nanoparticles in agriculture and the environmental risks and toxicity that they will pose for life.

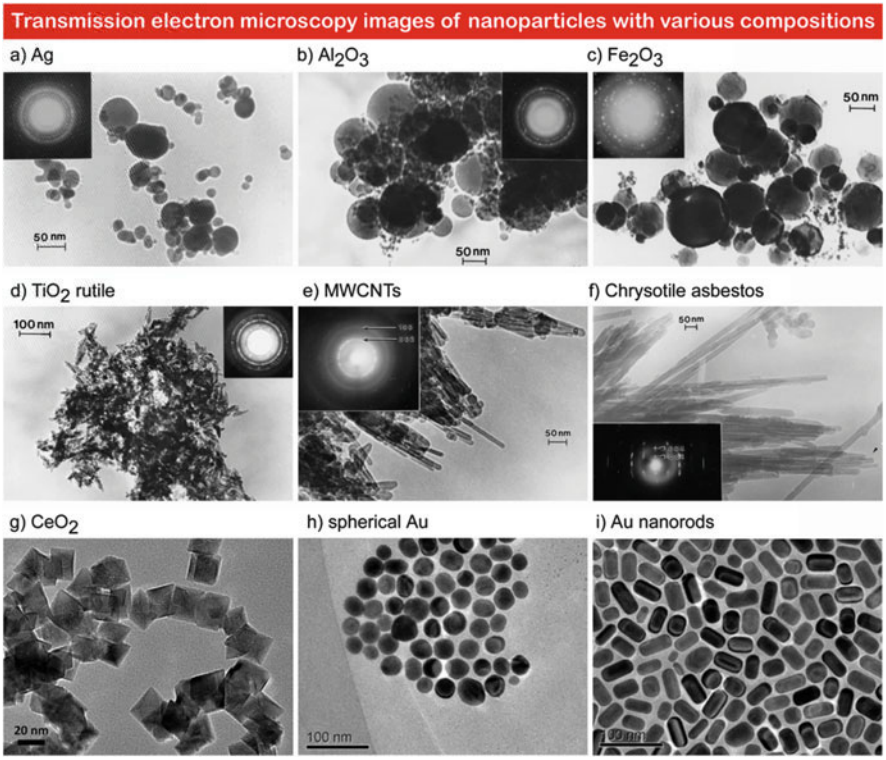
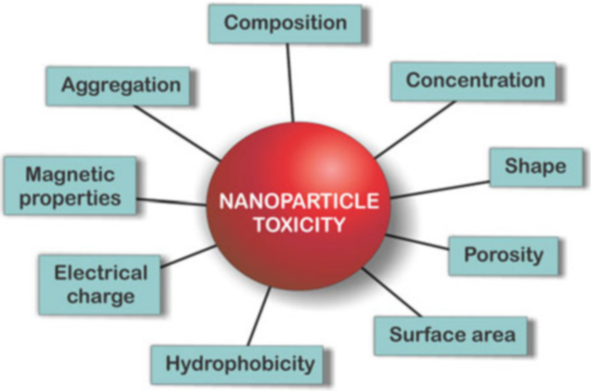



**Fig. 1.1** Transmission electron microscopy images of nanoparticles of (**a**) Ag, (**b**) $Al_2O_3$, (**c**) $Fe_2O_3$, (**d**) $TiO_2$ rutile, (**e**) MWCNTs, and (**f**) chrysotile asbestos. Inserts are showing selected area electron diffraction (SAED) patterns that indicate the degree of crystallinity of nanoparticles. Notice the similarity between the morphology of MWCNTs and asbestos. Images (**a**–**d**) are reprinted from Soto K. F. et al. 2005. Comparative in vitro cytotoxicity assessment of some manufactured nanoparticulate materials characterized by transmission electron microscopy. Journal of Nanoparticle Research, 7, 145–169, with permission from Springer (Soto et al. 2005). Images (**e**–**f**) are reproduced from Murr L. E. & Soto K. F. 2004. TEM comparison of chrysotile (asbestos) nanotubes and carbon nanotubes. Journal of Materials Science, 39, 4941–4947. Copyright 2004 Kluwer Academic Publishers. With permission of Springer (Murr and Soto 2004). (**g**) $CeO_2$ nanoparticles. Reprinted from Environmental Pollution, vol. 198, Rui Y. et al., Transformation of ceria nanoparticles in cucumber plants is influenced by phosphate, pp. 8–14, Copyright (2015), with permission from Elsevier (Rui et al. 2015). (**h**) Gold nanospheres and (**i**) gold nanorods; images (**h**–**i**) adapted from Biomaterials, Vol 31, issue 30, Qiu Y. et al, Surface chemistry and aspect ratio mediated cellular uptake of Au nanorods, Pages 7606–7619, Copyright (2010), with permission from Elsevier (Qiu et al. 2010)

**Fig. 1.2** Nanoparticle toxicity is determined by its physicochemical and morphological characteristics




## 1.2 Nanoparticle Physicochemical Properties

Nanoparticle interaction with their environment and uptake and toxicity in plants, humans, and animals depend on their size, aggregation, composition, concentration, shape, porosity, surface area, hydrophobicity, electrical charge, and magnetic properties, as illustrated schematically in Fig. 1.2.

