Sustainable Plant Nutrition in a Changing World

Vishnu D. Rajput
Krishan K. Verma
Neetu Sharma
Tatiana Minkina *Editors*

The Role of Nanoparticles in Plant Nutrition under Soil Pollution

Nanoscience in Nutrient Use Efficiency

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Preface

Nanotechnology, with its research and outcomes, has become one of the most important fields in the forefront of all disciplines of sciences. The promising results of research hold great potential for providing breakthroughs that will revolutionize the scientific progresses in all fields. *The Role of Nanoparticles in Plant Nutrition Under Soil Pollution* presents a comprehensive review of the role of nanotechnology in agriculture in a compilation of 16 chapters related to importance, recycling, and transformation of nanoparticles, role of nanotechnology in increasing yield and growth, and nanoparticles as bioremediation agents. Each chapter provides a detailed perspective of principle, procedure, glitches, and solutions of diverse topics with illustrative work in the form of figures and tables for students, researchers, and professionals. The purpose of this book is to provide a brief introduction to the application of nanotechnology in the field of agriculture that allows students, academicians, and researchers to obtain insights into the developments in this area. The topics include the global importance, bioavailability and transformation process, interaction with soil pollutants and their impact on soil systems, use of nanoelements in combating plant nutrition, and biofortification. The other important areas covered include nano-biosensors, interaction of nanoparticles with plant hormones, and impact of nanoparticles on genetic makeup of the plant system along with risks and concerns of their usage in agriculture. This book includes recent research and innovations along with case studies that will help readers grasp the updated content in a better way.

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About the Editors

Vishnu D. Rajput is working as an associate professor (leading researcher) at Sothern Federal University, Russia. His ongoing research is based on soil contaminations, that is, potentially toxic elements, and metallic nanoparticles, and investigating the bioaccumulation, bio/geo-transformations, uptake, translocation, and toxic effects of metallic nanoparticles on plant physiology, morphology, anatomy, the ultrastructure of cellular and subcellular organelles, cytomorphometric modifications, and DNA damage. He comprehensively detailed the state of research in environmental science in regard to how nanoparticles/heavy metals interact with plants, soil, microbial community, and the larger environment. He has published (total of 290 scientific publications) 167 peer-reviewed highly rated full-length articles, 15 books, 60 chapters (Scopus indexed), and 37 conference articles and achieve h-index: 18 by Scopus with 1320 citations, till April 2022. He is an internationally recognized reviewer (peer reviewed 180 manuscripts and has received an outstanding reviewing certificate from Elsevier, Springer and Plants-MDPI. He is an editorial board member of various high-impact journals. Dr. Rajput has received "Certificate for Appreciation" 2019, 2021; "Certificate of Honor 2020" and Diploma Award 2021 by Southern Federal University, Russia, for "Outstanding Contribution in Academic, Creative Research, and Publication activities". He has also received "Highly qualified Specialist" status by Russin Govt. https://www.researchgate.net/profile/Vishnu-Rajput; https://www.scopus.com/authid/detail.uri?authorId=56516545100

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Tatiana Minkina is the head of Soil Science and Land Evaluation Department at Southern Federal University. She is the head of international master's degree educational program "Management and estimation of land resources" (2015–2022, accreditation by ACQUIN). Her area of scientific interest is soil science, biogeochemistry of trace elements, environmental soil chemistry, soil monitoring, assessment, modeling, and remediation using physicochemical treatment methods. She was awarded in 2021 with Diploma of the Ministry of Education and Science of the Russian Federation for many years of long-term work for development and improvement of the educational process and significant contribution to the training of highly qualified specialists. Currently, she is handling projects funded by the

Russian Scientific Foundation, Ministry of Education and Science of the Russian Federation, and Russian Foundation of Basic Research. She is a member of the Expert Group of Russian Academy of Science, the International Committee on Contamination Land, Eurasian Soil Science Societies, the International Committee on Protection of the Environment, and the International Scientific Committee of the International Conferences on Biogeochemistry of Trace Elements. Her total scientific publications are as follows: 957 (total 957, 389 in English); Scopus—268, WoS—196, and citing index: Scopus—1976, h-index—21; WoS—1452, h-index—20. She is the invited editor of an open access journal from MDPI, *Water* (ISSN 2073-4441; impact factor: 3.229; SJR 0.718), and editorial board member of *Geochemistry: Environment, Exploration*, *Analysis* (ISSN: 1467-7873; impact factor: 1.545; SJR: 0.346), and the *Eurasian Journal of Soil Science* (e-ISSN: 2147–4249; SJR 0.24). https://www.researchgate.net/profile/Tatiana-Minkina; https://www.scopus.com/authid/detail.uri?authorId=15063165400

Chapter 1
Global Importance and Cycling of Nanoparticles

Uzma Kafeel, Urfi Jahan, Fariha Raghib, and Fareed Ahmad Khan

1 Introduction

A nanoparticle is a matter particle between 1 and 100 nanometers (nm) in diameter. At times the word is intended for bigger particles, up to 500 nm, or fibers and tubes that are smaller than 100 nm in only two directions (Vert et al. 2012). Nanoparticles are distinguishable because their infinitesimal size derives very diverse physical or chemical properties, like colloidal properties, optical or electrical properties. Nanoparticles are produced both naturally or synthesized as engineered materials. Naturally occurring nanoparticles (NNPs) are made through cosmological, geological, meteorological, and biological ways (Simakov et al. 2015; Simakov 2018). Engineered nanoparticles (ENPs) are produced as pure particles or composites and in several shapes and sizes and surface structures which are additionally conjugated to different bioactive molecules, forming an estimable number of variants with indefinite potential for biological uses (Ha et al. 2013), including better procedures for decreasing pollution, water management, environmental sensing, bioremediation, and making alternate energy resources more economical. The exceptional characteristics of nanoparticles facilitate these innovative technologies to encounter environmental tasks with a viable approach (Pathakoti et al. 2018). Given the mounting prominence of nanoparticles in research and developmental activities, risks associated with health, safety, and the environment should be highly considered. Accordingly, rules for safe handling, usage, and disposal of nanoparticles should be provided and strictly monitored in research and occupational sites to lessen the threats from health, safety, and environmental exposures. The chapter

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broadly centers on the environmental applications of nanoparticles and emphasizes their safe disposal and cycling.

2 Global Importance of Nanoparticles

2.1 Soil Remediation

In the present decade (2021–2030), which is declared as the UN decade for Ecosystem restoration, the remediation of soil systems is of utmost concern (Rajput et al. 2021). Improper management of metropolitan and industrial waste, unrestrained and laid-back chemical discharge, commonly due to industrial activity, and too much treatment of pesticides and fertilizers in crop production lead to soil deterioration. In current times, soil pollution is of grave concern, and the need to conserve soil quality is pivotal for ecosystems and human health (Galdames et al. 2020). Heavy metal (HM) pollution is alarming, owing to their toxicity, non-biodegradability, and accumulation (Naikoo et al. 2020). HMs hinder various physiological processes comprising disruption of cell functions, modifications in enzyme specificity, damaging cell membrane and DNA configuration (Bruins et al. 2004; Naikoo et al. 2019a; Raghib et al. 2020). Some plants accumulate and endure high levels of HMs due to their proficient biochemical tolerance mechanisms which makes them superb contenders for phytoremediation of contaminated soils (Naikoo et al. 2019b). Even though useful, these conventional strategies are time-consuming and costly. Remediation with nanoparticles is considered a favorable approach for the decontamination of HM-contaminated soils (Xue et al. 2018; Fajardo et al. 2019). It is more operative and economical than conventional approaches because of the better reactivity of nanoparticles plus the option of in-situ management.

Three widely used nanoparticles in soil remediation are nanoscale zero-valent iron (nZVI) particles, nanoscale calcium peroxide (CaO_2), and nanoscale metal oxides used for the degradation of halogenated organic compounds, destruction of organics, and adsorption of metals, respectively (Mueller and Nowack. 2010). Fajardo et al. (2019) reported the effectiveness of nanoparticle remediation in soil contaminated with HMs. Chemical analysis showed that adding nZVI stabilized elevated zinc concentrations (Zn) and lead (Pb) used in the study (Carmen et al. 2019). After some weeks of nZVI application, when the bioavailability and toxicity of HMs are reduced, bioremediation can be done subsequently to enhance detoxification and improve the nano remediation strategy's efficiency for restoring contaminated sites. Applications of nZVI particles have attained favorable results, making them predominantly useful for remediation of subsurface contaminants. Degradation of many such deterrent halogenated aliphatic hydrocarbons with nZVI, for example, the degradation mechanism of cis-dichloroethylene (cis-DCE), trichloroethylene (TCE), tetrachloroethylene (PCE), and trans-dichloroethylene (trans-DCE), has been studied and reported (Arnold and Roberts 2000). Bare nZVI particles also reduce nitrate concentrations (Galdames et al. 2020).

Iron nanoparticles (FeNP) showed promising results in remediation of soils contaminated with chlorinated organic compounds, metals (Lowry and Johnson 2004; Zhang 2003), and arsenic (As) (Shipley et al. 2010). Magnetite (Fe_3O_4) and hematite (Fe_2O_3) nanoparticles effectively remove arsenic (As^{3+}), (As^{5+}), cadmium (Cd), chromium (Cr), cobalt (Co), nickel (Ni), selenium (Se), molybdenum (Mo), vanadium (V), lead (Pb), antimony (Sb), thallium (Tl), thorium (Th), and uranium (U) to negligible concentrations, suggesting their budding potential in remediation of HM-contaminated soils (Shipley et al. 2010). CaO_2 nanoparticles act as oxidants in treating soils containing different carbon-based pollutants, such as heating oil, gasoline, ethylene glycol, methyl tertiary butyl ether, and solvents. Also, they are highly effective in removing aromatics and are used in advanced bioremediation. The O_2 released in the reaction of CaO_2 with H_2O helps in forming an aerobic atmosphere backing up natural bioremediation by aerobic organism's existent in soil (Mueller and Nowack 2010).

2.2 *Water Treatment*

Using nanoparticles in water and wastewater treatment has been considered extensively due to their minuscule size and vast specific surface areas. Nanoparticles have remarkable adsorption capacities, high reactivity, and mobility (Khan and Siddiqui 2020a, b). Various nanoparticles have successfully removed bacteria, heavy metals, inorganic anions, and organic contaminants present in water (Tang et al. 2014; Liu et al. 2014; Yan et al. 2015; Kalhapure et al. 2015). Nanomaterials widely used for water and wastewater treatment include carbon nanotubes (CNTs), metal oxide nanoparticles, nanocomposites, and zero-valent metal nanoparticles (Lu et al. 2016). Silver nanoparticles (Ag NPs) are widely used to disinfect water, acting as an excellent antimicrobial agent. Ag NPs stick to the bacterial cell wall, enter it, cause structural modifications in the cell membrane, and increase its permeability (Quang et al. 2013). Among many zero-valent metal nanoparticles, nZVI and nZVZ (nano zero-valent zinc) are better-reducing agents relative to various redox-labile pollutants (Yang et al. 2019).

Despite a weaker reduction potential, Fe possesses many noticeable benefits over Zn among exceptional adsorption properties, oxidation, precipitation, and is cost-effective. nZVI is efficient in eliminating a wide series of contaminants, together with halogenated organic compounds (Liang et al. 2014), nitroaromatic compounds (Xiong et al. 2015), organic dyes (Hoag et al. 2009), phenols (Wang et al. 2013), heavy metals (Galdames et al. 2020), inorganic anions such as phosphates (Markova et al. 2013) and nitrates (Muradova et al. 2016), metalloids and radio elements (Ling and Zhang 2015). CNTs are also likely substitutes for treating wastewater owing to their large surface area, ease of chemical and physical modification, and rapid adsorption kinetics (Lu et al. 2016). They have excellent adsorption effects toward Mn^{7+} (Yadav and Srivastava 2017), Tl^{1+} (Pu et al. 2013), Cu^{2+} (Tang et al. 2012), Pb^{2+} (Kabbashi et al. 2009), and Cr^{6+} (Tuzen and Soylak 2007).

Although each nanoparticle discussed above has its own advantages, their respective disadvantages cannot be ignored. CNTs can only be used with secondary medium or matrix to form structural components as it is difficult for CNTs to suspend evenly in different solvents. Besides, nanoparticles frequently face difficulty in aggregation, oxidation, poor separation, and an extreme pressure drop when cast-off in flow-through systems and fixed-bed (Yunus et al. 2012). To avoid such issues and improve elimination efficiency, nanocomposites are considered an operative strategy for treating water and wastewater (Galdames et al. 2020). Water and wastewater treatment demand safe, continuingly stable, and cheap materials. Research is still ongoing to acquire desired nanocomposites. An in-depth study and understanding mechanisms of the interaction vis-à-vis the hosts and guests of nanocomposites is vital to lead the synthesis of nanocomposites productively.

2.3 Air Pollution Control

Nanomaterials act as potential super adsorbents to confiscate various kinds of organic and inorganic air contaminants. Toxic gases present in ambient air are cleaned through nanoparticles. An example of such usage in harmful gas cleaning is the adsorption by CNTs and gold (Au) particles. CNTs are single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). SWNTs are chemical sensors for nitrogen dioxide (NO_2) and ammonia (NH_3), and MWNTs are used as hydrogen (H_2) storage (Yunus et al. 2012). CNTs give suggestively better outcomes than activated carbon and aluminum oxide (γ -$Al_2O_{3)}$ in confiscating dioxins (Bhushan 2010), NO_x (Long and Yang 2001), sulfur dioxide (SO_2), and carbon dioxide (CO_2) (White et al. 2003; Aaron and Tsouris 2005). This advancement of CNTs is perhaps attributable to their curved surface equated with flat sheets, which provide more vital interactive forces between pollutants and CNTs (Yunus et al. 2012). In addition to NO_2 and SO_2, there are several atmospheric pollutants, such as nitrous acid (Indarto 2012), polyaromatic compounds (Santiago and Indarto 2008; Indarto et al. 2009), volatile organic compounds (VOCs) (Sinha and Suzuki 2007), and soot (Indarto 2009) that nanoparticles effectively adsorb.

Combination of very porous manganese oxide (MnO) and Au nanoparticles (which are grown in it) at room temperature is beneficial for removing VOCs from the air (Sinha and Suzuki 2007). This accomplishment is due to porous MnO, which has a considerably larger surface area than all earlier known compounds. The presence of Au nanoparticles reduces the barrier of radical formation. This novel combination unlocked the opportunity for further nano-metal compounds. Isopropyl alcohol (IPA) is used in manufacturing semiconductors and optoelectronic devices. Lack of air pollution control causes IPA vapors to be released into the atmosphere without any remediation. These vapors are carcinogenic and cause skin irritations in humans. Hsu and Lu (2007) oxidized SWNTs in a solution of hydrochloric acid (HCl), nitric acid (HNO_3), and sodium hypochlorite (NaClO), which was used to adsorb IPA vapors. After being oxidized by HCl, HNO_3, and NaClO solution, physicochemical properties of SWNTs considerably enhanced, resulting in reduced pore size simultaneously increasing the surface of functional groups, the surface area of micropores, and the dynamic surface of the base. Subsequently, SWNTs adsorb even more IPA vapors from the air stream (Hsu and Lu 2007). Nanowires like Si nanowires (SiNWs) are adept tools for chemical and biological sensors (Smart et al. 2006). Their minuscule dimension and capability to identify several analytes in actual sensors can help detect chemical and biological pathogens in air, water, and food.

2.4 Agriculture and Crop Productivity

In recent years, nanoparticles have played a substantial role in food security, food safety, and global food production using nanoscale micronutrients in exploring the relationship between nutritional status and crop diseases. Besides enhancing crop yield, nanoparticles can exploit the benefits of agriculture means through able products such as pesticides, soil and plant sensors, and disease management (Khan and Siddiqui 2020a, b; Raghib et al. 2020; Khan et al. 2021). Nanoparticles lessen the applied quantity of plant safety products, curtail nutrient damages in fertilization, and upsurge crop harvests through enhanced nutrient management (Predoi et al. 2020). Nanoparticles optimize soils deficient in elements like Fe, Zn, Se, P, Ca, and Mg (Gogos et al. 2012). In recent years, nanoparticles have been used to make several nano-products that are used as fertilizers, for example, active nano-grade organic fine humic [CN 1472176-A] (Yang et al. 2007), oxide nano rare earth [CN1686957-A] (Wang et al. 2011), nanosilver [KR 000265-A] (Jo et al. 2009), and nano-selenium [U.S. 0326153-A] (Li et al. 2012).