It is important to note that nanoparticles suffer chemical transformation in the soil, within the plants, and within organisms in general. They are able to undergo various transformations, for example, acquiring a protein corona or changing their oxidation state, depending on their environment conditions. These transformations dictate ultimately their uptake, translocation, and toxicity. Even nanoparticles that may be considered stable are still able to change chemically, and their beneficial properties might become detrimental. For example, under hydroponic conditions Ce(IV)$O_2$ in cucumber plants is reduced to Ce(III) (Rui et al. 2015). $CeO_2$ nanoparticles in hydroponic cucumber plants treated with phosphate suffer chemical transformation, being located outside the epidermis, while in phosphate free plants, they were observed only in the intercellular spaces and vacuole of root (Rui et al. 2015).

## 1.3 Nanoparticles in Agriculture

### 1.3.1 Pesticides and Fertilizers

The topic of nanoparticle applications in agriculture emerged around the year 2000 (Gogos et al. 2012). Nanoparticles used in agriculture can be solid (such as metal and their oxides) or nonsolids (such as lipid or polymer) (Gogos et al. 2012). They are used for plant crop protection and for soil/water remediation (Fig. 1.3). Nanoparticles in plant protection are used as fungicides, herbicides, and insecticides, as depicted in Fig. 1.4. Nanoparticles can be the active ingredient or an additive that

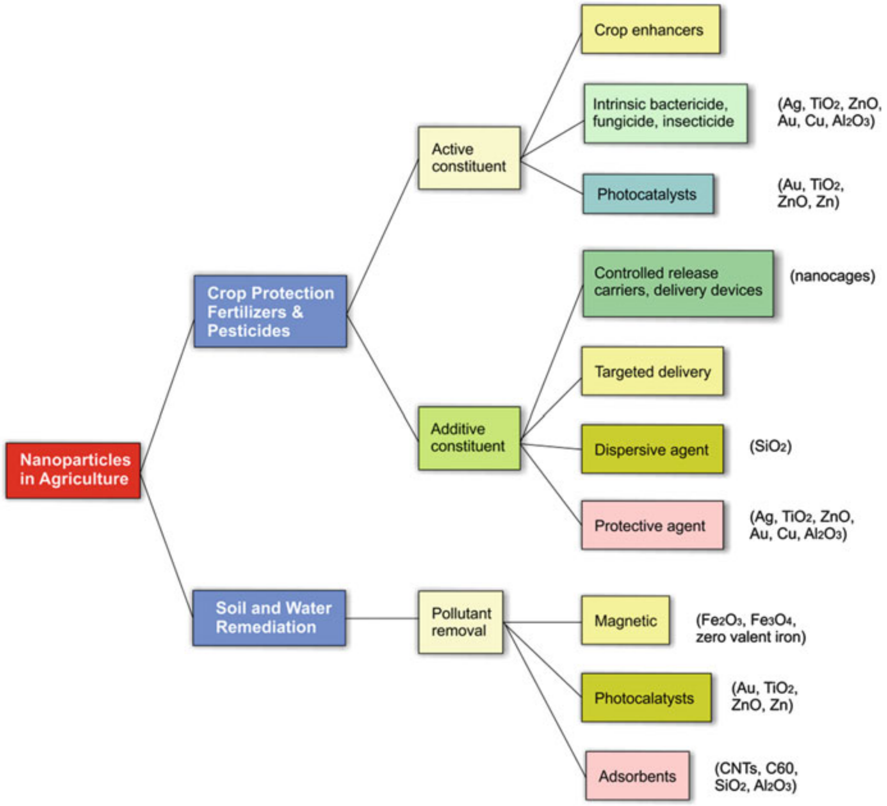



**Fig. 1.3** Schematics for the applications of nanoparticles in agriculture for plant protection and soil and water remediation

can act for the controlled release of the main ingredient, as dispersing agent, targeted delivery agent, protective agent, or photocatalyst.

Figure 1.3 shows a schematic of nanoparticle function used in agriculture together with examples of nanoparticle compositions. Figure 1.4 shows comparative results of nanoparticles used in agriculture. Nanoparticles can act as active constituents and additives: they can serve as delivery devices that targeting specific tissues, nanopesticides (small particles of pesticides), and nanocages filled with pesticides act as controlled release devices. Nanoparticles themselves can have pesticidal properties when in nanoform, such as Ag, Au, $TiO_2$, Cu, and ZnO, several of these having photocatalytic properties. They can be pesticide additives that serve for enhancing the solubility of active ingredients. Some nanoparticles can also be used for soil and water remediation (Aragay et al. 2012). Due to their high surface area, adsorption capacity, and electromagnetic properties, nanoparticles are prospected for the adsorption of organic and inorganic pollutants from soil and water (Gupta and Saleh 2013). Among them are metal-containing particles, CNTs,

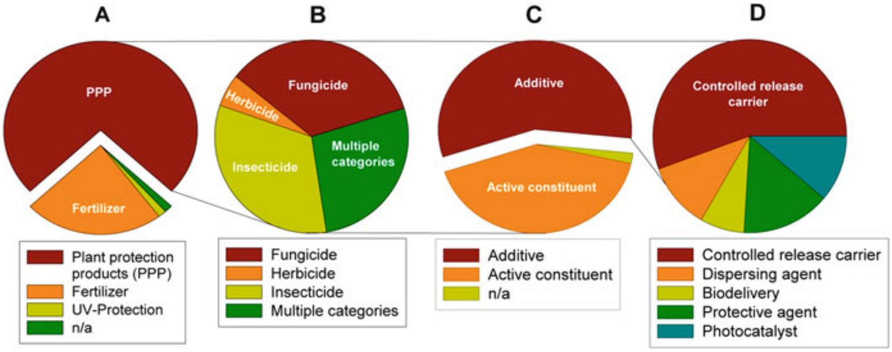



**Fig. 1.4** Comparative results of nanoparticles used in agriculture. (**a**) Applications of nanoparticles in agriculture. (**b**) Types of plant protection products containing nanoparticles, (**c**) the function of nanoparticles within these products, (**d**) the role of the additive nanoparticles in plant protection products. Reprinted with permission from Gogos A. et al., Nanomaterials in Plant Protection and Fertilization: Current State, Foreseen Applications, and Research Priorities. Journal of Agricultural and Food Chemistry, vol. 60, pp. 9781–9792. Copyright (2012) American Chemical Society (Gogos et al. 2012)