Nanofertilizers control the discharge and organization of nutrient fluctuation over time with their uptake, curtailing the loss of nutrients through soil or air (Tarafdar et al. 2014). There is a constructive effect on crop development and pathogen inhibitions relative to Ag, Mg, Si, TiO_2, or ZnO nanoparticles (He et al. 2011; Yin et al. 2011; Jaberzadeh et al. 2013; Delfani et al. 2014; Janmohammadi et al. 2015). Foliar application of ZnO nanofertilizer on Pearl millet enhanced shoot length by 16%, root length by 4.5%, chlorophyll content by 24%, and soluble leaf protein by 38% (Tarafdar et al. 2014). ZnO NPs are also useful in controlling pathogen growth, are less toxic than AgNP sand, and enhance soil fertility. Usage of ZnO NPs resulted in complete disturbance of cell functions of fungi *Botrytis cinerea* and *Penicillium expansum,* distorting hyphae and fungal complexity (He et al. 2011). The antifungal action of AgNPs is described by their amassing in the fungal hyphae, which disrupts cell functions, an extreme mechanism associated with a higher ion discharge on the amplified nanoparticle surface area (Yin 2011). A dose of 50 μg/ml MWCNTs on tomato roots resulted in improved fresh and dry weight and altering gene expressions (Khodakovskaya 2011).

The foliar application and root application of Fe_2O_3 nanoparticles on soybean resulted in root elongation and better photosynthetic parameters (Alidoust and Isoda

2013). Exposure of spinach roots to TiO_2 nanoparticles enhanced growth rate, photosynthetic rate, chlorophyll content, and RuBisCo activity (Linglan et al. 2008). An additionally capable candidate is TiO_2 NPs because of their assembled photocatalytic and antimicrobial activity. Application of TiO_2 NPs suppressed septicity of *Penicillium cubensis* on cucumber by 90% and increased photosynthetic activity by 32% (Cui et al. 2009). The application of cerium oxide (CeO_2) nanoparticles on cucumber leaves exhibited increased leaf-root translocation signifying phloem-based transportation in the plant (Hong 2014). Zn nanoparticles protected rice plants from ROS impairment by improving levels of antioxidant enzyme actions during germination.

Consequently, Zn nanoparticles-treated seeds exhibited more significant potential for germination (Azarin et al. 2022). To achieve higher crop production, the development of varieties for effective nutrient use can supplement agricultural tactics (Al Tawaha et al. 2020). Tomato plants infected with *Phytothphora infestans* tested for the effect of CuO_2 nanoparticles revealed 74% disease suppression and 58% improvement in nutrient quality (Gianoussi et al. 2013). The problem of in-plant translocation is worth mentioning, i.e., the way foliar application of nanoscale nutrients affects root pathogens, is still under study in the sense that pathogens can be released after root to shoot transfer or induced host resistance. Fertilizing nanoparticles' activity is subjective to the physical and chemical features of the surroundings, i.e., soil, air, and water. The original properties of nanoparticles may transform because of interactions with both biotic and abiotic soil constituents. These adaptations may impact the stability of nanoparticles, their availability to plants, and their transport and aggregation.

2.5 *Reducing Heavy Metal Contamination*

Soil and groundwater pollution by toxic heavy metals (HMs) remains one of the most challenging environmental concerns faced worldwide. Due to the magnitude and potential of the toxication legacy and high contaminant mobility, it is practically not possible to sequester metals from polluted locations cost-effectively. Nanoparticles are applied in situ and become special assistance for deep toxic zones or inaccessible with traditional methods (Carmen et al. 2019). The stabilized nanoparticles commendably hold up leachability and bio-accessibility of HMs in water, soil, and other porous media. Chromium (Cr) has been extensively identified in groundwater and soils. The US Environmental Protection Agency (USEPA) set a maximum pollutant quantity of 0.1 mg/L for total Cr in drinkable water to diminish human exposure as Criswater-soluble and mobile. Conventionally Cr^{6+} is removed from water by reducing it to its less noxious form, Cr^{3+}, following precipitation (Guha and Bhargawa 2005). Researchers have revealed that Fe^{2+} can effectively reduce Cr^{6+}. Reduction of Cr^{6+} to Cr^{3+} by coarse ZVI particles and non-stabilized or amassed ZVI nanoparticles have been examined in labs and field research (Alowitz and Scherer 2002; Blowes et al. 1997; Melitas et al. 2001; Ponder et al. 2000).

Amending CMC-stabilized ZVI nanoparticles in Cr^{6+} laden soil can substantively decrease chromate leachability (Xu and Zhao 2007). Minor quantity of the stabilized nanoparticles diminished the Cr^{6+} leachability, simultaneously converting all leached Cr^{6+} to Cr^{3+}. (Xu and Zhao 2007). Lead (Pb), placed as the second most harmful element according to the ATSDRs Substance Priority List 2019, is a widespread and potentially toxic contaminant. Present-day remediation skills depend mainly on diggings and relatively pricey landfills and are often ecologically troublesome. Liu and Zhao (2007) combined and verified vivianite nanoparticles (a new category of nanoscale iron phosphate) with carboxymethylcellulose (CMC) as a stabilizer. Results showed that CMC-stabilized nanoparticles successfully decrease the TCLP leachability and PBET bioaccessibility of Pb^{2+} in three representative soils (calcareous, neutral, and acidic). The TCLP leachability of Pb^{2+} was reduced by 85–95%, and the bio-accessibility by 30–45%. Adding chloride (Cl) in the treatment further decreased the TCLP leachable Pb^{2+} in soils, suggesting the formation of chloro-pyromorphite minerals. Interaction of ZnO nanoparticles and AM fungi decreased Pb toxicity in wheat by increasing antioxidants and restricting Pb uptake (Raghib et al. 2020).

Using nanoparticles reduces almost 50 percent phosphate discharge in the surroundings (Xu et al. 2014). Xu and Wang (2017) studied different dynamics on graphene oxide (GO) adsorption performance to confiscate heavy metals during batch trials, with pH, a dose of the adsorbent, interaction time, temperature, and existing ions. It was concluded that GO was an effective adsorbent for Zn^{2+}. Zhao et al. (2011) combined multi-layered GO nanosheets and used them to adsorb Cd^{2+} and Co^{2+} in water. Correspondingly, the maximum adsorption capacities of Cd^{2+} and Co^{2+} onto GO were 106 and 68 mg/g. Lisha and Anshup (2009) examined the elimination effect toward Hg^{2+} by using Au nanoparticles sustained on Al. The elimination capacity of Au nanoparticles toward Hg extended up to 4.7 g/g, much greater than common adsorbents. Au nanoparticles were recovered proficiently, signifying that Au nanoparticles sustained on Al can be useful in wastewater treatment.

Application of super-paramagnetic Fe_2O_3 nanoparticles to treat acid mine drainage (AMD) completely removed Al^{3+}, Mg^{2+}, Mn^{2+}, and 80% of Ni^{2+} and Zn^{2+} (Kefeni et al. 2018). Fe_2O_3 nanoparticles are non-toxic, highly stable, and outstanding metal adsorbers, hence a likely candidate to decontaminate wastewater polluted with heavy metals (Yang et al. 2019). In a study, Fe_3O_4 and Fe_2O_3 nanoparticles were detected to eliminate arsenic (As) via column studies. A retardation factor of about 6742 showed high adsorption of As by Fe_3O_4 nanoparticles in the column. High retardation factor, strong adsorption, and impervious desorption suggest that Fe_3O_4 and Fe_2O_3 nanoparticles can be used to remove as through in situ techniques (Shipley et al. 2010).

2.6 Clean Energy and Environment

A continuous stock of energy is required to satisfy the rapidly expanding economy. This has posed an enormous burden on the existing energy setup and the environment. The unwarranted depletion of limited fossil fuels tends to desiccate energy resources and causes severe environmental pollution and global warming (Xia et al. 2014). Most developing nations have vast renewable and non-renewable energy resources, yet many are challenged with critical energy problems. Precisely, energy resource in the form of electricity in many of these countries is so low, affecting trade and industrial activities, and further stunts the whole nation's development. Nanoparticles can offer cleaner, more reasonable, effective, and steadfast approaches to harness renewable energy resources. Developing countries could overcome energy supply challenges and head toward energy self-reliance, alongside decreasing dependency on conventional, environment contaminating energy resources. Such concerns have compelled us to strive for next-generation energy sources. Recent signs of progress in research and development to commercialize a huge range of nanomaterials have been groundbreaking. With the expansion and commercialization of nanoparticles, many devices have been developed to produce, store, transfer, and even conserve energy for a sustainable future (Ranjan et al. 2021).

Nanoparticles have appeared as ultimate platforms to resolve energy conversion issues in solar cells and fuel cells, improve energy storage of lithium-ion batteries and supercapacitors and clean the environment as green catalysts, sensors, pollution prevention, and remediation (Xia et al. 2014). Photons move electrons from a material; electrons flow through wires as an electric current. Nanoparticles significantly improve the efficiency of these processes. ZnO nanoparticle, a transparent conductor, is favorable for use in solar energy approaches, including the photocatalytic splitting of H_2O molecules to discharge hydrogen fuel (Pal and Thapa 2019). CNTs, fullerenes, and quantum dots are being used to create lighter solar cells, inexpensive and more effective. The ratio of increased surface area to volume of these materials increases solar emission capturing by uncovering more conducting surfaces to solar radiation (Zhang et al. 2015). Using nano lead selenide results in releasing more electrons and more electricity to be released when hit by a photon of light with external quantum proficiencies exceeding 120% (Davis et al. 2015).

Nanocomposites of cobalt oxide (Co_3O_4) nanoparticles fixed to conducting graphene as a progressive anode material for better performance of lithium (Li) ion batteries revealed longer battery performance through great revocable capacity, admirable cyclic performance, and noble rate competency, emphasizing the prominence of electrochemically active Co_3O_4 nanoparticles and graphene for energy storage in lithium-ion batteries (Wu et al. 2010). CNTs are excellent substitutes for conventional graphite electrodes in batteries. They have a large surface area, better electrical conductivity, and undeviating geometry making them very reachable to battery electrolytes causing amplified electrical output (Amin et al. 2020). CNTs increase the conductivity of electrolytes resulting in increased energy output therefore, more potent, smaller, and light-weight batteries are widely used in a range of applications (Amin et al. 2020). Nanobatteries can recharge about sixty times faster than standard batteries.

Several of these can function over a wide range of temperatures than is currently available (Echiegu 2016), are also used to optimize and improve the wind turbine blades making them durable, longer, and less heavy to enhance the efficiency of wind turbines and the amount of electricity generated. This remarkable innovation allows future wind turbines to harvest ultra-mega sources of clean energy. Besides, CNTs can also be used as sensors to monitor these huge blades (Brahim 2020). Ding et al. (2014) developed nanostructures called PlaCSH (plasmonic cavity with subwavelength hole-array) to intensify the LEDs' brightness, productivity, and clearness. These amplified the yield of light abstraction to 60%, which is 57% greater than normal LEDs, simultaneously increasing the clarity by 400%. Higher illumination also dismisses the heating problem triggered by the light confined in normal LEDs. Plasmonic cavities can achieve these results because of nano size, metallic structures can control light in such a way those large materials or non-metallic nanostructures cannot. Nanomaterials have made geothermal energy more hands-on by leasing effectual energy production nearer to the surface and at low temperatures. The heat-retaining characteristics of the fluid are improved with nanoparticles. Adding nanoparticles to the fluid increases its capacity to preserve heat, improving efficiency and profitability (Ahmadi et al. 2019).

3 Global Production and Cycling of Nanoparticles

Nanoparticles are a major part of the material flows in the global economy. A report by Allied Market Research expectantly shows the nanomaterial market to grow above $55 billion by the year 2022 (Fig. 1.1) from $15 billion in 2015, growing at a compound annual growth rate (CAGR) of 21% during this period. The USA is expected to keep the leading position until the year 2022, with the nanomaterials market proceeds budding at a rate of 19%. Among Asian countries, China and India are estimated to be the quickest growing nanomaterial markets; however, China is

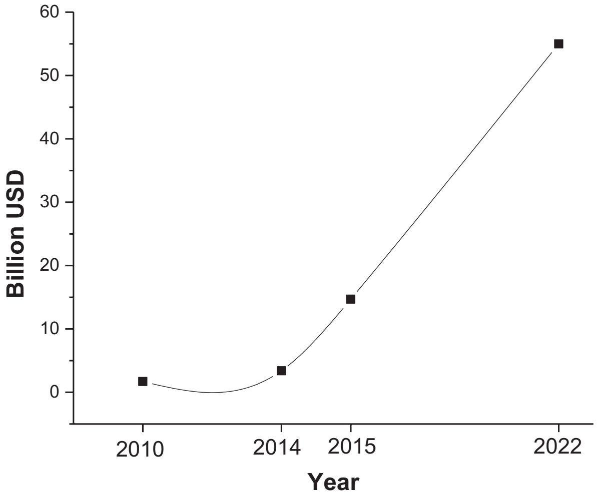

Fig. 1.1 Total worth of nanomaterials in USD (billion) in different years

expected to be the second biggest market for nanomaterials after the USA with over 12% share of the worldwide demand by 2022 (Inshakova and Inshakov 2017). Technology readiness levels (TRL) quantified that carbon-based nanoparticles have a diverse multitude of current uses. In contrast, metal and non-metal oxide-based nanoparticles are the most commonly used in industrial production (Allied Market Research 2016). Around 25% of the nanoparticles introduced in the markets are integrated with TiO_2, SiO_2, and Ag nanoparticles (StatNano 2017). TiO_2 and SiO_2 are the most used up metal and metal-oxide-based nanoparticles, respectively. Ag nanoparticles are considered to be the most commercialized nanoparticles, accounting for over 50% of the global nanomaterial consumer products (Global Market Insights Inc. 2017), with an expected growth market at a CAGR of closely 13% from 2016 to 2024 (Industry Report Forecast 2017). Major areas of Ag nanoparticles consumption are healthcare & life sciences, food & beverages, electronics & IT sectors, and packaging industries (Inshakova and Inshakov 2017). Carbon-based nanomaterials are mostly utilized in coatings, pigments, paints, followed by cosmetics, optics, electronics, clean energy, and the environment (Keller et al. 2013). The industries with top opportunities for applying novel nanoproducts in producing final goods are aerospace, automobiles, electronics, defense, energy storage, and sporting goods industries (Allied Market Research 2016).

Electronics production is estimated to constitute the top stake in the market-approximately 30% in nanoparticle utilization. In contrast, the aerospace industry is the fastest emerging sector in the predicted period because of the growing use of metal oxide nanoparticles, polymer nanocomposites, and anti-corrosion coatings in the aircraft industry (Inshakova and Inshakov 2017). At present, we are procuring the profits of material use reduction, enhanced energy efficiency, and improved performance in numerous prevailing and novel technologies which have been aided by nanoparticle application (Keller et al. 2013). Nanoparticles infiltrate the global economy nevertheless; it is important to understand their environmental repercussions. In 2018, Bundschuh reported that out of 26,00,00,000 to 309,00,00,000 kilograms of global nanoparticle production, about 63–90% ended up in landfills, with the remaining 8–28% discharged into soils, 0.5–7% in water forms, and 0.1–1.5% in the atmosphere. After discharge of nanoparticles in the environment deliberately or accidentally, at different stages throughout the products life cycle, i.e., manufacturing, integration into nano-assisted products and product utilization stage and at the end phase of the life cycle (Gottschalk et al. 2015; Keller and Lazareva 2014) they interact with different constituents of the surroundings and undergo dynamic makeover (Bundschuh et al. 2018). Most nanoparticles like Ag, TiO_2, and ZnO are discharged into the surroundings at the utilization stage. Carbon-based nanoparticles have high adsorption affinities for organic and inorganic pollutants present in the environment. Contact with such pollutants modifies their transference and reactivity (Canesi et al. 2015; Sigmund et al. 2018).