$C_{60}$, and zeolites. Magnetic nanoparticles, such as iron oxide ($Fe_3O_4$) and zerovalent iron, are unique agents for water treatment (Xu et al. 2012; Deng et al. 2014). Magnetic nanoparticles are used for selected pollutant removal. Heavy metal pollutants are adsorbed by nanoparticles of $Fe_2O_3$, $Fe_3O_4$, $SiO_2$, and $Al_2O_3$ (Bakshi et al. 2015).

Some nanoparticles are found to be beneficial for plant protection and growth of selected plants, as discussed in Sect. 1.6. Unfortunately, the same types of nanoparticles are shown to be toxic to animals, humans, and some plants, such as carbon nanotubes (CNTs), Ag, titanium dioxide ($TiO_2$), silica ($SiO_2$), and alumina ($Al_2O_3$), as seen in Sect. 1.7.

The use of nanoparticles in agriculture should be limited by legislation. Very concerning is the increasing number of patents being filed related to nano-agrichemicals. The buildup of nanoparticles in plants, soil, water, and the environment, their trophic transfer, will detrimentally and irreversibly affect the health of humans and animals as well as plants. Many nanoparticles are shown to enter edible plants, and once they are in the food chain, they are likely to cause adverse health effects. It is imperative that regulatory agencies address and control the utilization of nanoparticles in agriculture (Kookana et al. 2014).

The reader interested in finding out more details about nanoparticles used in agriculture as agrichemicals, crop enhancers, crop protection, and soil and water remediation, can research the following reviews: Iavicoli et al. (2017), Khot et al. (2012), Liu and Lal (2015), Servin et al. (2015), Deng et al. (2014), Aragay et al. (2012), Gogos et al. (2012), Kah and Hofmann (2014), Ruttkay-Nedecky et al. (2017), and Wang et al. (2016).

### 1.3.2 Nanoparticle Soil Interaction and Accumulation

The use of nanoparticles in agriculture results in their accumulation in soil and the environment in general as well as trophic transfer. We must specify that when speaking about soil and nanoparticles, we are referring to man-made nanoparticles. Within the soil there are a multitude of natural nano- and microparticles, some of them having beneficial properties for the soil fertility. For example, clay nanoparticles may prevent leakage of nutrients in the groundwater by forming electrostatic bonds with them (Bernhardt et al. 2010).

Several types of nanoparticles are known for their antibacterial properties; hence their availability in soil is likely to affect soil bacteria, which are essential for their role in various ecosystems (Dinesh et al. 2012). The negative effects on endophytic bacteria symbionts are of special concern (Deng et al. 2014). Nanoparticles in soil will modify their properties in a dynamic manner, affecting their aggregation, dispersibility, dimensions, surface area, charge, and chemistry, which will affect their transport and availability.

Nanoparticle interaction with the soil and their bactericidal properties depends on the soil properties (Bakshi et al. 2015; Layet et al. 2017; Schlich and Hund-Rinke 2015). For example, silver nanoparticle toxicity against ammonia-oxidizing bacteria decreases for soils with higher clay content and larger pH. As a result, the toxicity of nanoparticles on plants may be affected by the soil type (Josko and Oleszczuk 2013).

The existence of nanoparticles with bactericidal properties in soil is likely to affect plants. It was found that the exposure of legumes to some nanoparticles severely lowers nitrogen fixation due to their bactericidal effects. Soybean plants exposed to ceria nanoparticles have a reduced nitrogen fixation correlated with almost absent bacteroids in its nodules (Priester et al. 2012).

## 1.4 Nanoparticle Uptake in Plants

### 1.4.1 Nanoparticle Uptake Routes

The interaction of nanoparticle with plants is a relatively new field of study. Nanoparticle uptake is plant specific. While the topic of uptake and transport of nanoparticles within plants is still not entirely understood, there is a consensus that it depends on the type of nanoparticle, their physicochemical properties, plant species, and the plant substrate—soil, hydroponics, or culture medium (Arruda et al. 2015; Aslani et al. 2014; Bakshi et al. 2015; Bernhardt et al. 2010; Chichiricco and Poma 2015; Deng et al. 2014; Dietz and Herth 2011; Ma et al. 2015; Miralles et al. 2012a, b; Navarro et al. 2008; Rico et al. 2011; Yadav et al. 2014; Schwab et al. 2015; Zuverza-Mena et al. 2017; Reddy et al. 2016).

It is known already that some nanoparticles translocate within the plants by forming complexes with membrane transporter proteins or root exudates (Yadav et al. 2014). Nanoparticle properties, such as size, porosity, hydrophobicity, and

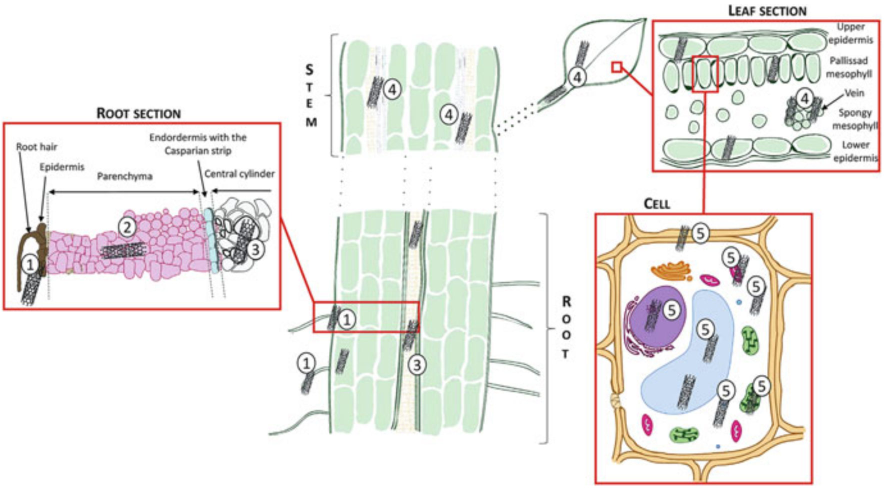



**Fig. 1.5** Schematics of the uptake and translocation of CNTs in plants. Image not at scale. Within the cell blue represents vacuole; green, chloroplasts; purple, nucleus; orange, smooth endoplasmic reticulum; blue, plasmode. *1*. The uptake of CNTs by plant roots can occur via osmotic pressures, capillary forces, pores on cell walls, intercellular plasmodesmata, or through direct penetration. *2*. Endocytosis allows CNTs to cross both cell wall and cell membrane. *3*. CNTs may use the vascular system together with water and nutrients and can translocate to the upper parts of the plants. *4*. CNTs may reach the upper part of plants. Their preferential location in leaves is the xylem. *5*. Inside the cells CNTs can be found in cytoplasm, cell wall, cell membrane, chloroplast, mitochondria, and plasmodes. Reprinted from Carbon, vol. 123, Line C. et al., Carbon nanotubes: Impacts and behaviour in the terrestrial ecosystem—A review, pp. 767–785. Copyright (2017), with permission from Elsevier (Line et al. 2017)

surface, are modulating the interaction of nanoparticles with plants. A schematic of nanoparticle uptake in plants is shown in Fig. 1.5 (Line et al. 2017).

Roots can uptake small nanoparticles through pores (with size around 5–20 nm) within the root epidermal cell walls—called the apoplastic route (Deng et al. 2014). Particles larger than the pore size will be stopped. Small nanoparticles that cross the cell walls may be subjected to osmotic pressure and capillary forces and diffuse through the apoplast and reach the endodermis (Lin et al. 2009; Deng et al. 2014).

Another route of nanoparticle uptake in plants is the symplastic pathway via the inner side of the plasma membrane. The cell wall is a porous matrix of polysaccharide fibers that can be crossed by nanoparticles that bind to protein carriers, via aquaporins, ion channels, and endocytosis, or by piercing the cell membrane and creating new pores (Tripathi et al. 2017; Rico et al. 2011; Wild and Jones 2009). Nanoparticles can migrate to neighboring cells through plasmodesmata (20–50 nm diameter channels) (Deng et al. 2014).

Another way of entry of nanoparticle in plants is via foliar through stomatal pores (Larue et al. 2014a, b; Hong et al. 2014). From leaves nanoparticles can translocate to other parts of the plants, including roots (Hong et al. 2014). Examples of plants that internalize nanoparticles through leaves are rapeseed, wheat, beans, corn, lettuce, and cucumber (Chichiricco and Poma 2015). Nanoparticles ranging from a few nanometers up to several hundred nanometers and with different compositions can be internalized through leaves, such as ceria, titania, iron oxide, zinc oxide, and silver (Chichiricco and Poma 2015).

Within the cells nanoparticles are shown to interact with cell organelles, and depending on their physicochemical properties, many produce oxidative stress, genotoxicity, and metabolic changes (Deng et al. 2014).

### 1.4.2 Nanoparticle Composition-Dependent Uptake in Plants

In the following, we will focus mostly on the nanoparticle uptake on crops due to their immediate trophic transfer to humans and animals. Many crops exposed to various nanoparticles have been shown to internalize them (Deng et al. 2014). Once inside, they translocate to various plant tissues: stems, leaves, petioles, flowers, and fruits (Deng et al. 2014). While there are some reports on beneficial effects on selected plants, there is an overwhelming evidence of adverse effects of nanoparticles on many crops.

Below are examples of studies showing the uptake of nanoparticles with various compositions in various edible plants:

- Au—tomato plants (Dan et al. 2015), tobacco (Judy et al. 2011; Sabo-Attwood et al. 2012), *Arabidopsis thaliana* (Avellan et al. 2017; Taylor et al. 2014), barley (Feichtmeier et al. 2015), rice, radish, pumpkin (Zhu et al. 2012)
- Ag—*Arabidopsis thaliana* (Geisler-Lee et al. 2013; Kaveh et al. 2013; Nair and Chung 2014), tomato (Antisari et al. 2015), wheat (Dimkpa et al. 2013b), lettuce (Larue et al. 2014a), mung bean and sorghum (Lee et al. 2012), rice (Mirzajani et al. 2013; Thuesombat et al. 2014), broad bean (Patlolla et al. 2012), corn, cabbage (Pokhrel and Dubey 2013), review (Cox et al. 2016)
- $CeO_2$—alfalfa, corn (Lopez-Moreno et al. 2010b; Wang et al. 2013b), cucumber (Zhang et al. 2011; Lopez-Moreno et al. 2010b; Rui et al. 2015; Hong et al. 2014), tomato (Antisari et al. 2015; Lopez-Moreno et al. 2010b; Wang et al. 2013b), soybean (Lopez-Moreno et al. 2010a), barley (Rico et al. 2015), lettuce (Gui et al. 2015; Zhang et al. 2015), wheat (Rico et al. 2014)
- MWCNTs—wheat (Miralles et al. 2012b; Larue et al. 2012b), rapeseed (Larue et al. 2012b), tomato (Khodakovskaya et al. 2013), red spinach (*Amaranthus tricolor* L), (Begum and Fugetsu 2012), lettuce, rice, cucumber (Begum et al. 2014), onion (Ghosh et al. 2015), alfalfa (Miralles et al. 2012b), corn (Yan et al. 2013), review (Line et al. 2017)
- $TiO_2$—corn (Asli and Neumann 2009), wheat (Du et al. 2011; Larue et al. 2012a, c), rapeseed (Larue et al. 2012a, c), lettuce (Larue et al. 2014b), *Arabidopsis thaliana* (Kurepa et al. 2010, Wang et al. 2011b), cucumber (Servin et al. 2012, 2013), tomato (Antisari et al. 2015), onion (Pakrashi et al. 2014; Ghosh et al. 2010), review (Cox et al. 2016; Jacob et al. 2013), tobacco (Ghosh et al. 2010)

- C60 or C70—*Arabidopsis thaliana* (Landa et al. 2012; Liu et al. 2010), bitter melon (Kole et al. 2013), rice (Lin et al. 2009), onion (Chen et al. 2010), review (Husen and Siddiqi 2014)
- Zn and ZnO—*Arabidopsis thaliana* (Landa et al. 2012), soybean (Lopez-Moreno et al. 2010a), radish, rape, lettuce, corn, cabbage (Pokhrel and Dubey 2013; Lin and Xing 2007), cucumber (Lin and Xing 2007), wheat (Dimkpa et al. 2013a; Du et al. 2011), cress (Josko and Oleszczuk 2013), onion (Kumari et al. 2011), garlic (Shaymurat et al. 2012)
- Carbon-Fe—pea, sunflower, tomato, wheat (Cifuentes et al. 2010)
- $Fe_3O_4$—pumpkin (Zhu et al. 2008), soybean (Ghafariyan et al. 2013), tomato (Antisari et al. 2015)
- $Al_2O_3$ or Al—onion, cress (Asztemborska et al. 2015), corn (Lin and Xing 2007; Asztemborska et al. 2015), review (Singh et al. 2017b)
- Co—tomato (Antisari et al. 2015), onion (Ghodake et al. 2011)
- Ni—tomato (Antisari et al. 2015; Faisal et al. 2013)
- $SnO_2$—tomato (Antisari et al. 2015)
- $CuO_2$—radish (Atha et al. 2012), wheat (Dimkpa et al. 2013a), rice (Shaw and Hossain 2013), review (Anjum et al. 2015)
- CdSe quantum dots—rice (Nair et al. 2011)
- Rare-earth $La_2O_3$, $Gd_2O_3$, $Yb_2O_3$—rape, radish, wheat, lettuce, cabbage, tomato, cucumber (Ma et al. 2010)

The accumulation of nanoparticles in plants is not yet entirely understood; however several trends are emerging (Deng et al. 2014). Nanoparticle uptake in plants is species specific and depends on the nanoparticle composition and their size. For example, tobacco uptakes Au nanoparticles, while wheat does not (Judy et al. 2012). One must emphasize that future research might show a different picture of nanoparticle uptake, as various researchers uses nanoparticles with different sizes, surface charge and functionalization, crystallinity, etc.

Nanoparticle uptake and toxicity in plants is composition specific. For example, the exposure of tomato plants to nanoparticles with various compositions ($CeO_2$, $Fe_3O_4$, $SnO_2$, $TiO_2$, Ag, Co, and Ni) has different effects on root growth, accumulation site, and fruit yield (Antisari et al. 2015). Longer roots are achieved after exposure to iron oxide nanoparticles, while the opposite effect is obtained by using tin oxide. While most metal nanoparticles accumulate in roots, silver and cobalt nanoparticles were found in below- and aboveground plant organs. Tomato fruits had higher amount of silver nanoparticles compared to other compositions (Antisari et al. 2015).

The uptake of nanoparticle by plants is a function of exposure condition, nanoparticle physicochemical properties, and plant species. Similar to the process in humans, the uptake and translocation of nanoparticles within plants can be very swift. The time of translocation from roots to shoots of carbon-coated magnetic nanoparticles in sunflower, tomato, pea, and wheat is less than 24 h (Cifuentes et al. 2010).

### 1.4.3 Nanoparticle Size-Dependent Plant Uptake

Particle size is one of the most important factors that determine the uptake of nanoparticles in plants. Smaller nanoparticles are internalized by plants, while larger ones are not (Zhu et al. 2008; Wang et al. 2011a). For example, in the case of $TiO_2$ nanoparticles with sizes between 14 and 655 nm, only the smallest ones are able to translocate through the entire wheat plant (Larue et al. 2012a). The ones smaller than 140 nm pass through wheat root epidermis, while those smaller than 36 nm can transfer through root parenchyma and translocate from root to shoot (Larue et al. 2012a). Another example is the uptake of ceria nanoparticles in cucumber (Zhang et al. 2011). Nanoparticles with sizes of 7 and 25 nm are both absorbed by cucumber roots and translocate to leaves; however a larger number of smaller nanoparticles are absorbed compared to larger ones (Zhang et al. 2011).