The undesirable casting-off of nanoparticles in surroundings is an impending risk to living beings (Abbas et al. 2019). Coatings, paints & pigments, and cosmetics together combined facilitate 41% of total global nanomaterial flows and likely

Table 1.1 Assessments of nanomaterials released into the environment (air, wastewater treatment plant (WWTP), and soil) during usage in various applications

Application	Air (%)	WWTP (%)	Soil (%)
Aerospace	5	90	5
Automobiles	5	90	5
Coatings, paints & pigments	1	60	35
Cosmetics	1	90	1
Electronics & optics	5	5	90
Energy & Environment	5	5	90
Medical	5	90	5
Packaging	0	5	95
Plastics	1	5	94
Textiles	5	95	0
Sensors	0	5	95

contributed 80–87% of total nanoparticle emissions to soil and 90–97% to water (Keller et al. 2013).

Wastewater treatment plants (WWTPs) serve as an important intermediate passage for some nanoparticles to move from soil and water and vice versa. 17–34% of nanoparticles likely pass through WWTPs, which results in 3–25% release of nanoparticles into water bodies through treated sewage, and 45–47% is discharged to soils through biosolids. The probable nanoparticle releases during use in different applications are presented in Table 1.1, which provides an estimate of the percent release into the atmosphere, water flowing to a WWTP, or release in soil from a waste product. Hence, understanding the behavior and transformation in WWTPs is crucial for the exact estimation of these emissions (Yousaf et al. 2020). United States National Research Council (USNRC) guideline states that "Critical elements of nanomaterial interactions should be considered while estimating the health risks and environmental safety of nanoparticles." (NRC 2012). These critical elements comprise nanoparticles' physical, chemical, and biological changes that oversee their kinesis, bioavailability, persistence, and harmfulness in the environment (Yousaf et al. 2020).

3.1 Guidelines for the Management of Nanoparticles

Rapid commercialization of nanoparticles offers limitless prospects for industrial advancements and economic progress. It holds many keys to old problems, especially in environmental protection, saving energy, agricultural productivity, contaminated soil, and water remediation, reducing hazardous metal wastes and harmful greenhouse gases. However, more expansion and ease of access to nano-based solutions bring several trials which should be brought to notice before further damage is done. Such trials consist of matters associated with monitoring, safe use, and discarding of nanoparticles. Some recommendations made are:

Proper Funding and Manufacturing

First of all, the research done on the influence of nanoparticles on the environment and health is not thought-out as essential and impressive as developing and synthesizing new nanoparticles. This outlook can be understood by observing and comparing the impact factors of research articles and how research funds are distributed. This attitude must change. To make progress and boost research in this area, an adequate amount of funds devoted to toxicity assessment and improvement of safe disposal techniques should be granted by governments, private organizations, or grant funding bodies to study nanomaterials' health and ecological effects (Faunce et al. 2017). Secondly, the company/institute developing the nanoproduct should conduct detailed studies before releasing the product for additional ecological and risk assessment. Proper lab tests should be performed to establish the presence/absence of biotic action or abiotic action is harmful and lethal to the object or not. Tests for product safety must be performed under several ecological settings (i.e., acidity levels, radiation effect, temperature, pressure, moisture, etc.). An authentic, official report clearly describes the chemical structure, industrial procedures, and the required chemicals useful in synthesizing the nanoparticle, analytical processes used to assess lethal and ecological effects of the nanoparticle, along with all up shots collected while performing experiments.

Their port should also mention if the product is safe to manufacture, use, disposal and recyclable (if recyclable, then procedures for recycling). The producer should carefully examine complete information from the readings and submit a concluding report to the controlling body. Experts agree that companies/institutes should be held accountable for assessing risks of their products to ascertain they are safe for manufacturing, using, and disposing off. In cases where such modus operandi do not occur, the corporation/individual using the nanoparticle must be indicted with the duty of completing the toxicity assessment and the developing dumping practices particular to that product (Faunce et al. 2017).

Setting National and International Standards

All countries must develop specific standards based on their different requirements, experiences, and environmental conditions. A nanoparticle could be particularly reactive or toxic under a given set of environmental conditions. National regulatory bodies must handle safe disposal, neutralization of nano-wastes, and systematically collect and preserve information from case studies, concerns, reports, and user grievances associated with the approved product.

Presently, only very few international policies standardize, monitor the safe use and disposal of nanoparticles. International bodies, such as International

Organisation for Standardisation (ISO), have started probing issues at hand and developing criteria linked to safe disposal and/or reprocessing on nano waste. Two important policies regarding nano waste disposal are: ISO/TS 80004, it describes the terminology used in nanotechnology and its uses and presents uniform standards and legislature. One more is ISO/TR 13121:2011. It is more definite as it refers to procedures for detecting, assessing, improving, creating resolutions, and sharing possible threats of developing and using synthetic nanomaterials. Besides, it recommends practices that corporations must follow to be transparent and responsible regarding the management of nanomaterials.

These policies are imperative in handling nanowastes, but they are clearly insufficient. Global support and investments could affect larger and incorporated international policies and schemes, and it will also enrich exchanging novel ideas, concerns, and clarifications. The Organisation for Economic Co-operation and Development (OECD) attempts to address the issue and bring a change in the safe use of nanomaterials by giving out testimonials, reports, and recommendations. Nonetheless, more dynamic science diplomacy is required to standardize the concern, especially at an early stage of product development (Faunce et al. 2017; Campos and Lopez 2019).

Safe Use

Following acceptable work practices help reduce exposure to nanoparticles to a great extent. When working in a lab with nanoparticles, one must always wear personal protective gear, including safety glasses/goggles, lab coats/disposable gowns, respirators/face shields (if the risk of potential aerosol exposure), and nitrile/rubber gloves. Needles used for injecting nanoparticles should not be bent, clipped, or recapped and must be straightaway dumped in sharps containers after use. Bench paper/cloth used during preparing nanoparticle stock should be resistant to limit potential workplace contamination in case of a slight spill. After each work shift, work areas should be cleaned using filtered vacuum cleaners or wet wipes, and pressurized air or dry sweeping should be avoided. Benchtops, safety cabinets, equipments, and lab surfaces should be cleaned regularly, and cleaning must be done in a way that obstructs workers' interaction with wastes. The disposing off nanowastes must conform with central, private, and local guidelines (Amoabediny et al. 2009).

Disposal

The chemical and physical attributes of nanoparticles and their physical properties compel us to recognize ideal removal, neutralization, and recycling procedures for every particle individually. For example, it should not be assumed that disposal measures for Fe_3O_4 nanoparticles shall be applied to TiO_2. Nanowaste removal involves broad investigation; it also needs stringent norms and practices to be adopted. Policymakers, sponsors, scientists, and researchers must come forward and work together for effective and viable principles. Governments should nationally and internationally unite their databases and work with technologists, manufacturers, consumers of nanoparticles to design and improve dependable treaties and strategies for responsible development. Excess stocks and additional waste materials containing contamination in high concentrations must be disposed of through the UTHSC-H Environmental Protection Program. Specific nanoparticles may be unaltered during metabolism hence all potentially contaminated animal remains, bedding, and other materials must be disposed of through incineration. In addition, all contaminated sharp tools and equipments must be placed in a proper sharps container and disposed of as bio-hazardous waste (Amoabediny et al. 2009).

4 Conclusion

Nanoparticles are providing paramount sustainability, health, and welfare expediencies around the globe. Their distinctive physical and chemical properties improve reactivity, strength, electrical features, and functionality. These advantages have ensued in nanoparticles being combined into an extensive series of user products that help protect the environment and climate globally by saving energy, increasing crop yields and agricultural productivity, remediating contaminated soil and water, and reducing hazardous metal wastes and harmful greenhouse gases. But the world has previously known complications that come with novel developments. With the questionable progress of genetically modified foods and the highly relevant microplastics calamity, more progress in applying nanoparticles must result in similar health and safety dilemmas. Health and environmental impacts must be our priority, but this is not an easy job. Even though normal risk evaluations exist for various nano products, every nanoparticle has unique properties, so their safety and disposal measures have to be evaluated following that concerns relating to caution, safe use, removal, and wherever likely, the actual reuse of nanoparticles should be addressed without bias. Widespread applications of nanoparticles have proved beneficial in various fields of sciences, but they are also ascertained hazardous to the surroundings and well-being of mortals. Therefore, it is the need of the hour to have an improved understanding of measures for the safe use and disposal of nanoparticles so that we can more confidently relish their benefits without compromising our environment.

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Chapter 2
Nanoparticles: Physiology, Chemistry, and Biochemistry

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1 Introduction

In the last two decades, the use of engineered nanoparticles increases in industrial, agricultural, and biomedical sectors (Maurer-Jones et al. 2013). The engineered nanoparticles are of different shapes and sizes that alter their properties from the naturally occurring materials (Auffan et al. 2009; Joshi et al. 2019; Singh et al. 2020). The extensive use of these nanoparticles makes their presence in the

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environment inevitable. The water bodies and soil are the most likely to get contaminated with excess nanomaterials that can enter indirectly from industrial discharge or directly from the nanomaterials used for agriculture. So, it is crucial to understand the impact of nanoparticles on different plant species before their release in the environment.

Over the last two decades, the application of nanotechnology in the agricultural field has been proven as an effective tool to ensure food security in a sustainable manner (Singh et al. 2021). Nanofertilizers are more efficient for crop production as they ensure high nutrient use efficiency (Zulfiqar et al. 2019). Site-directed, controlled delivery of these nanofertilizers minimizes the use of fertilizers and increases crop production in a highly efficient manner. The emergence of biopesticides offers the protection of plants without much damage to the natural ecosystem as it offers a reduced amount of active ingredient and high efficacy (Kookana et al. 2014). On the other hand, the use of nanosensors can help to detect the microclimate change in the crop field and can alert the farmer before any biotic or abiotic stress hits the threshold and affect crop production (Pérez-de-Luque et al. 2012; Pérez-de-Luque and Hermosín 2013). The development of nanosensors has improved human control over soil and plant health and contributed to precision farming and sustainable agriculture (Chen et al. 2016).

The increasing use of NPs is directly related to their accumulation in the environment. Besides the NPs used in agriculture, various other NPs that are used in different industries also enter in air, water, and soil by different means. Industrial wastes tend to end up in water bodies that increase the chances of NPs contamination. Soil is the ultimate sink of NPs, which receives the NPs directly or indirectly (Remédios et al. 2012). Plants are the base of the ecosystem and directly in contact with soil, water, and air. Any negative effects of nanomaterials on plants can ultimately affect animals and human beings (Judy et al. 2012; Hawthorne et al. 2014; De la Torre Roche et al. 2015; Tangaa et al. 2016). Hence, it is imperative to intensively study the role of NPs on the plant, before their intensive use in the natural environment. Also, it is important to examine the effect of NPs on microflora present in soil because in the nature, growth and development of plants are affected by them. Any positive or negative effect on them can ultimately affect the crop plants. In this chapter, we will describe the effect of various NPs on plants physiology and their effect on plant microbial associations.

2 Entry and Translocation of Nanoparticles (NPs) in Plant System

Nanoparticles are more reactive than their molecular form due to their smaller size and higher surface to volume ratio (Taylor et al. 2015). The uptake of NPs by plants is dependent on several factors including the nature of nanoparticles and

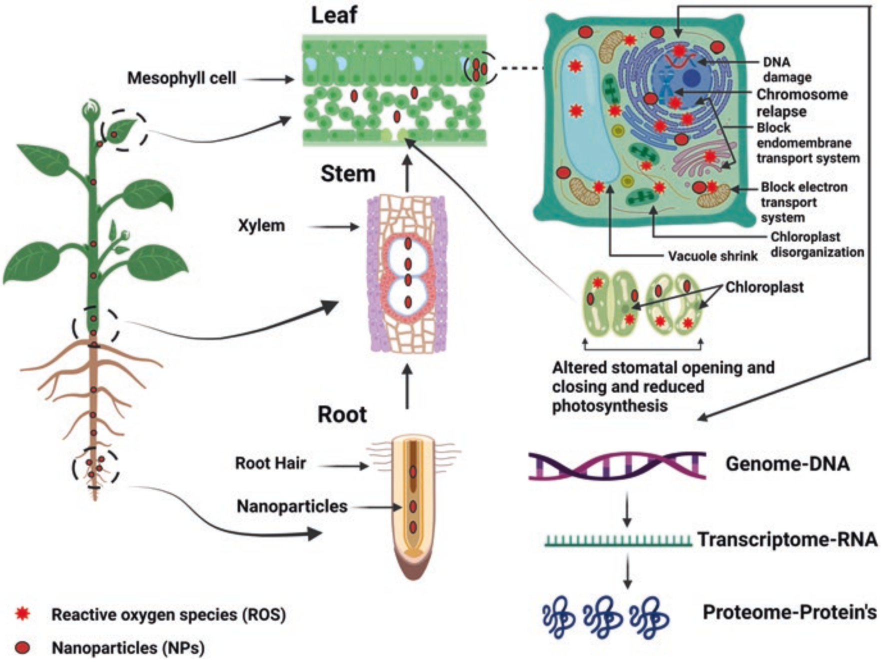

Fig. 2.1 Diagrammatic representation of translocation nanoparticle inside the plant cell from root to leaf, and effect of nanoparticle at a physiological, biochemical, and molecular level

their interaction with environment, along with the physiology of plant species (Pérez-de-Luque 2017).

The NPs are generally taken up by plant roots and translocated through vascular tissues to aerial parts of the plant (Fig. 2.1). The uptake and penetration of NPs in plant cells is directly dependent on their size. The small NPs, ranging between 5 and20 nm, can penetrate through the plant cell wall (Dietz and Herth 2011). Few studies reported about the maximum dimensions allowed by plants for the movements and accumulation of NPs inside the plant cells. Usually, 40–50 nm is the size limit of NPs to enter in the plant cells (González-Melendi et al. 2008; Corredor et al. 2009; Sabo-Attwood et al. 2012; Taylor et al. 2015). The morphology of NPs and the means of delivery are also important for their transport in plants. Raliya et al. (2016) had demonstrated that the morphology of gold nanoparticles (nAu) plays a significant role in its translocation in watermelon. The chemical property of NP is an additional factor influencing its interaction with plant cells. The attachment of NPs to the surface of negatively charged plant cell wall is directly dependent on the surface charge of NPs. Zhu et al. (2021) found that the absorption of ZnO onto the leave surface and cell wall of wheat was enhanced by the smaller size and positive charges. In order to understand the uptake, translocation, and accumulation of NPs in plants, standardized laboratory experiments are needed to correlate the physicochemical properties of NPs with their effect on plant tissues.

The NPs of smaller size (3–5 nm) can pass directly through the root epidermis or they penetrate to the plant root along with osmotic pressure and capillary force. The small pores in the cell wall of roots permit the entrance of small-sized NPs while some NPs could form new pores in the root cell wall and enter through it (Du et al. 2011). After crossing the cell wall, NPs enter in extracellular spaces and make their passage to the vascular system. After reaching the vascular bundle, the NPs enter in xylem and they are transferred to shoot and other aerial parts (Ali et al. 2021). When the NPs enter in the cell, they travel from cell to cell through plasmodesmata (Perez-de-Luque 2017). The NPs that cannot enter in the cell are accumulating on the Casparian strip (Wang et al. 2012; Raliya et al. 2016).

NPs can also enter through the stomata or cuticle present on the aerial part of the plant, especially leaves (Larue et al. 2014). The foliar absorption of NPs is dependent on the leaf morphology. The presence of cuticle, wax, trichrome, and leaf exudates are some important factors, which affect the adherence and entrance of NPs from leaves (Larue et al. 2014). The cuticle allows the entrance of NPs smaller than 5 nm while the NPs of 10 nm range can enter through stomata (Ali et al. 2021). The NPs entered through aerial tissues are transported through phloem along with sugar transportation and can accumulate in root, grains, fruits, and young leaves (Wang et al. 2013; Raliya et al. 2016).