### 1.4.4 Nanoparticle Crystalline Structure-Dependent Plant Uptake

Nanoparticles with the same composition but different crystalline structure can suffer a different uptake and translocation in plants. For example, titanium dioxide nanoparticles in anatase and rutile crystalline form are differentially translocated in cucumber plants (Servin et al. 2012). The anatase nanoparticles remained mainly in the roots, while the rutile nanoparticles translocated and accumulated mostly in the aerial tissue of cucumber.

### 1.4.5 Nanoparticle Charge-Dependent Plant Uptake

Studies show that the uptake of nanoparticles in plants is a function of nanoparticle surface charge or functionalization. Nanoparticles can be neutral; have a positive charge, in which case are called cationic; or have a negative charge—being called anionic. There seems to be a different behavior in the uptake of nanoparticles according to their charge by woody plants compared to herbaceous plants.

**Woody Plants** A recent study on the uptake of CdSe/CdZnS quantum dots coated with cationic polyethylenimine (PEI) or poly(ethylene glycol) of anionic poly (acrylic acid) (PAA-EG) in poplar trees shows that both types of nanoparticles are internalized after 2-day exposure (Wang et al. 2014). Cationic quantum dot absorption is tenfolds faster than anionic nanoparticles, most likely due to electrostatic forces between positively charged quantum dots and the negatively charged root cell wall (Wang et al. 2014). Slower absorption of anionic quantum dots might be a result of the repulsive electrostatic forces between the negatively charged root surface and the negatively charged nanoparticles.

**Herbaceous Plants** Interestingly, the uptake of cationic and anionic nanoparticles in herbaceous plants differs from the one in woody plants (Koelmel et al. 2013; Zhu et al. 2012).

Rice under hydroponic conditions uptakes and bioaccumulates 2 nm gold nanoparticles. Their distribution is a function of the nanoparticle surface charge (Koelmel et al. 2013). The accumulation in roots follows the order AuNP (+) > AuNP(0) > AuNP(−), where "+," "0," and "−" denoted positive, zero, and negative electrical charged nanoparticles, respectively. In contrast, the rice shoots showed a reverse order of nanoparticle charge uptake compared to the roots, having a preferential uptake of anionic nanoparticles.

Similar results were obtained in a study on the uptake of (6−10 nm) gold nanoparticles with different surface charge under hydroponic conditions in rice, radish, pumpkin, and perennial ryegrass (Zhu et al. 2012). Nanoparticle uptake is surface charge and plant specific. Cationic nanoparticles translocate mainly in plant roots, while anionic nanoparticles suffer uptake mainly in plant shoots. A larger number of nanoparticles are found in radish and ryegrass roots than rice and pumpkin roots. Nanoparticles accumulate in rice shoots in larger amounts compared to none in radish and pumpkin shoots (Zhu et al. 2012).

Cerium oxide nanoparticles (4 nm in size) also have a preferential uptake and tissue localization in wheat according to their surface charge (Spielman-Sun et al. 2017). Positively charged $CeO_2$ adhere to wheat roots the strongest, while negatively charged and neutral nanoparticles have higher concentrations in leaves compared to plants exposed to cationic $CeO_2$.

Therefore, the trend for herbaceous plants is to absorb positively charged nanoparticles in roots, while the shoots, stems, and leaves uptake mainly negatively charged nanoparticles.

## 1.5 Detrimental Effect of Nanoparticles in Plants

### 1.5.1 Composition and Plant-Specific Phytotoxicity

The interaction between plants and nanoparticles may range from subtle to notable changes in plant morphology, physiology, biochemistry, and genetics (Deng et al. 2014). Plant morphology changes include germination index (germination time and rate), root elongation, shoot and root biomass, root tip morphology, etc. (Deng et al. 2014).

Many studies indicate a detrimental effect of nanoparticles in many plant species, while a minority is trying to promote the use of nanoparticles for selected beneficial effects in a few plants. It is important to note that while some plants will have beneficial effects as a result of exposure to a type of nanoparticle, other plants are negatively affected by the same nanoparticles.

Many types of nanoparticles are phytotoxic, inhibiting plant growth and physiological, biochemical, and genetic traits (Tripathi et al. 2017; Brar et al. 2010; Deng et al. 2014). Table 1.1 shows examples of edible plants adversely affected by

**Table 1.1** Detrimental effects of nanoparticles on selected crops

| | Au | Ag | CNT | $C_{60}$ | $TiO_2$ | $CeO_2$ | ZnO | $CuO_2$ | $Fe_3O_4$ |
|---|---|---|---|---|---|---|---|---|---|
| Alfalfa (*Medicago sativa*) | | | | | D | D | D | D | |
| *Arabidopsis thaliana* | D | D | D | | | D | D | *D* | D |
| Barley (*Hordeum vulgare*) | D | D | | | | D | | D | D |
| Corn (*Zea mays*) | | D | | D | D | D | D | D | |
| Cress (*Lepidium sativum*) | | | | | D | | D | | D |
| Cucumber (*Cucumis sativus*) | | D | D | | D | D | D | D | D |
| Lettuce (*Lactuca sativa*) | | D | D | | D | D | D | D | D |
| Onion (*Allium cepa*) | | D | D | D | D | | D | D | |
| Pumpkin (*Cucurbita*) | | | | | | | | | D |
| Radish (*Raphanus raphanistrum*) | | D | | | D | D | D | D | D |
| Red spinach (*Amaranthus tricolor*) | | | D | | | | | D | D |
| Rice (*Oryza sativa*) | D | D | D | D | D | D | D | D | |
| Soybean (*Glycine max*) | D | | D | D | | D | D | D | D |
| Tomato (*Lycopersicon esculentum*) | D | D | D | | D | D | D | | D |
| Wheat (*Triticum aestivum*) | | D | D | | D | D | D | D | D |

D—found detrimental in at least one of the growth inhibition, physiological and biochemical traits, and toxicity at genetic level

nanoparticles with several compositions that are promoted or already being used as agrichemicals (Au, Ag, CNT, $C_{60}$, $CeO_2$, ZnO, $CuO_2$, $Fe_3O_4$). Here "D" refers to detrimental.