The translocation and accumulation of NPs depend upon the plant species and the characteristics of nanomaterial. Accumulation of the same NP was observed in different parts in different plant species (Cifuentes et al. 2010; Zhu et al. 2012). For example, the accumulation of nAu was found in the shoots of *Oryza sativa* while in *Cucurbita pepo* and *Raphanus raphanistrum* nAu accumulation was not found in shoots (Zhu et al. 2012).

3 Physiological Alterations in Plants in Response to Nanoparticles

After entering in plant system, the NPs interact with plants at the cellular and subcellular level, resulting in various morphological and physiological changes. In order to access the effect of NPs, percentage of germination, root elongation, total biomass, and leaf numbers are generally considered physiological parameters (Lee et al. 2010). NPs can affect the plant physiology positively or negatively in a dose-dependent manner and also dependent on plant species.

NPs cover a wide range of materials, but only few of metal and metal oxides nanoparticles are extensively used in various industries. NPs of silver, titanium and its oxide, zinc oxide, iron oxide, aluminum oxide, etc., are the few NPs that are entering in the environment due to their excessive use in different processes. Hence, it is important to understand their physiological impact on the plant. Various methods of NP application, such as foliar application, seed treatment, application in soil, growth media, or in hydroponics, were used to examine the impact of NPs on plant

Table 2.1 Nanoparticles (NPs) and their effect on different plant species

Type of NPs	Concentration	Crop species	Physiological effect	References
nAg	0.5–5 mg/kg	*Triticum aestivum*	Increased branching in roots Increased ROS generation	Dimkpa et al. (2013)
nAg	0.5–10 mg/kg	*Spirodela polyrhiza*	Increased ROS accumulation and activities of peroxidase, SOD, and glutathione	Jiang et al. (2014)
nAg	0.01–1 mg/kg	*Capsicum annuum*	Reduced plant growth Elevated cytokinin concentration	Vinkovic´et al. (2017)
nAg	40 mg/l	*Lolium mutiforum*	Damaged epidermis and root cap	Yin et al. (2012)
nAg	10 mg/l	*Eruca sativa*	Increased root length	Vannini et al. (2013)
nAg	10–100 ppm	*Bacopa monnieri*	Reduction in total protein content in root and shoots	Krishnaraj et al. (2012)
nAl_2O_3	10–1000 mg/l	*Triticum aestivum*	Increased activities of catalase and SOD at 200 and 500 mg/l concentrations	Riahi-Madvar et al. (2012)
$nCeO_2$	500 mg/kg	*Oryza sativa*	Decrease in starch, glutalin, lauric acid, valeric acid, prolamin Fe and S in rice grains	Rico et al. (2013)
$nCeO_2$	100, 400 mg/kg	*Triticum aestivum*	Reduced chlorophyll level Increase in catalase and SOD activities Changed root and leaf cell microstructure, delayed flowering, and high protein content in grains	Du et al. (2015)
$nCeO_2$	62.5–500 mg/kg	*Solenum lycopersicum*	Induced catalase activity and chlorophyll content in leaves Increased stem length	Barrios et al. (2016)
$nCeO_2$	0–500 mg/kg	*Phaseolus vulgaris*	Increased antioxidant activities in aerial tissues	Majumdar et al. (2016)
nCu	200–1000 mg/l	-*Phaseolus radiates* -*Triticum aestivum*	Reduced growth of roots and seedlings Roots were more affected than shoots *T. aestivum* showed more responsive than *P. radiates*	Lee et al. (2008)
nCuO	2.5–1000 mg/l	*Oryza sativa*	Decreased thylakoid number/grana Decreased photosynthesis rate, transpiration rate, stomatal conductivity Increased activities of SOD and ascorbate peroxidase	Costa and Sharma (2016)
nCuO	10–200 mg/l	*Lemna minor*	Increased activities of catalase, SOD and peroxidase Induced lipid peroxidation Reduced plant growth	Song et al. (2016)

(continued)

Table 2.1 (continued)

Type of NPs	Concentration	Crop species	Physiological effect	References
nCuO	20, 50 mg/l	*Arabidopsis thaliana*	Among Col-0, WS-2, and Bay-0, Col-0 was the most sensitive ecotype nCuO inhibited the growth of all ecotypes Presence of nCuO was detected from root to seeds	Wang et al. (2016a, b, c)
nCuO	3–300 mg/l	*Triticum aestivum*	Shorting of division and elongation zones in root	Adams et al. (2017)
nFe_2O_3	5–20 mg/l	*Triticum aestivum*	Exposed plants to NPs had a positive response for preventing oxidative damage	Iannone et al. (2016)
nFe_2O_3	20–100 mg/l	*Zea mays*	Germination index was found to be dose-dependent. Exposure to 20 and 50 mg/L of NPs increased the germination, but exposure to 100 mg/L of NPs decreased it	Li et al. (2016)
TiO_2	300 mg/l	*Zea mays*	Inhibited leaf growth Root water transport was physically affected	Asli and Neumann (2009)
TiO_2	100 mg/l	*Linum usitatissimum*	Reduced seed germination, root length, and root biomass	Clément et al. (2013)
TiO_2	200 mg/l	*Mentha piperita*	Negatively affect the germination percentage and shoot length Increase in chlorophyll and carotenoid content	Samadi et al. (2014)
TiO_2	0–1000 mg/kg	*Solenum lycopersicum*	Dose-dependent increase in height, root length, and biomass 100 mg/kg of TiO_2 positively affect the lycopene content and fruit size Chlorophyll content was increased on 750 mg/kg of TiO_2	Raliya et al. (2016)
ZnO	10–1000 mg/l	Lolium perenne	Inhibited root elongation in dose-dependent manner Seedling biomass decreased at >20 mg/L concentration	Lin and Xing (2008)
ZnO	200–800 mg/l	*Allium cepa*	Increased cytotoxicity in root cells. Increased DNA degradation Increased ROS accumulation and activity of glutathione peroxidase, but decreased catalase activity	Ghosh et al. (2016)

physiology (Table 2.1). Also, various concentrations and sizes of NPs were used to find the threshold level of NPs for different species (Raliya et al. 2016).

Silver nanoparticles (nAg) are extensively used in the preparation of antimicrobial agents, food packaging materials, fabrics, paint, detergents, etc. (Rai et al. 2009; Wijnhoven et al. 2009). Through the industrial waste, nAg can easily enter in the ecosystem and ultimately can affect the plants. It has been observed that the lower concentration of nAg (30 μg/ml) cannot affect the rice, while the higher concentration can affect the cell structure (Mirzajani et al. 2013). Also, it has been observed that the nAg with lower size (˃30 nm) has higher toxic effect on plant and inhibits the growth of root and shoot in different plant species. On contrary, the nAg particles with higher size were able to enhance the growth of root and shoot (Jasim et al. 2017). These results indicate that the penetration and accumulation of nAg in the plant cell can cause a negative impact on plant growth, while its presence in the surrounding has a positive effect on plants.

The higher concentration of NPs can negatively affect plant growth. The increased concentration of NPs can cause stress in plants and in turn, can elevate the production of reactive oxygen species (ROS) as a defense response. There are several studies showing that nAg and nCu/CuO can elevate the level of ROS and various antioxidants in plants (Dimkpa et al. 2013; Jiang et al. 2014; Nair and Chung 2014; Shaw et al. 2014; Cvjetko et al. 2017; Tripathi et al. 2017). These NPs can also affect the expression of genes related to the synthesis of antioxidant. For example, in *Arabidopsis thaliana,* the expression of various genes related to oxidative stress was changed by applying a high concentration of nCuO (Nair and Chung 2014). The application of NPs can also affect the level of hormones, such as auxin and cytokinin (Yin et al. 2012; Vinkovi’c et al. 2017).

Titanium oxide (TiO_2) is known for its photocatalytic property and hence, foliar application of it has shown a positive impact on plants. Foliar application of TiO_2 in tomato resulted in an enhanced growth of the plant with an increase in fruit yield and chlorophyll content (Raliya et al. 2016). Similar to nAg and nCu, at high concentration the phytotoxic response of TiO_2 was observed in plants (Rafique et al. 2014). Application of TiO_2 in colloidal form was observed to inhibit transpiration rate and root growth by physically affecting the root-water interaction (Asli and Neumann 2009).

These studies suggest that the NPs can have impacts on the physiology, morphology, and biochemistry of plants. The effects of NPs on plants can depend upon their size, concentration, and mode of application. It was also observed that the response of the same NPs can differ in genetically diverse plant species (Lee et al. 2008; Van et al. 2016; Wang et al. 2016b). These studies also indicate that the internalization and high accumulation of NPs in plant cells can cause phytotoxic effects in plants, but at lower concentration these NPs can improve plant growth and yield. Application of NPs at lower concentration can help the plant to mitigate various stresses (Jaberzadeh et al. 2013).

4 Molecular and Biochemical Changes in Plants in Response to Cellular Internalization of Nanoparticles

Once the NPs internalize within the plant cells, they start interfering with various metabolic processes. Various reports show that the excess accumulation of NPs in the cell causes oxidative stress and increased production of ROS (Hossain et al. 2015).

NPs present within the cell can enter in the cell organelles. The electron transport chain present on the membrane of mitochondria and chloroplast can be interrupted by the NPs, which ultimately cause oxidative burst (Faisal et al. 2013; Ghosh et al. 2016; Rastogi et al. 2017). This oxidative burst causes the increased production of ROS that ultimately causes the lipid peroxidation, DNA-strand breaks, and cell death (Van Breusegem and Dat 2006; Cvjetko et al. 2017; Saha and Dutta Gupta 2017). The production of ROS also activates the stress regulatory mechanism in plants. The balance between production and scavenging mechanism of ROS determines the level of stress tolerance in plant species (Sharma et al. 2012). The increased level of ROS induces the antioxidant mechanism of cell and as a result, the level of various antioxidant enzymes (peroxidase, catalase, superoxide dismutase (SOD), etc.) and non-enzymatic molecules (ascorbate, glutathione, carotenoids, tocopherols, etc.) increase, to maintain the cellular oxidative state (Sharma et al. 2012).

There are several reports showing an increase in the activities of antioxidant enzymes associated with the application of NPs in plants (Table 2.1). Effects of nickel oxide nanoparticles (nNiO) were examined on tomato. Increased level of ROS, SOD, glutathione, and lipid peroxidation was observed in nNiO-treated tomato plants (Faisal et al. 2013). Application of nAg affected the photosystem II in *Spirodela polyrhiza* that decreases the fixation of solar energy and promotes the production of ROS in chloroplasts (Jiang et al. 2014). Similarly, nCuO damaged the PSII in rice. The osmotic and oxidative stress was confirmed in nCuO-treated rice plants by the increased level of malondialdehyde, proline, SOD, and ascorbate peroxidase (Costa and Sharma 2016).

Hormonal signaling is liked with the ROS and integrated with the stress signaling pathway. The synthesis of various hormones is differentially regulated by various environmental stresses (O'Brien and Benková 2013). In *Arabidopsis*, the level of auxin and cytokinin was decreased in shoot, while the level of zeatin, salicylic acid, and abscisic acid (ABA) was increased in presence of nZnO (Vankova et al. 2017). In response to nFe_2O_3 exposure, an increase in indole acetic acid and ABA was reported in the roots of non-transgenic and transgenic rice (Gui et al. 2015). On contrary, a decrease in phytohormone level was found in seedlings of rice in response to nanocarbon tubes (Hao et al. 2016). These outcomes indicate that the NPs can influence the hormonal synthesis in plants. It has been hypothesized that plants sense the presence of NPs as stress and in response to that they synthesize more stress-related hormones (Vankova et al. 2017). Plant roots are directly in contact with the NPs present in soil/water; hence they are more adversely affected than shoots (Pokhrel and Dubey 2013; Qian et al. 2013; Shaw et al. 2014; Tripathi et al. 2017; Vinkovi'c et al. 2017).

Molecular changes in plants due to NPs are dependent upon their uptake and translocation. NPs of smaller size can penetrate and internalize in the cells by endocytosis. Interaction of NPs with cell organelles like mitochondria, chloroplast, etc., can cause oxidative stress (Fig. 2.1). Various molecular and biochemical changes occur in the plant due to this oxidative stress. The growth and survival of plants depend upon the level of ROS generated in response to NP stress. ROS production at an optimal level can enhance the synthesis of various antioxidant compounds and provide resistance to various stresses. On the other hand, a higher level of ROS can induce apoptosis, cell damage, and ultimately affect plant growth and yield (Foyer and Shigeoka 2011). Hence, intensive studies on the translocation and accumulation of NPs in different plant species at different concentrations are required before their use in the natural environment.

5 Biochemical Alterations in Primary and Secondary Metabolites

In the previous section of this chapter, we mentioned the increase in ROS production as a result of NP-plant interaction. There are several evidences showing ROS-mediated signaling for secondary metabolite production (Simon et al. 2010; Jacobo-Velazquez et al. 2015). Also, ROS can act as a signaling molecule of brassinosteroids (BRs), jasmonic acid (JA), salicylic acid (SA), ethylene, etc., that can modulate the synthesis of secondary metabolites (Wu and Ge 2004; Xia et al. 2009; Maruta et al. 2012; Baxter et al. 2014; Zhang et al. 2016).

Although there is a link between ROS and secondary metabolite production, there are very few reports showing the production of secondary metabolites can be affected by NPs. However, there are few studies related to the alteration in secondary metabolites in plants in response to NPs (Table 2.2). There are many evidences showing the change in SA, JA, BR level, etc., in plants, which are indirectly liked with secondary metabolite production. The level of SA was increased while JA was decreased in *Arabidopsis* treated with nZnO (Vankova et al. 2017). nAg can reduce the production of ethylene biosynthesis by affecting the production of ACC and ACC oxidase 2 (Syu et al. 2014).