Table 1.2 shows examples of plant-specific detrimental effects of nanoparticles as a result of plant exposure to nanoparticles with several compositions. These range from adverse effects in their physiological, biochemical, and genetic traits. Noble metal nanoparticles, such as Au, induce necrosis in tobacco plants (Sabo-Attwood et al. 2012). Exposure to Ag nanoparticles leads to retarded germination in rice and corn (Thuesombat et al. 2014; Pokhrel and Dubey 2013) and reduction in mitotic index and fragmented chromosomes in onion (Kumari et al. 2009). Carbon-based nanoparticles (CNTs, $C_{60}$) lead to cellular toxicity in rice, spinach, and onion (Shen et al. 2010; Begum and Fugetsu 2012; Chen et al. 2010), reduction in biomass for zucchini (Stampoulis et al. 2009), and delayed flowering together with decreased yield (Lin et al. 2009). Exposure to $TiO_2$ nanoparticle results in damaged chloroplast and reduced photosynthetic rate in spinach (Lei et al. 2008), stress in cucumber

**Table 1.2** Examples of detrimental effects as a result of plant exposure to different nanoparticles

| NPC | Size (nm) | Plant | Effect | References |
|---|---|---|---|---|
| Au | 3 | Tobacco | Necrosis | Sabo-Attwood et al. (2012) |
| Ag | 20 | Rice | Seed germination | Thuesombat et al. (2014) |
| | 11 | Corn | Retarded germination | Pokhrel and Dubey (2013) |
| | <100 | Onion | Fragmented chromosomes, reduction in mitotic index | Kumari et al. (2009) |
| CNT | 1–2 | Arabidopsis | Cell death | Shen et al. (2010) |
| | | Rice | Delayed flowering, decreased yield | Lin et al. (2009) |
| | | Rice | DNA damage, cell viability | Shen et al. (2010) |
| | | Zucchini | 60% reduction in biomass | Stampoulis et al. (2009) |
| | | Spinach | Cell damage | Begum and Fugetsu (2012) |
| $C_{60}$ | | Onion cells | Necrosis | Chen et al. (2010) |
| $TiO_2$ | 27 | Cucumber | Stress | Servin et al. (2013) |
| | 30 | Corn | Inhibited leaf growth | Asli and Neumann (2009) |
| | | Corn | DNA damage | Castiglione et al. (2011) |
| | 5 | Spinach | Damaged chloroplast, reduced photosynthetic rate | Lei et al. (2008) |
| | 100 | Onion | DNA damage | Ghosh et al. (2010) |
| $CeO_2$ | 7 | Soybean | Genotoxicity | Lopez-Moreno et al. (2010a) |
| | 8 | Cucumber | Stress | Hong et al. (2014) |
| | 8 | Rice | Stress | Rico et al. (2013) |
| | 8 | Wheat | Nutrition | Rico et al. (2014) |
| | 10 | Cucumber | Nutrition | Zhao et al. (2014) |
| | 10–30 | Tomato | Detrimental effects on second-generation plants | Wang et al. (2013b) |
| ZnO | 20 | Corn | Plant growth | Lin and Xing (2007) |
| | <100 | Onion | Genotoxicity | Kumari et al. (2011) |
| | 8 | Soybean | Plant growth | Lopez-Moreno et al. (2010a) |
| | <50 | Soybean | Seed formation | Yoon et al. (2014) |
| | 4 | Garlic | Genotoxicity | Shaymurat et al. (2012) |
| | 10 | Green peas | Chlorophyll/stress | Mukherjee et al. (2014) |
| | 100 | Rice | Root length/formation | Boonyanitipong et al. (2011) |
| | 30,50 | Chinese cabbage | Root and shoot formation | Xiang et al. (2015) |
| | <50 | Buckwheat | Genotoxicity | Lee et al. (2013) |

(continued)

**Table 1.2** (continued)

| NPC | Size (nm) | Plant | Effect | References |
|---|---|---|---|---|
| CuO, Cu | <50 | Rice | Stress | Shaw and Hossain (2013) |
| | | Zucchini | 77% reduced root length<br>90% reduced biomass | Stampoulis et al. (2009) |
| | <100 | Radish | Decreased root growth, DNA damage | Atha et al. (2012) |
| | <50 | Buckwheat | Genotoxicity | Lee et al. (2013) |
| Ni | 23,34 | Tomato | Stress, mitochondria, cell damage | Faisal et al. (2013) |