Proteomic studies of some plant species exposed to NPs had shown the change in expression of primary and secondary metabolites. Application of Al_2O_3, ZnO, and Ag nanoparticles caused alteration in the amount of 104 proteins related to secondary metabolites in soybean roots (Hossain et al. 2016). Application of nZnO increased the proline content, soluble phenols, and phenylalanine ammonia-lyase in tomato (Pejam et al. 2021). In *Artemisia annua*, the expression of artemisinin was increased by 3.9-fold after the application of nAg in root culture (Zhang et al. 2013). An increase in diosgenin concentration was obtained in fenugreek after nAg

Table 2.2 Effect of nanoparticles (NPs) on primary and secondary metabolite production

NPs	Plant species	Organ/ tissue	Effects	References
nAg	*Calendula officinalis*	Areal parts	Enhanced saponin, decreased anthocyanin, flavonoid, and carotenoid	Ghanati and Bakhtiarian (2014)
nAg	*Prunella vulgaris*	Calli culture	Increased total phenols, DPPH-radical scavenging activity	Fazal et al. (2019)
nAg	*Corylus avellana*	Hazel cells	Increased taxon, baccatin, and lipid peroxidation. Decreased total soluble phenols and total flavonoids	Jamshidi and Ghanati (2017)
nAg, $nAgNO_3$	*Cucumis anguria*	Hairy roots	Increase in total phenols (caffeic, syringic, hydroxybenzoic acid, chlorogenic, β-resorcylic, ferulic, vanillic acid, protocatechuic, t-cinnamic, o-coumaric, and ρ-coumaric)	Chung et al. (2018)
nAg	*Isatis constricta*	Plantlets	Increase in tryptanthrin and indigo that reduced upon 10 and 15 days post-treatment	Karakas (2020)
nAg	*Caralluma tuberculata*	Calli culture	Increase in total phenols, SOD, CAT, APX, etc.	Ali et al. (2019)
nAu	*Prunella vulgaris*	Calli culture	Increase in total phenols, flavonoids, and DPPH-radical-mediated scavenging	Fazal et al. (2019)
$nCeO_2$	*Solanum lycopersicum*	Fruits	Increase in lycopene, decrease in reducing sugar and starch content	Barrios et al. (2016)
nCu	*Solenum lycopersicum*	Fruits, leaves and seedlings	Increase in lycopene content and activity of catalase	Juarez-Maldonado et al. (2016)
nCu	*Capsicum annuum*	Fruits	Increase in antioxidant content, total phenol content, and flavonoids	Pinedo-Guerrero et al. (2017)
nCu	*Cucumis sativus*	Fruits	Increase in various amino acids, fructose, fructose, proline, and benzoic acid. Decrease in lysine and methionine.	Zhao et al. (2017)
nCuO	*Withania somnifera*	Shoots and roots	Increase in antioxidants, total phenols, and flavonoid content	Singh et al. (2018)
nSiO2, nTiO2	*Tanacetum parthenium*	Leaves	Increase in parthenolide, increased expression of *COST*, *TpGAS*, and *TpCarS* genes related to biosynthesis pathways of β-caryophyllen and parthenolide	Khajavi et al. (2019)
nSiO2, nTiO2	*Argania spinos*	Callus culture	Enhance tocopherol accumulation	Hegazi et al. (2020)

(continued)

Table 2.2 (continued)

NPs	Plant species	Organ/ tissue	Effects	References
nSe	*Apium graveolens*	Stem and leaves	Increase in total antioxidant capacity, total phenols, proteins, vitamin C, jasmonic acid, aspartic acid, chlorophyll, beta-carotenes, glutamic acid, flavonoids, soluble sugar, ariginine, tryptophan, and proline	Li et al. (2020)
nTiO2	*Abelmoschus esculentus*	Roots, stem, and leaves	Increase in activity of SOD, but reduced glutathione reductase (GR) and ascorbate peroxidase (APX) activities in roots. Increased level of malondialdehyde and GR activity, but reduced activity of APX in leaves	Ogunkunle et al. (2020)
nZnO	*Stevia rebaudian*	Shoots	Increase in total reducing power, total antioxidant activity, total flavonoids, total phenols, rebaudioside A, stevioside content, and inhibition of DPPH	Ahmad et al. (2020)
nZnO	*Momordica charantia*	Shoots	Increased antioxidant enzyme activities, carbohydrate, phenols, carotenoids, flavonoids, anthocyanins, and proline content	Sharifi-Rad et al. (2020)
nZnO	*Camelina sativa*	Root-shoot	Increase in total phenols, phosphorus, calcium, zinc, carotenoids, and anthocyanins. Decrease in antioxidant capacity and total flavonoids	Hezaveh et al. (2020)

application (Jasim et al. 2017). Effects of NPs were examined on lower non-vascular members of plant kingdom. It was found that the application of $nTiO_2$ can increase the secretion of phenolic compound in *Arthrospira platensis* (cynobacteria) and *Haematococcus pluvialis* (micoalga) (Comotto et al. 2014).

Although, the studies suggest that NPs are capable of modulating the synthesis of secondary metabolites but the exact mechanism is not clearly understood. Synthesis of secondary metabolites is a defense mechanism of plants against any stress. NPs, after entering in the cell, might interfere with the electron transport system present in mitochondrial and chloroplast membrane, create oxidative stress, and ultimately generate ROS, which can generate secondary metabolite, directly or indirectly.

6 Effect of Nanoparticles in Rhizospheric Environment

Soil is the habitat of diverse microorganisms, which are associated with plants growth and development. Among these soil microorganisms, rhizobia and mycorrhiza are the most important microorganisms that interact with the roots of plants in rhizosphere. Almost all the vascular plant roots establish the symbiotic relationship with arbuscular mycorrhizal fungi (AMF) (Brundrett and Tedersoo 2018). This association helps the plant to access less available minerals in soil, viz. phosphate, improve plant growth, and tolerance to abiotic/biotic stress (Hildebrandt et al. 2007; Smith et al. 2009; Miransari 2010). On the other hand, the symbiotic association of rhizobium with legumes plays a significant role in atmospheric N-fixation. Knowing the importance of rhizobium and mycorrhizal symbiotic association with plants to maintain the health of soil, it is crucial to examine the effect of NPs on these microorganisms.

There is only hand full of studies showing the effect of NPs on symbiotic association of rhizobium and mycorrhiza with plants. Most of the studies show that the presence of NPs has negative impact on rhizobium and mycorrhiza while few show the positive effect of NPs on these microorganisms (Table 2.2). The effect of NPs on mycorrhiza and rhizobium is dependent upon the physicochemical properties of NPs, concentration of NPs, species of fungus and bacteria, and the properties of soil (Tian et al. 2019).

The impact of NPs on mycorrhizal colonization or rhizobial association with plants is dependent on the size and concentration of soil, microbial species, and physicochemical properties of soil. The concentration and size of nanoparticles have a crucial impact on these symbionts. To understand the mechanism by which NPs can affect these microorganisms in the natural environment, it is important to characterize NPs in the possible exposure conditions.

Soil microorganisms are crucial to sustainable agriculture and their association with plants is vital for the growth and development of plants. Hence, it is important to examine the effect of NPs on these microorganisms, individually as well as the effect of NPs on their association with plants. At this point, we know that NPs can affect the symbiotic association of plant-mycorrhiza and legume-mycorrhiza in a positive and negative way. In most of the experiments, unrealistically high concentrations of NPs are used to examine the effect on mycorrhiza (Tian et al. 2019). Also, the experiments with rhizobia were performed in soil-less media (Tian et al. 2019). For a better understanding of the impacts of NPs on soil microorganisms, more studies are required that are closed to natural environmental conditions.

7 Major Concerns

Nowadays, nanoparticles are used in every industry and becoming the part of our lives. The ultimate sink for these NPs is our environment, i.e., air, water, and soil and from there it enters in plants. Hence, it is imperative to observe the impact of NPs on plants. Several studies have reported that the lower concentrations of NPs can positively affect plant growth while its high concentration can cause phytotoxicity. Excessive use of NPs can increase their concentration in the environment. So, it is important to characterize the NPs, their stability in the environment.

Table 2.3 Effects of nanoparticles (NPs) on plants in rhizospheric environment

NPs	Symbiotic partners	Effect	References
nAg	White clover-*Glomus caledonium*	+ve	Feng et al. (2013)
nAg	Faba bean-*Rhizobium leguminosarum*	−ve	Abd-Alla et al. (2016)
nAg	Faba bean-*Glomus aggregatum*	−ve	Abd-Alla et al. (2016)
nAg	Alfaalfa-*Sinorhizobium meliloti*	−ve	Mohaddam et al. (2017)
nAg	Tomato-AMF	−ve	Noori et al. (2017)
nAu	Tomato-AMF	−ve	Judy et al. (2015)
nCeO	Soybean-*Bradyrhizobium japonicum*	No effect	Priester et al. (2012)
nCeO	Red clover-AMF	No effect	Moll et al. (2016)
$nCu(OH)_2$	Bean- *Rhizobium leguminosarum*	−ve	Baijukya and Semu (1998)
nFe_3O_4	Soybean-*Bradyrhizobium japonicum*	+ve	Ghalamboran (2011)
nFe_3O_4	Soybean- *Rhizobium* sp.	No effect	Burke et al. (2015)
nFe_3O_4	Pea- *Rhizobium leguminosarum*	Varied from −ve to +ve, dependent upon the dose and days of inoculation	Sarabia-Castillo and Fernández-Luqueño (2016)
nFeO	Clove-*Glomus caledonium*	+ve to no effect (dose dependent)	Feng et al. (2013)
nMo	Chickpea-*Bradyrhizobium japonicum*	+ve	Taran et al. (2014)
$nTiO_2$	Pea- *Rhizobium leguminosarum*	−ve	Fan et al. (2014)
$nTiO_2$	Wheat-AMF	No effect	Kingenfuss (2014)
$nTiO_2$	Soybean- *Rhizobium* sp.	No effect	Burke et al. (2015)
$nTiO_2$	Soybean-AMF	No effect	Burke et al. (2015)
$nTiO_2$	Reds clove-AMF	No effect	Moll et al. (2016)
$nTiO_2$	Pea- *Rhizobium leguminosarum*	−ve	Sarabia-Castillo and Fernández-Luqueño (2016)
$nTiO_2$	Rice-AMF	−ve	Priyanka et al. (2017)
nZnO	Soybean-*Bradyrhizobium japonicum*	No effect to +ve	Priester et al. (2012)
nZnO	Pea- *Rhizobium leguminosarum*	−ve	Huang et al. (2014)

(continued)

Table 2.3 (continued)

NPs	Symbiotic partners	Effect	References
nZnO	Tomato-AMF	No effect	Watts-Williams et al. (2014)
nZnO	Maize-*Funneliformis mosseae*	−ve	Li et al. (2016)
nZnO	Soybean-*Funneliformis mosseae*	−ve	Jing et al. (2016)
nZnO	Pea- *Rhizobium leguminosarum*	−ve	Sarabia-Castillo and Fernández-Luqueño (2016)
nZnO	Maize- *Glomus caledonium/versiforme*	No effect to −ve (dose-dependent)	Wang et al. (2016a, b and c)

The assessment of the impact of NPs on plants is very complicated as it is species-specific (Pérez-de-Luque 2017). Also, the results obtained from experiments done in control conditions, using hydroponics or soil-less media, can differ while using in the field. Crop fields are inhabited by several microorganisms that affect plant growth. Application of NPs in the field can influence the microflora (Table 2.3) so their impact on the plant can differ in the field from the laboratory experiments.

Before the use of NPs in agriculture, experimentation is needed in more realistic conditions. The physicochemical changes of NPs in soil and their long-term effects on mycorrhiza and rhizobia should be investigated. The mechanism of translocation and internalization of NPs in different plant tissues and induction of secondary metabolite pathways by them are still not clearly explained. Studies suggested that NPs can be used to improve the synthesis of bioactive compounds (Table 2.2). This can be a great strategy to enhance the synthesis of commercially important bioactive compounds. But, the potential impact of the NPs as an elicitor of secondary metabolite production needs more studies to assess the overall impact on ecosystem. Furthermore, to bring the NPs in regular agricultural practices, large-scale experiments are required for the better understanding of the NP-plant interaction on the basis of concentration, size, the exposure period of NPs, and its impact on other components of soil.

8 Conclusion

Technological innovation is essential to fill the gap between food production and the exponentially increasing world population. Nanotechnology is one of the promising fields with broader applications. An increase in the use of NPs in industries is ultimately going to end up in our environment. Once they enter in soil, they will affect our crops and ultimately become a part of our food chain. Hence, it is imperative to thoroughly investigate the impacts of commonly used NPs on plants along with their microenvironment. The studies showed that they can affect plant growth and its physiology in positive, negative, or in neutral ways. Also, the effect of the same NPs can vary from species to species.

Similar to plants, the effect of NPs on the microbiome also varies from species to species and can affect positively or negatively in a dose-dependent manner. Before the use of NPs in large-scale crop field, it is crucial to examine the holistic effect of that NP in particular species along with its effect on microbial population present along with that crop. This chapter shows that the study of NPs in agriculture is expanding. Although, more studies are needed to explain the mode of interaction of NPs with different bio-molecules and their impact on gene expressions.

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Chapter 3
Impact of Nanoparticles on Soil Ecosystems

Wenjie Ren, Haoran Liu, and Ying Teng

1 Introduction

Nanomaterials, with dimension less than 100 nm, have become one of the focuses of concerns in various fields. Due to the unique physiochemical, electronical and mechanical properties, etc., a range of carbon-based, metal, and metal oxide-based nanomaterials have been developed and applied in medical products, electronical appliances, cosmetics, textile, agricultural fertilizers, environmental remediation agents, and so on. Increasing amount of nanomaterials in these wide areas inevitably release nanoparticles (NPs) to the environment during the production, application, disposal, and recycling. Soil is usually considered as the ultimate sink of most contaminants, including nanoparticles (Hochella et al. 2019). Nanoparticles can enter the soil ecosystem in a variety of ways, such as application of nanomaterials in agrochemicals, sewage irrigation, aerosol deposition, and agricultural utilization of municipal sludge (Terekhova et al. 2017). Besides, more and more engineered nanomaterials have been successfully applied in agricultural production and contaminated soil remediation for the past 10 years (Medina-Pérez et al. 2019; Zhao et al. 2020). These will introduce nanoparticles directly to soil system as well. According to statistics, only silver nanoparticles (Ag NP_S) have been directly

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discarded for hundreds of tons and enter the natural soil all around the world every year (Moon et al. 2019). As a remarkable number of nanoparticles enter the soil, their ecological risk to the soil ecosystem draws increasing attention.

Nanoparticles in soil might change soil's physiochemical properties, affecting the habitat of soil biota. Biological systems are subsequently continuously exposed to nanoparticles in soil. Nanoparticles may enter plants and animals with biological activities and induce specific toxicological effects, affect soil microbial communities, and further the biogeochemical cycles in soil. In the past 20 years, especially in the past decade, the impact of nanoparticles on the soil ecosystem has been increasingly studied. Indeed, we now know that nanoparticles exhibit certain toxicological effects on soil biota, but not fully understood.

Moreover, there are usually not consistent conclusions for the impact of nanoparticles on soil biota. Herein, we summarize the toxicity effects of nanoparticles on the soil ecosystem from several aspects, including phytotoxicity, soil fauna toxicity, and soil microbial toxicity. Furthermore, the corresponding toxicity mechanisms are also discussed.

2 Effect of Nanoparticles on Soil Physiochemical Properties

Soil is a complex system comprising of clay minerals, organic matter, and organisms, and harbors definite resistance and restorability from the influence of exogenous nanoparticles. After receiving a certain amount of metal nanoparticles, soil pH might be affected by the enhancement of ion release in the soil. If carbon nanoparticles harbor acidic surface functional groups, such as carboxyl and hydroxyl, they would lead to a certain level of acidification in soil theoretically while it is still difficult for carbon nanoparticles to greatly change soil pH unless they are added with a large quantity. Moreover, the change is relatively limited and mainly depends on the nature of the soil itself. The self-regulation of the soil ecosystem can sometimes counteract the effect. Nevertheless, other physicochemical properties are still likely to be affected by nanoparticles, e.g., organic matter content, nutrient level, and so on.

The content of organic carbon is an important indicator to measure the balance of the soil-plant-microbe system. In the silty-clay soil with high organic matter, TiO_2 NPs are able to cause a significant decrease in carbon mineralization in the soil, thereby promoting the accumulation of organic matter (Simonin et al. 2015). High concentrations of C60 have also been reported to increase the content of organic matter in the soil, leading to an imbalance of the ecosystem (Chen et al. 2019). Besides, an increasing number of researches have demonstrated that nanoparticles could exert a specific influence on the nitrogen cycle in the soil, especially metal nanoparticles. For example, Ag NPs could inhibit certain nitrogen fixing, nitrifying and denitrifying microbes in vitro and are able to disrupt these functional processes in the soil. The current state of knowledge regarding the effect of Ag NPs on the nitrogen cycle has been reviewed by McGee (2020), so we do not expound these herein. Silver sulfide (Ag_2S) NPs can reduce the quantity of denitrifiers in the soil, thus affecting the nitrogen cycle in the soil ecosystem and causing nitrate and nitrite in the soil hardly to be reduced to nitrogen (N_2) (Wu et al. 2020a). Except metal nanoparticles, carbon nanoparticles have also been reported to affect the nitrogen cycle in soil by affecting the nitrogen fixation of legumes. The nitrogen fixation potential of plants can be reduced by more than 30% under the stress of carbon nanoparticles (Wang et al. 2017), which leads to a decrease in nitrogen entering the soil from the air through the legume-rhizobium system, so a reasonable conjecture can be made that carbon nanoparticles might lead to the C:N ratio increase in soil-legume systems.

In addition to the nitrogen cycle, other biogeochemical cycles have also been found to be affected by metal nanoparticles, such as the cycles of sulfur and microelements. For example, ZnO NPs could reduce the abundance of *Sulfitobacter* in the soil, causing the disturbance of the sulfur cycle in the soil (Wu et al. 2020b). Engineering nanoparticles may improve the utilization of nutrients in the soil by animals and plants. This means that the nutrient loss rate in the soil is increased, and the fertility is rapidly reduced (Conway and Keller 2016). After titanium dioxide (TiO_2) NPs were added to the soil, the content of metal and nonmetal elements in the soil would decrease, e.g., Mn, Fe, and P (Bellani et al. 2020). The influencing extent of nanoparticles on soil physiochemical properties also depends on the properties of nanoparticles, e.g., structure, molecular size, and hydrophobicity. Solid nanoparticles may be difficult to decompose ions, whereas dissolved nanoparticles allow their ions to rapidly affect the ionic balance of the soil. All these effects caused by nanoparticles could directly affect the absorption and utilization of nutrients by plants and animals as well as the circulation of substances in the whole soil ecosystem.

However, microorganisms, plants, and animals are not necessarily "accomplices" when soil function is under the stress of nanoparticles. Nanoparticles tend to transfer and be transformed in the soil, diluting the content of nanoparticles in another way. This dilution process protects organisms from direct exposure to high concentrations of nanoparticles, while low concentrations of nanoparticles do not necessarily cause harmful effect on organisms. Some plants and animals have the ability to achieve resistance to low levels of nanoparticles through their epidermal cells (Zhao et al. 2016). This is the dilution of the soil that gives these organisms a chance to exert their self-protection. This reflects a kind of protective effect of soil on organisms. However, the related researches concerning the ecological risk from the viewpoint of the integrated soil ecosystem are still quite limited, which are necessary to be further explored in the future.

3 Effect of Nanoparticles on Plant Growth and Development

Plants, as the dominating primary producers, play a vital role in the sustainable development of the terrestrial ecosystem. They could provide oxygen and food for animals through photosynthesis, and their root exudates and residues drive the assembly and geological distribution of the soil microbial community. Therefore, it is quite important to investigate the phytotoxicity effects of nanoparticles for elucidating the ecological risk of nanoparticles to soil system. So far, a large number of papers have been published concerning the impact of nanoparticles on plant growth, development as well as physiological and biochemical characteristics. It could be found that the phytotoxicity effect of nanoparticles is closely related to nanoparticle type. Obvious difference could be found between metal nanoparticles and carbon nanoparticles.

3.1 Absorption and Accumulation of Nanoparticles in Plants

Nanoparticles have been reported to be absorbed by plants in two passways, including root uptake and foliar uptake. Roots are the main organ for plants to absorb nanoparticles, while there is no contribution ratio between root and foliar absorptive amount.

Dang et al. (2019) determined the uptake passways of Ag_2S NPs and Ag NPs into plants by stable isotope tracer technique, and indicated that the accumulation amount in ^{109}AgNP-treated leaves from root uptake accounted for less than 29%, whereas almost all of Ag in untreated plants was originated from root uptake of Ag_2S NPs. Stable isotope tracer technique has enabled the differentiation of the uptake passway of nanoparticles in plants. However, the related reports are still quite limited, needing to be further investigated. Cell wall, with the largest pore in the range of 5–20 nm, is the first barrier through which nanoparticles enter into the interior plant. It has been generally accepted that nanoparticles with the particle size less than 5 nm can penetrate cell wall pores and reach epidermal cells, as has been reported for Ag NPs (Antisari et al. 2015), AgS NPs (Stegemeier et al. 2017), and CeO_2 NPs (López-Moreno et al. 2010).

However, an increasing number of researches demonstrate that nanoparticles with a larger size could be detected in plant cells as well. They found that nanoparticles may enlarge the cell wall pores or change their permeability, facilitating the uptake of nanoparticles by plant cells. Besides, nanoparticles could also pass through the bilayer lipid membranes of cells via endocytosis. Hu et al. (2020b) found that nanoparticles (e.g., CDs, CeO_2, and SiO_2) translocated across the leaf epidermal barrier through stomatal or cuticular passways, and then move toward the epidermis, extracellular space, or organelles (e.g., chloroplasts) through two passways, namely, apoplastic pathway (through the extracellular space between cell walls) and symplastic passway (through the cytosol) (Fig. 3.1). These types of nanoparticles could be rapidly absorbed by the stomata and cuticle of cotton and maize leaves. This process might be less than 10 min. If the nanoparticles were positively charged (>15 mV), the efficiency transfer by leaf guard cells, extracellular space, and chloroplast could reach the highest (Hu et al. 2020b).

Exposure to metal nanoparticles can affect the concentration of metal elements in plants. For example, the concentrations of both metal ions present a substantial

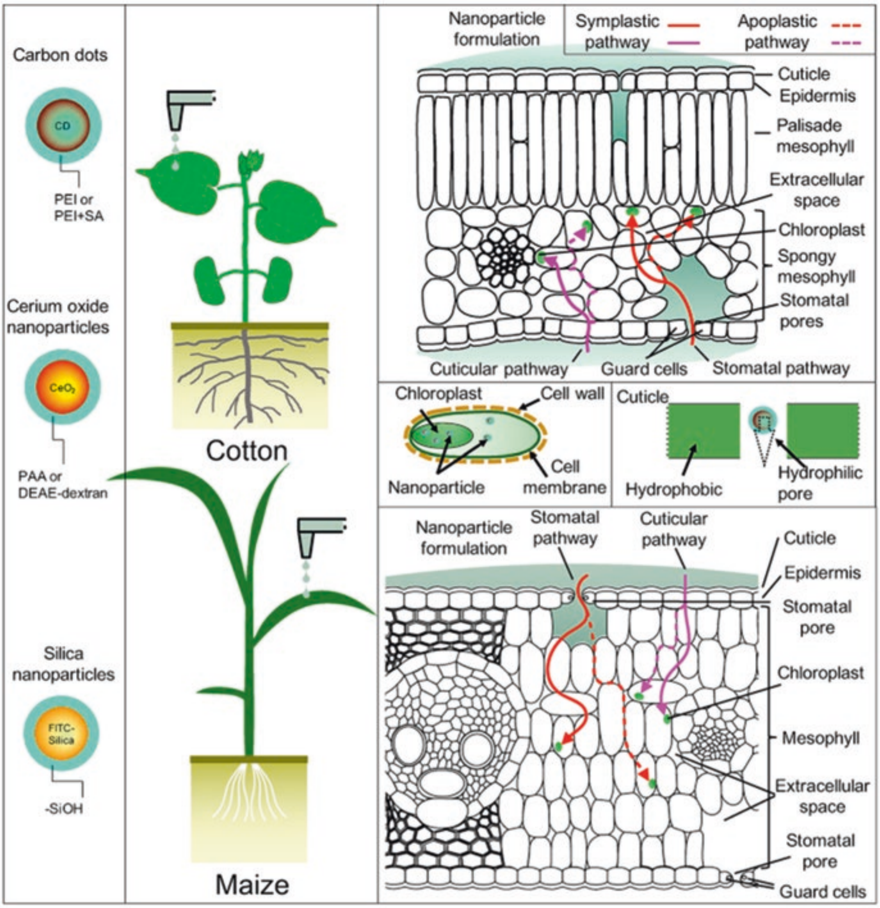

Fig. 3.1 Nanoparticle translocation pathways and distribution in plant leaves. (Reprinted with permission from Hu et al. (2020b). Copyright (2021) American Chemical Society)

increase in plants upon exposure to 1000 mg/L of Cu NPs and Ag NPs (Stampoulis et al. 2009). Based on these phenomena, low concentrations of metal nanoparticles can be used to prepare nano-fertilizers, supplying the appropriate amount of metal ions needed by plants, according to the types of metal ions to reach growth requirement levels of plants. Similar to metal or metal oxide nanoparticles, carbon nanoparticles can also be absorbed and utilized by plant roots. However, carbon nanoparticles are mainly concentrated in plant roots and only a very small amount of carbon nanoparticles can enter the rest of plant organs, especially leaves, which leads to a limited translocation of carbon nanoparticles spread along food chains.

The transport and fate of carbon nanoparticles are dependent on nanoparticle types, showing the selectivity of layer, size, and charge. Cañas et al. (2008) found that the absorption of single-walled carbon nanotubes (SWCNTs) by plants is very slow, and no visible accumulation of SWCNTs was observed in plant roots within 48 h. The transfer of graphene oxide (GO) from roots to other organs is also relatively difficult. Only a very limited amount of GO can be transferred from wheat roots to stems and leaves, and GO accumulated in the roots may be slowly eliminated to the external environment (Chen et al. 2017). *Arabidopsis* also showed strong resistance for GO transport to stems and leaves (Zhao et al. 2015). Huang et al. (2018) also found the highest accumulation of few-layer graphene (FLG) in rice roots through the tracking of carbon-14 label. FLG can translocate within the rice seedlings to penetrate the cell wall and shoot membrane and enter the chloroplast. After nanoparticles were absorbed in interior plants, three aspects have been reported for the fate of nanoparticles: a) remaining in the interior plant; b) degraded by carotene or other enzymes in plants; c) discharged to the external environment. Nevertheless, the relative contributions of these aspects have not been clearly elucidated.

3.2 Impact of Nanoparticles on Plant Growth and Development and Interaction Mechanisms

Impact of Nanoparticles on Plant Growth and Development

A variety of nanoparticles, such as ZnO NPs, CeO_2 NPs, CuO NPs, carbon nanotubes, and graphene, have been reported to exert a hormesis effect on plant growth and development parameters, e.g., germination, root and shoot length, biomass, and yield, that is, low-concentration promoting and high-concentration inhibiting.

For example, ZnO NPs at lower concentrations (10 and 25 mg/L) could promote seed germination and seedling growth of *Vicia faba* (Youssef and Elamawi 2020), improve yield and quality of soybeans, and solve malnutrition problems (Yusefi-Tanha et al. 2020); $Cu(OH)_2$ nanowire can improve the growth of alfalfa at the level of 80 and 280 mg/kg, especially the absorption of nutrients (Cota-Ruiz et al. 2020); $nTiO_2$ caused an increase in the fresh weight of carrot leaves (Wang et al. 2021a). These indicate that metal nanoparticles have the potential to be applied for the improvement of soil lacking specific metal elements. However, higher concentrations (100 and 200 mg/L) of ZnO NPs markedly induced micronuclei, vacuolated nuclei formation and chromosomal aberration, which includes chromosomal breakage, chromosomal bridges, ring chromosomes, laggard chromosomes, and stickiness. Besides, ZnO NPs at the concentration of 400 mg/kg can also cause severe oxidative stress in soybeans, especially the spherical 38 nm ZnO NPs (Yusefi-Tanha et al. 2020). Surface-modified titanium dioxide nanoparticles ($nTiO_2$) caused a decrease in the fresh biomass of taproot and the increase of abnormal division of carrot taproots at a higher concentration of 400 mg/kg (Wang et al. 2021a, b). Exposure to Cu NPs and Ag NPs at 1000 mg/L can cause the root length, transpiration, and biomass of *Cucurbita pepo* to be greatly reduced by more than 75% (Stampoulis et al. 2009).

Compared with metal or metal oxide nanoparticles, previous studies concerning the effect of carbon nanoparticles on plants were mostly performed in the range of relatively higher concentrations. For the most part, carbon nanoparticles have a negative impact on plant growth or development at higher concentrations. GO can lead to a decrease in the maximum root length and the number of lateral roots in wheat, as well as abnormal reactions such as whitening, wrinkles, and oxidative stress in root tips (Weng et al. 2020). Both few-layer graphene (FLG) and GO can inhibit the germination of Hazel (*Corylus avellana L.*) pollen, and furthermore GO can also suppress the growth of pollen tubes (Carniel et al. 2020). GO at 0.1 mg/L had a positive effect on the formation of apple roots, while it reduced root growth (Li et al. 2018). GO has no obvious effect on *Arabidopsis* seed germination, root and shoot growth, and flowering (Zhao et al. 2015). However, the combined exposure of GO and other substances (PEG 6000 or NaCl) can have significant inhibition effects on *Arabidopsis* seedlings than a single exposure of other substances, leading to the reduction of fresh weight and root length (Wang et al. 2014).

As indicated in Table 3.1, we summarized various results for the effects of nanoparticles on plants in the recent years. It could be apparently demonstrated that these effects and corresponding mechanisms are highly dependent on multiple factors, such as nanoparticle type, surface properties, dose, plant species, exposure pathways and duration as well as environmental conditions (Cota-Ruiz et al. 2020; Jordan et al. 2020; Yusefi-Tanha et al. 2020). Surface properties like size, shape, solubility, specific surface area, surface charge, and reactivity are key factors for assessing the phytotoxicity of nanoparticles (Carniel et al. 2020). The original functional carbon nanodots (FCNs) have a limited promotion effect on plant growth, while quantum-sized FCNs are more easily absorbed by plants and produce more positive effects (Chen et al. 2020). Besides, the growing stage of plants is also an important influencing factor for the effect of nanoparticles. For instance, multiwalled nanotubes (MWNTs) can cause the delay of early plant growth and flowering, but do not affect the later growth of plants (Jordan et al. 2020). Graphene can speed up the germination of seeds and increase the germination rate. However, it leads to a decrease in the biomass of seedlings (Zhang et al. 2015). Although a large number of researches have paid close attention to these influencing factors, it is still difficult to identify the most crucial factor for plant phytotoxicity. More plant species should be considered in the future, especially in the full life cycle. Multiple mechanisms have been proposed and clarified concerning the hormesis effect of nanoparticles on plants from molecular level, tissue level to individual level. Herein, the promoting and inhibiting mechanisms were elucidated respectively.

Promoting Mechanisms

1. Nanoparticles can enhance water transfer characteristics in plants. This mechanism has been reported mostly for carbon nanoparticles, including GO and hydrated graphene ribbon (HGR). Most of the carbon nanoparticles harbor oxygen-containing functional groups, which facilitate the collection of water.