*NPC* nanoparticle composition

(Servin et al. 2013), inhibited leaf growth, and DNA damage in corn (Asli and Neumann 2009; Castiglione et al. 2011). $CeO_2$ nanoparticle adversely affects the nutrition and genetics of soybean, cucumber, rice, and wheat (Lopez-Moreno et al. 2010a; Hong et al. 2014; Rico et al. 2013, 2014; Zhao et al. 2014). ZnO is genotoxic to onion, garlic, and buckwheat (Kumari et al. 2011; Shaymurat et al. 2012; Lee et al. 2013); affects the seed formation in soybean (Yoon et al. 2014); inhibits plant growth in corn, soybean, rice, and cabbage (Lin and Xing 2007; Lopez-Moreno et al. 2010a; Boonyanitipong et al. 2011; Xiang et al. 2015); and affects chlorophyll in green peas (Mukherjee et al. 2014). CuO is genotoxic to radish and buckwheat (Atha et al. 2012; Lee et al. 2013), produces stress in rice (Shaw and Hossain 2013), and severely reduces root length (77%) and biomass (90%) in zucchini (Stampoulis et al. 2009). Nickel nanoparticles induce stress and damage of mitochondria and cells in tomato (Faisal et al. 2013).

A type of nanoparticle can sometimes have both beneficial and detrimental effects on the same plant. For example, barley exposed to $CeO_2$ nanoparticles (500 mg/kg) led to a more than 300% increase in shoot biomass; however it formed no grain (Rico et al. 2015).

In the following subchapters, we will elaborate on the adverse effects of nanoparticles on plant physiological, biochemical, and genetic traits.

### 1.5.2 Plant Growth Inhibition

Phytotoxicity related to growth inhibition manifests in reduced biomass; decreased germination and leaf growth; reduced root elongation, root biomass, root tip morphology, and shoot growth; delayed flowering; and decreased yield among others (Tripathi et al. 2017). The adverse biochemical traits involve the generation of reactive oxygen species, lipid peroxidation, decreased rate of transpiration, disturbed mitosis, breakdown of cell wall, reduction in chlorophyll content, and reduced photosynthesis (Tripathi et al. 2017). Toxicity at genetic level involves reduction in mitotic index, sticky and fragmented chromosomes, chromosome aberrations, alteration of genes, damaged DNA structure, and decreased cell viability (Tripathi et al. 2017). Examples of toxic effects of nanoparticle on plants are given in Table 1.2.

Some adverse effects of nanoparticles on plant growth are easily assessed by measuring the germination index, the elongation of roots and shoots, root biomass, root tip morphology, total biomass, and flowering (Deng et al. 2014).

For plants exposed to nanoparticles from soil or hydroponically, an important indicator of toxicity is the shoot and root biomass. While studies use different exposure times and doses, the general conclusion is that phytotoxicity is plant and nanoparticle specific. This toxicity can be due to the release and subsequent accumulation of ions in plant tissue and/or nanoparticle uptake and translocation (Deng et al. 2014). Nanoparticles with various compositions have an adverse effect on seedling roots and shoot elongation, mainly due to the adsorption of nanoparticles into the roots. Among phytotoxic materials to roots and shoots are gold, silver, zinc oxide, copper oxide, alumina, and carbon nanotubes (Begum and Fugetsu 2012; Begum et al. 2012; Burklew et al. 2012; Feichtmeier et al. 2015; Deng et al. 2014; Dimkpa et al. 2013b; Ghodake et al. 2011).

Figure 1.6 shows photographs of plants detrimentally affected by exposure to nanoparticles. Figure 1.6a–h illustrates the trend of decreased shoot and root length in a concentration-dependent manner in tomato and cauliflower exposed to CuO nanoparticles (Singh et al. 2017a), wheat exposed to Ag nanoparticles (Dimkpa et al. 2013b), barley seedlings exposed to Au nanoparticles (Feichtmeier et al. 2015), red spinach exposed to MWCNTs (Begum and Fugetsu 2012), rice exposed to MWCNTs (Begum et al. 2012), and rice exposed to CuO nanoparticles (Shaw and Hossain 2013). Figure 1.6i–j shows various aberrant features observed in onion after exposure to titanium dioxide nanoparticles, such as chromosome break and nuclear blebbing (Pakrashi et al. 2014).

It is important to note that nanophytotoxicity is material and species specific. This can be seen in a study comparing the toxic effects of several rare-earth oxide nanoparticles ($CeO_2$, $La_2O_3$, $Gd_2O_3$, $Yb_2O_3$) on several crops (cabbage, cucumber, lettuce, radish, rape, tomato, wheat) (Ma et al. 2010). For example, only the root elongation of lettuce is affected by $CeO_2$, while all remaining ($La_2O_3$, $Gd_2O_3$, $Yb_2O_3$) nanoparticles lead to a large reduction in root elongations for all studied plants.

Silver nanoparticles are known for their antibacterial, antifungal activity and are consequently used extensively as agrichemicals. As a result, the existence of Ag nanoparticles in soil can have an effect upon soil microbiota (such as nitrogen-fixing bacteria) that will in turn affect the physicochemical characteristics of soil and plants (Anjum et al. 2013). Silver nanoparticles can be internalized and accumulate in edible plants and consequently enter the food chain. Some plants exposed to silver nanoparticles show reduced germination, biomass, transpiration, shoot and root length, and cytotoxicity involving modifications in gene expression, oxidative stress, decreased mitosis, chromosomal abnormalities, and cell death (Anjum et al. 2013; Arruda et al. 2015; Thuesombat et al. 2014; Pokhrel and Dubey 2013; Kumari et al. 2009). Silver nanoparticles have a concentration-dependent growth inhibition effect upon mung bean and sorghum (Lee et al. 2012).

MWCNTs are the type of nanoparticle that shows the entire array of effects on plants, ranging from beneficial to detrimental. They are promoted for their use in