Table 3.1 Effects of representative NPs on plants

Characterization of NPs				Materials and methods			Effects on plants			
Types of NPs	Diameter(nm)	Zeta potential (mV)	Wrappage	Tested concentration	Medium	Plant species	Toxicological endpoints	Promotional concentration (target of action)	Inhibitory concentration (target of action)	References
Metal or metal oxide NPs										
Ag	30.1–65		20 nm 0.3% PVP	0–2000 mg/kg	Sandy loam and silt loam	Northern wheatgrass (*E. lanceolatus*) and red clover (*T. pratense*)	Seedling emergence, root and shoot length		389 (root length), 1104 (shoot length) and >1923 mg/kg (seeding emergence)	Jessica et al. (2016)
CeO_2	7.5–11.7	14.9–34.6	DiI-AD[1]	0.5 mg/L	Standard soil mix (Sunshine, LC1 mix).	Cotton (*Gossypium hirsutum* L.) and maize (*Zea mays* L.)	Leaf cells in the epidermis, extracellular space, or organelles (e.g., chloroplasts)		0.5 mg/L	Hu et al. (2020b)
CeO_2	1.8–10.8	−43.5 ~ −40.3	DiI-P[1]	0.5 mg/L	Standard soil mix (Sunshine, LC1 mix).	Cotton (*Gossypium hirsutum* L.) and Maize (*Zea mays* L.)	Leaf cells in the epidermis, extracellular space, or organelles (e.g., chloroplasts)		0.5 mg/L	Hu et al. (2020b)
Co_3O_4	<50	−30		269.3–1000 mg/kg	OECD Soil	Tomato (*L. lycopersicum*) and maize (*Zea mays* L.)	Germination and growth		269.3–1000 mg/kg	Bouguerra et al. (2019)
CuO	25, 50, 250	−51.5 ~ −52.6		0–500 mg/kg	Soil	Soybean (*Glycine max* L.)	Seed yield, antioxidant biomarkers (SOD, CAT, POX, APX[1])		50–500 mg/kg	Yusefi-Tanha et al. (2020)

Characterization of NPs				Materials and methods			Effects on plants			
Types of NPs	Diameter(nm)	Zeta potential (mV)	Wrappage	Tested concentration	Medium	Plant species	Toxicological endpoints	Promotional concentration (target of action)	Inhibitory concentration (target of action)	References
$Cu(OH)_2$ Nanowires	50	24.1 ± 0.32		80–280 mg/kg	Soil	Alfalfa (*Medicago sativa*)	Nutrients in roots and leaves	80–280 mg/kg		Cota-Ruiz et al. (2020)
Fe $S = 70–100\ m^2/g$	50–100			5 mg/L (leaf spray)	Cd-contaminated soil	Wheat (*Triticum aestivum* L.)	Straw and grain yields, chlorophyll, carotenoids contents and antioxidants activities, bio-fortification of Fe increase, the decrease of Cd uptake	5 mg/L		Hussain et al. (2021)
FeO	19–40			25–100 mg/kg	Cd-contaminated soil	Wheat (*Triticum aestivum* L.)	Length and nutrient concentrations (N, P, K) increase; Cd uptake decrease	100 mg/kg		Manzoor et al. (2021)
Fe_3O_4	30			100 mg/kg	Soil	Maize (*Zea mays* L.)	Chlorophyll b content and biomass increase	100 mg/kg		Zhao et al. (2019)
Pb^2 $S = 64.91\ m^2/g$	<1000			0–200 mg/L	Alkaline soil suspension	Maize (*Zea mays* L.)	Accumulation of Pb and Cu in shoots and roots		25–200 mg/L	Li et al. (2021)
S				50–200 mg/kg	Soil	Broad bean (*Vicia faba* L.)	Total length and quantity of leaves	200 mg/kg		Kahlel et al. (2020)

(continued)

Table 3.1 (continued)

Characterization of NPs				Materials and methods			Effects on plants			
Types of NPs	Diameter(nm)	Zeta potential (mV)	Wrappage	Tested concentration	Medium	Plant species	Toxicological endpoints	Promotional concentration (target of action)	Inhibitory concentration (target of action)	References
Si $S = 70–100\ m^2/g$	≤50			300 mg/L (leaf spray)	Cd-contaminated soil	Wheat (*Triticum aestivum* L.)	Straw and grain yields, chlorophyll, carotenoids contents and antioxidants activities increase, the decrease of Cd uptake	300 mg/L		Hussain et al. (2021)
SiO_2	18.0 ± 13.5	−45.8 ± 1.8	FITC[4]	0.5 mg/L (leaf spray)	Standard soil mix (Sunshine, LC1 mix).	Cotton (*Gossypium hirsutum* L.) and maize (*Zea mays* L.)	Leaf cells in the epidermis, extracellular space, or organelles (e.g., chloroplasts)		0.5 mg/L	Hu et al. (2020b)
SiO_2	20			100 mg/kg	Soil	Maize (*Zea mays* L.)	Amino acid perturbations in leaves		100 mg/kg	Zhao et al. (2019)
TiO_2	50 ± 25		Al_2O_3, glycerol or, dimethicone[3]	100–400 mg/kg	Natural soil and potting soil (5:1)	Carrots (*Daucus carota* subsp. *sativus*)	Biomass of leaves, biomass and taproot splitting of roots	100 mg/kg (biomass of leaves)	400 mg/kg (biomass and taproot splitting of roots)	(Wang et al. 2021a, b)
TiO_2	<100			100–300 mg/kg	Soil	Soybean (*Glycine max* L.)	^{133}Cs accumulation in shoot		100–300 mg/kg	Singh and Lee (2018)

Characterization of NPs				Materials and methods			Effects on plants			
Types of NPs	Diameter(nm)	Zeta potential (mV)	Wrappage	Tested concentration	Medium	Plant species	Toxicological endpoints	Promotional concentration (target of action)	Inhibitory concentration (target of action)	References
TiO_2	20–30			100–500 mg/L (leaf spray)	Artificial soil	Benth (*Nicotiana benthamiana*)	Biomass and leaf area	100–200 mg/L		Adeel et al. (2021)
TiO_2 (anatase)	20–80		Non-humified compounds	80–800 mg/kg	Soil (sand 93.3%, clay 2.1%)	Pea (*Pisum sativum* L.)	N absorption in shoots, inorganic ions absorption in roots (Mn, K, Zn, P) and shoots (Mn, N)	80–800 mg/kg (N absorption in shoots)	80–800 mg/kg (inorganic ions absorption in roots (Mn, K, Zn, P) and shoots (Mn, N))	Bellani et al. (2020)
TiO_2 (rutile)	20–100		Non-humified compounds	80–800 mg/kg	Soil (sand 93.3%, clay 2.1%)	Pea (*Pisum sativum* L.)	N absorption in shoots, inorganic ions absorption in roots (Mn, K, Zn, P) and shoots (Mn, N)	80–800 mg/kg (N absorption in shoots)	80–800 mg/kg (Inorganic ions absorption in roots (Mn, K, Zn, P) and shoots (Mn, N))	Bellani et al. (2020)
TiO_2 (aggregates)	100–300			80–800 mg/kg	Soil (sand 93.3%, clay 2.1%)	Pea (*Pisum sativum* L.)	N absorption in shoots, inorganic ions absorption in roots (Mn, K, Zn, P) and shoots (Mn, N)	80–800 mg/kg (N absorption in shoots)	80–800 mg/kg (inorganic ions absorption in roots (Mn, K, Zn, P) and shoots (Mn, N))	Bellani et al. (2020)

(continued)

Table 3.1 (continued)

Characterization of NPs				Materials and methods			Effects on plants			
Types of NPs	Diameter(nm)	Zeta potential (mV)	Wrappage	Tested concentration	Medium	Plant species	Toxicological endpoints	Promotional concentration (target of action)	Inhibitory concentration (target of action)	References
TiO_2	5–10			100 mg/kg	Soil	Maize (*Zea mays* L.)	Malondialdehyde (MDA) content decrease and amino acid perturbations in leaves		100 mg/kg	Zhao et al. (2019)
TiO_2 mixed phosphorous fertilizer	26.5			500–750 mg/kg	Silt-loam and Clay	Rice (*Oryza sativa* L.)	Shoot length, biomass, phosphorous uptake and rice grain protein content	500–750 mg/kg		Waani et al. (2021)
Zinc ferrite ($ZnFe_2O_4$) with AMF	20–30			5 μM	Soil	Pea (*Pisum sativum*)	Roots and shoots fresh weights	5 μM		Abdelhameed et al. (2021)
ZnO				50 mg/kg	Soil	Broad bean (*Vicia faba* L.)	Total length and quantity of leaves	50 mg/kg		Kahlel et al. (2020)
ZnO $S = 70–100\ m^2/g$	20–30			25 mg/L (leaf spray)	Cd-contaminated soil	Wheat (*Triticum aestivum* L.)	Straw and grain yields, chlorophyll, carotenoids contents and antioxidants activities, bio-fortification of Zn, Cd uptake	25 mg/L		Hussain et al. (2021)
Carbon NPs										

Characterization of NPs				Materials and methods			Effects on plants			
Types of NPs	Diameter(nm)	Zeta potential (mV)	Wrappage	Tested concentration	Medium	Plant species	Toxicological endpoints	Promotional concentration (target of action)	Inhibitory concentration (target of action)	References
Nano-C $S = 1200\ m^2/g$	20–70			0–20 g/kg	Mixture of peat, vermiculite and perlite (3:1:1) with neutral salts	Alfalfa (*Medicago sativa* L.)	The dry weight, fresh weight, seedling length, and antioxidant enzyme activities	5 g/kg	10–20 g/kg	Chen and Wang (2021)
C60	50			100–200 mg/L (leaf spray)	Artificial soil	Benth (*Nicotiana benthamiana*)	Biomass and leaf area, viral coat protein transcript abundance, GFP mRNA expression, abscisic acid, and salicylic acid	100–200 mg/L		Adeel et al. (2021)
CDs[1]	1.7–5.5		PEI[1]	0.5–5 mg/L (leaf spray)	Standard soil mix (Sunshine, LC1 mix).	Cotton (*Gossypium hirsutum* L.) and maize (*Zea mays* L.)	Leaf cells in the epidermis, extracellular space, or organelles (e.g., chloroplasts)		0.5–5 mg/L	Hu et al. (2020b)
CDs	1.9–6.4		SA-PEI[1]	0.5–5 mg/L (leaf spray)	Standard soil mix (Sunshine, LC1 mix).	Cotton (*Gossypium hirsutum* L.) and maize (*Zea mays* L.)	Leaf cells in the epidermis, extracellular space, or organelles (e.g., chloroplasts)		0.5 mg/L	Hu et al. (2020b)

(continued)

Table 3.1 (continued)

Characterization of NPs				Materials and methods			Effects on plants			
Types of NPs	Diameter(nm)	Zeta potential (mV)	Wrappage	Tested concentration	Medium	Plant species	Toxicological endpoints	Promotional concentration (target of action)	Inhibitory concentration (target of action)	References
GNS $S = 161.3\ m^2/g$				100–300 mg/L (leaf spray)	Soil	Pepper (*Capsicum annuum* L.) and eggplant (*Solanum melongena* L.)	Number of branches plant and fruits, large starch granules, mitochondrial number adjacent to chloroplasts, SOD, CAT, POX, APX in leaves	100–300 mg/L (number of branches plant and fruits)	100–300 mg/L (large starch granules, mitochondrial number adjacent to chloroplasts, SOD, CAT, POX, APX in leaves)	Younes et al. (2019)
GO				50–200 mg/L	Soil	Spinach (*Spinacia oleracea*) and chive (*Allium schoenoprasum*)	Germination and biomass of seedlings	50–200 mg/L		He et al. (2018)
MWNTs $S = 500–2000\ m^2/g$	30–50		-COOH	1–10 mg/kg	Soil	Tomato (*L. lycopersicum*)	Early growth and flowering		1–10 mg/kg	Jordan et al. (2020)
MWNTs	20–30			100–200 mg/L (leaf spray)	Artificial soil	Benth (*Nicotiana benthamiana*)	Biomass and leaf area, viral coat protein transcript abundance, GFP mRNA expression, abscisic acid, and salicylic acid	100–200 mg/L		Adeel et al. (2021)

Characterization of NPs				Materials and methods			Effects on plants			
Types of NPs	Diameter(nm)	Zeta potential (mV)	Wrappage	Tested concentration	Medium	Plant species	Toxicological endpoints	Promotional concentration (target of action)	Inhibitory concentration (target of action)	References
SWNTs $T = 5000–3 \times 10^4$ nm	1–4			1–10 mg/kg	Soil	Tomato (*L. lycopersicum*)	Salicylic acid	10 mg/kg		Jordan et al. (2020)

Note:

1. *DiI* (2Z)-2-[(E)-3-(3,3-dimethyl-1-octadecylindol-1-ium-2-yl) prop-2-enylidene]-3,3-dimethyl-1-octadecylindole perchlorate, Invitrogen, *Dil-AD* DiI labeled aminated dextran-coated material, *Dil-P* DiI labeled poly(acrylic acid)-coated material, *SOD* superoxide dismutase enzyme, *CAT* catalase, *POX* guaiacol peroxidase, *APX* ascorbate peroxidase, *CDs* carbon dots, *PEI* polyethyleneimine coated material, *SA-PEI* succinic anhydride-modified PEI
2. There are also small amounts of Cr, Cu, and Zn in the sample

Moreover, the hydrophobic SP^2 and SP^3 hybrid structures are in favor of the transport of water into seeds (He et al. 2018). He et al. (2018) indicated that GO at 0–200 mg/L could promote the germination and growth of spinach and leek by means of hydrophilicity and water transfer characteristics. Besides, Zhou and Hu (2017) found that GO stress may increase the expression of aquaporin genes in plants, providing powerful evidence at the molecular level.

2. Nanoparticles can stimulate the uptake of micro- and macro-nutrients in plant tissues. For metal or metal oxide nanoparticles, elemental release following the direct uptake of nanoparticles or the uptake of metal ions after the transformation of nanoparticles in soil can lead to accumulation of the corresponding elements in plant tissues. Previous researches suggested that Fe_3O_4, ZnO, CuO, and Si NPs could increase the contents of these respective metals in leaves or roots (Hussain et al. 2021; Kahlel et al. 2020; Yusefi-Tanha et al. 2020; Zhao et al. 2019). Based on these, some metal nanoparticles can be used as nano-fertilizers to improve nutrient deficiencies in the soil. Moreover, Si NPs significantly increased N, K, and Si contents in root, stem, and leaves in an experiment with cucumber growth (Alsaeedi et al. 2019). The ionomics and especially ionome-genome interactions, developing rapidly in recent years, can provide further insights for the mechanism elucidation in this field.
3. Nanoparticles can improve the physiological activities of plants themselves, and strengthen their resistance to biotic or abiotic stresses. Nanoparticles are able to increase not only the absorption and transport of nutrients in plant but also the metabolic and biochemical pathways of nutritional quality (synthesis of carbohydrates, amino acids, and fatty acids). Besides, nanoparticles might improve phytohormone biosynthesis, differential gene expression for elemental transporters, primary and secondary metabolisms, and antioxidant enzyme activity in plants. ZnO NPs and single-walled carbon nanohorns (SWCNHs) have been reported to improve the salt tolerance of *Sophora alopecuroides* seedlings, but different mechanisms were revealed. ZnO NPs can lead to the increase of soluble sugar content and leaf Zn content (Wan et al. 2020), whereas SWCNHs enhanced PSII activity and protein content (Wan et al. 2020). Low concentration of graphene nanosheets (GNS) (0.1–0.3 g/L) is able to regulate some enzyme activities in the leaves, e.g., catalase and ascorbate peroxidase, thereby promoting the healthy growth of pepper and eggplant cells (Younes et al. 2019). Our previous study also found that a low dose of sulfonated graphene could scavenge reactive oxygen species (ROS) in roots and improve maize health state (Ren et al. 2016). Graphene could enter into the chloroplasts and thylakoids of rice leaves and help enhance the fluorescence intensity of chlorophyll (Lu et al. 2020).

Inhibiting Mechanisms

1. After higher concentrations of nanoparticles enter plant cells, their released toxic metal ions (mainly for metal or metal oxide nanoparticles) and the nanoparticles in interior cells can induce ROS generation in plants. Figure 3.2 demonstrated

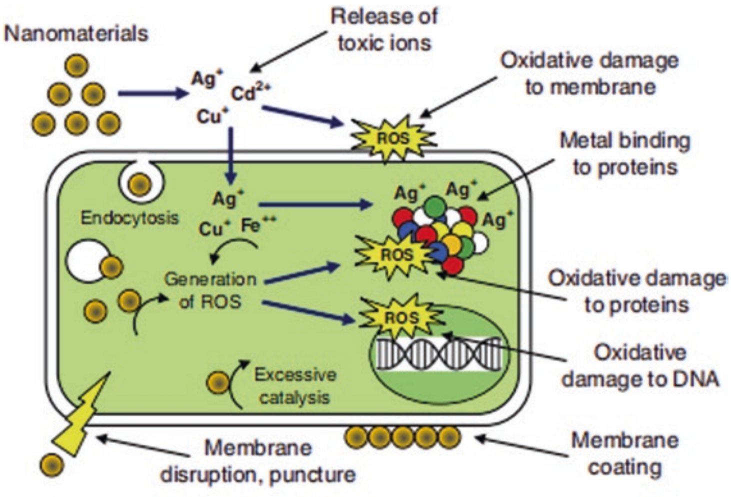

Fig. 3.2 Nanoparticles induced damage to plant cells through ROS generation (Reprinted with permission from Van Aken (2015). Copyright (2021) Elsevier)

the ROS-induced damage mechanisms of nanoparticles on the plant (Van Aken 2015). High levels of ROS might lead to activation of defense systems in plants, such as antioxidant enzymes, phase I + II detoxifying enzymes, and heat shock proteins. Thereupon, some peroxidation products like malondialdehyde (MDA) may increase to a certain extent. Once ROS could not be removed by these enzymes or other defense systems, they would attack cell membranes, proteins, DNA, or organelles, resulting in cellular damage or even cell death (Katti et al. 2015).

2. Higher concentrations of metal nanoparticles can not only lead to the accumulation of toxic metal ions in various plant organs, but also hinder the absorption of macro- or microelements (e.g., Mn and Zn). For example, the intake and accumulation of some metal elements in carrots may be out of balance upon exposure to $nTiO_2$, e.g., the decrease of Mg, Zn, and N accumulation in taproots (Bellani et al. 2020; Wang et al. 2021a, b). This may be because the uptake of Ti by plants directly affects the accumulation of other metal elements in roots, leading to the forced transfer of these metal elements to the rest of the plant. Carbon nanoparticles have been reported to break the guanine-cytosine (Gua-Cyt) hydrogen bond (Katti et al. 2015), and thereby inhibit the expression of nitrate transporters (NRTs), reducing the absorption of N in wheat (Weng et al. 2020).
3. Nanoparticles can disturb or even destruct normal physiological activities, including plant mitosis, photosynthesis, various functional enzymes, and so on. CeO_2 NPs can decrease chlorophyll fluorescence parameters and change the structure of chlorophyll thylakoid, leading to the decrease of energy conversion in Calvin cycle and chlorophyll synthesis of soybeans (Li et al. 2020). These finally caused a significant reduction in the photosynthetic capacity of plants.

ZnO NPs embody the clastogenic and aneugenic nature for root cells of broad bean (*Vicia faba*). Higher concentrations of ZnO NPs can significantly induce chromosomal aberrations (e.g., chromosome breakage and annular chromosomes) as well as the formation of cellular micronucleus and vacuolar nuclei. In addition, ZnO NPs can alter the expression of various functional enzyme lines in plant cells, interfere with mitosis. Consequently, mitotic index and cell cycle can be significantly altered, indirectly inhibiting plant growth (Youssef and Elamawi 2020). Carbon nanoparticles have been also reported to reduce endogenous plant hormones in rice (Hao et al. 2016), and cause clastogenic/aneugenic effects.

4. Nanoparticles may affect the structure and function of symbiotic microbiome of plants. Some beneficial microbial communities play a crucial role in plant growth and development. The disturbance of these microbial communities would lead to the harmful effect on plants. For instance, exposure to GO can directly reduce the abundance, uniformity, and diversity of beneficial endophytic bacterial populations in rice roots even at the concentration of 5 mg/L (Du et al. 2020b).

3.3 Impact of Nanoparticles on Soil Fauna

Soil fauna is a type of important consumer in the soil ecosystem and plays a large role in pedological mass circulation, such as nutrient cycle. Soil fauna is usually directly exposed to nanoparticles because most of them live in the top soil, which is also the nanoparticles' main distribution range. Compared with the phytotoxicity effect, it attracts obviously less attention concerning the toxicity of nanoparticles on soil fauna. At present, the animal species more concerned mainly focus on earthworm, nematode, and cricket. In this section, we introduce the impact of nanoparticles on soil fauna from the following aspects: the absorption and accumulation of nanoparticles, short-term acute toxic effect, and long-term toxic effect.

Uptake and Accumulation of Nanoparticles in Terrestrial Animals

Food is the main way for terrestrial animals to absorb nanoparticles. Their food come from a wide range of sources, especially the material contained in topsoil. For example, earthworms in annelids eat humus, animal waste, soil bacteria, and the decomposition products of these materials. The coelomic cells of earthworms may take up nanoparticles through endocytosis. Nanoparticles in interior earthworm would be subjected to intercellular degradation or exocytosis. However, uptake and bioaccumulation of nanoparticles in terrestrial animals exhibited inconsistent results. Related parameters are strongly affected by nanoparticle types, soil properties, and nanoparticle concentrations.

Not all nanoparticles accumulate rapidly and in large quantities in terrestrial animals. The accumulation rate and amount may be influenced by the molecular size of nanoparticles. The macromolecular size of C60 impeded its bioaccumulation in earthworm (*Eisenia fetida*), leading to a quite low accumulation of C60 in earthworms. Petersen et al. (2008) compared the bioaccumulation of CNTs with that of common pollutant pyrene in earthworm, and found that the bioaccumulation factor of CNTs was two orders of magnitude smaller than that of pyrene. CNTs are not susceptible to be absorbed by biological tissues and form equilibrium distribution in earthworm, whereas remain in the guts of earthworm. Besides, soil properties may affect the uptake and accumulation of nanoparticles by soil animals to a larger extent. Previous researches were mostly performed with only a kind of soil. More soil types and nanoparticle types should be deeply studied to reveal universal law.

Short-term Acute Toxic Effect of Nanoparticles on Terrestrial Animals

In spite of various test conditions (soil types, nanoparticle characterization, animal species, exposure concentration, and exposure duration) among previous reports, most researches confirmed that the survival and growth of adult terrestrial animals were not influenced by the nanoparticles added to the soil. Some typical effects of nanoparticles have been summarized in Table 3.2, in which we could observe that most of the nanoparticles have an adverse effect on behavior, physiological and biochemical activities as well as some indexes at cellular level under acute exposure for a short term. Terrestrial animals try to avoid nanoparticles, which can cause damage to their surface cells. For example, high concentration (1000 mg/kg) of nano-cobalt oxide (Co_3O_4) could cause a significant avoidance effect in the invertebrate *Eisenia andrei* (Bouguerra et al. 2019). When nanoparticles enter earthworm cells, they can lead to DNA breakage and organelle damage (Yadav 2017). Dziewięcka et al. (2018) demonstrated that exposure to 200 mg/kg GO could induce obvious oxidative stress in *Acheta domesticus* after 10 days of feeding. They observed a significant increase in catalase (CAT) and total antioxidant capacity (TAC). *Achita* cell cycle in all stages was disturbed and 35% of DNA was damaged. Besides, the degeneration appeared in a large quantity of gut and testicular cells. This indicates that continuous consumption of GO in a short period of time can cause multiple and fatal harm to terrestrial animals. Moreover, nanoparticles might affect the structure and function of gut microflora in terrestrial animals and further regulate the soil biochemical process these animals get involved in. Wu et al. (2020a) reported that Ag_2S NPs can reduce the relative abundance of denitrifiers in the intestinal tract of earthworms, and inhibit the replication process of nitrification and denitrification genes in earthworms, leading to a significant decrease in N_2O emission. This process interferes with the denitrification of earthworm intestinal microorganisms and may lead to the increase of nitrification intermediate products in earthworms.

Even for the same kind of nanoparticles, nanoparticle-induced toxic effect still may exhibit apparent difference. Zhang et al. (2020a) indicated that multi-layer graphenes (MLGs) with different morphologies cause obviously differential toxic effect on earthworms. Different morphologies result in different hydrophobicity degree. MLGs with poor hydrophobicity are susceptible to be avoided by earthworms, generating a decrease in the quantity of cocoons formation, cell activity in the worm coelom, and the potential of mitochondrial membrane, whereas MLGs with good hydrophobicity can adhere to and destroy worm membranes, which lead to oxidative damage of worm membranes Besides nanoparticle properties, animal genotype is also an important influencing factor for the toxic effect of nanoparticles. Even in the same species, there may be different degrees of damage and self-repair due to the ability of different genotypes to resist external stimuli. Under the duress of the nanoparticles, this gap can be noticeable. Flasz et al. (2020) observed that the cell mortality rate and DNA damage rate of long-living *Acheta* were lower than those of wild *Acheta* after continuous ingest of GO, while the catalase activity was relatively higher for the former. This indicates that long-living *Acheta* has a stronger response to oxidative stress and is more liable to survive under GO stress. Furthermore, long-living *Acheta* is more adaptable to nanoparticles stress than common wild *Acheta* due to a more special homeostasis maintenance mechanism. After GO was removed from the food, catalase activity in long-living *Acheta* dropped to a controlled level, but this did not appear in wild *Acheta* and its total Vg protein expression remained at a high level, due to a protein repair mechanism taken by *Acheta* cells suffered from GO damage. Terrestrial animals usually have self-regulation function under nanoparticle stress. This process is mostly by means of the production or increase of proteins. Exposure to GO can activate antimicrobial proteins in nematode gut, e.g., Lys-1, Lys-8, and SPP-1, which play an important role in protecting animals against nanoparticles threat (Ren et al. 2017). The reports concerning the self-regulation mechanisms of terrestrial animals upon exposure to nanoparticles are still fairly limited, and deserve to be deeply studied.

Long-term Toxic Effect of Nanoparticles on Terrestrial Animals

In addition to the short-term and immediate effects, the long-term effects of nanoparticles on terrestrial animals cannot be ignored, because long-term exposure at low doses is the dominant exposure mode in the real soil environment. Although terrestrial animals have certain self-regulation mechanisms to reduce the toxicity of nanoparticles to themselves by enzymes production and up-regulation, nanoparticles can still alter the genes of animals in a long term, and seriously affect the reproduction function. Long-term exposure to GO can damage the gonads of terrestrial animals and significantly reduce their fertility (Dziewięcka et al. 2018). CuO NPs have been shown to induce a decrease in reproductive output of *Enchytraeus crypticus*, while the decrease extent was less than that induced by $CuCl_2$, suggesting the specific effect of nanoparticles in terrestrial animals (Bicho et al. 2020). Moreover, this specificity does not mean more toxicity and may even be less toxic than corresponding metal inorganic substances. The specificity is reflected in different ways that NPs affect organisms, including the type and location of genes and proteins (Bicho et al. 2016).

Upon exposure to nanoparticles for a long term, the impact of nanoparticles on terrestrial animals is probably not limited to a single period of time. It may appear in the full life cycle and even from generation to generation, displaying some certain intergenerational effects. Multigenerational (MG) test design is applied to measure long-term, multigenerational exposure toxicity of nanoparticles to terrestrial animals. Dziewięcka et al. (2020) indicated that long-term exposure to GO at low dose (0.2–20 mg/g) can lead to significant changes in some physiological and biochemical indexes of *Achita* from the second generation, e.g., body weight, antioxidant enzyme activity, and hatching capacity. Moreover, the DNA damage appeared from the third generation. This indicates that GO affects the genomic stability of *Achita* and induces genotype variation, causing changes in various indicators from generation to generation and damaging DNA gradually. Except carbon nanoparticles, metal or metal oxide nanoparticles can also suppress the success rate of hatching, the survival rate of larvae and adults, and reproduction of soil invertebrates, e.g., Ag NPs (NM300K) (Bicho et al. 2016) and CuO NPs (Bicho et al. 2020). *Enchytraeus crypticus* reduced reproductive yield by 10% after exposure to CuO NPs.

After five successive generations of CuO NPs exposure and two generations of clean medium propagation (224 days in total), *E. crypticus* DNA showed global methylation. Changes in appearance and genes are passed on to the next generation, including targets for oxidative stress and detoxification genes. This reflects the cross-generational effect of Cu NPs on *E. crypticus* (Bicho et al. 2020). The full life cycle test can better help to explore the influence of nanoparticles on various life cycles of organisms; however, there are still quite limited relative reports. It needs further more researches referring to various terrestrial animals and more types of nanoparticles.

3.4 Impact of Nanoparticles on Soil Microbial Communities

Microorganism is an important kind of organism in the soil ecological cycle, especially in material decomposing and transformation, and biogeochemistry cycles. In contrast to plants and animals, microorganisms are usually single-cell organisms and exist as microbial communities in the soil environment. To date, some studies have been performed on the effect of nanoparticles on soil microbial communities, which were summarized in this section.

Effect of Nanoparticles on the Structure of Soil Microbial Communities

Most of the nanoparticles have been reported to exhibit strong antimicrobial properties to individual microorganisms, because of the following mechanisms: (1) destroy cell wall or cell membrane through physical puncture (Chen et al. 2019); (2) induce the cell to produce reactive oxygen species, damaging cell structure and organelles (Mortimer et al. 2020); (3) disrupt the common function of cells, e.g., interfere with the transmission of electrons between cells and unbalance the anti-oxidation of microbial cells (Borkowski et al. 2015). However, an increasing number of

Table 3.2 Effects of representative NPs on soil fauna

NP types	Diameter (nm)	Zeta potential (mV)	Wrappage	Animal species	Medium	Tested concentration	Toxic effect	References
Ag	<100			Nematode (*Caenorhabditis elegans*)	Soil	0–5 mg/kg	Inhibit length and brood size of nematodes and survival at 5 mg/kg	Moon et al. (2019)
Ag	20–50		PVP, CIT[a]	Nematode (*Caenorhabditis elegans*)	SSPW (simulated soil pore water)	0.1–1 mg/L	Inhibit reproduction at 0.31–0.86 mg/L (EC_{50} of 20 nm Ag NPs) and 0.41–0.55 mg/L (EC_{50} of 50 nm Ag NPs)	Schultz et al. (2020)
Ag	30.1–65		20 nm 0.3% PVP	*Eisenia andrei*	Soil	0–2000 mg/kg	Show avoidance behavior at concentrations above 32 mg/kg; inhibit juvenile production and dry mass at concentrations above 49 mg/kg and no survival at 2000 mg/kg.	Jessica et al. (2016)
Ag_2S	95.4	−22.2		Earthworms (*Eisenia fetida* and *Pontoscolex corethrurus*)	Soil	0–300 mg/kg	Inhibit gut (N_2O emissions reduced), the denitrification function of the EW gut microbiota, and the cycling of N in soil-based systems at 30–300 mg/kg	Wu et al. (2020a)

NP types	Diameter (nm)	Zeta potential (mV)	Wrappage	Animal species	Medium	Tested concentration	Toxic effect	References
Ag_2S	20–50		PVP, CIT[a]	Nematode (*Caenorhabditis elegans*)	SSPW	1–100 mg/L	Inhibit reproduction by the impact of bacterial food source at 2.82–32.52 mg/L (EC_{50} of 20 nm Ag_2S NPs), 5.28–7.82 mg/L (EC_{50} of 50 nm Ag_2S NPs)	Schultz et al. (2020)
Co_3O_4	<50	−30		Earthworms (*Eisenia fetida*)	Peat, dry and defaunated horse manure	0–1000 mg/kg	Inhibit germination at 269.3–1000 mg/kg; show significant avoidance at 1000 mg/kg; induce oxidative stress and enhance lipid peroxidation No effect on reproductive outputs	Bouguerra et al. (2019)
CdTe QDs[a]	$<2.5 \times 10^5$		COOH, NH^{4+}, PEG[a]	Earthworms (*Eisenia fetida*)	Soil	50–2000 mg/kg	Inhibit juvenile survival ($EC_{50=}$65 mg/kg)	Tatsi et al. (2020)
Fe_3O_4	20–50			Earthworms (*Eisenia fetida*)	Soil	1.5 wt% of the soil	Avoidance behavior	Liu et al. (2020)

(continued)

Table 3.2 (continued)

NP types	Diameter (nm)	Zeta potential (mV)	Wrappage	Animal species	Medium	Tested concentration	Toxic effect	References
TiO_2	25			Earthworms (*Eisenia fetida*)	Soil	500–5000 mg/kg	Inhibit survival and exercise (locomotion (head trash frequency) becomes higher at 500 mg/kg and lower at 5000 mg/kg) Promote life span and irritation resistance of surviving individuals at 5000 mg/kg	Hu et al. (2020a)
GO	500–5000			*Acheta domesticus*	Soil	20–200 μg/g	Short-term: Induce induce the antioxidative defense, DNA damage, and numerous degenerative, changes gut and gonads; Long-term: low cell vitality in the next generation and multigenerational harmful effects at 200 μg/g.	Dziewięcka et al. (2018)
MLGs[a]	2800–7400			Earthworms (*Eisenia fetida*)	Soil	0.2% and 1% of dry soil	Inhibit cocoon and coelomocytes	Zhang et al. (2020a)

NP types	Diameter (nm)	Zeta potential (mV)	Wrappage	Animal species	Medium	Tested concentration	Toxic effect	References
MWCNTs	30–70		PEI (polyethylenimine)–Ac (acetyl groups) and PEI-Suc (succinamic acid groups)	Earthworms (*Eisenia fetida*)	Soil	0.3 mg/kg (MWCNTs) and 0.5 mg/kg (MWCNTs-PEI)	Limited absorption and impact	Petersen et al. (2011)
Nano-hydroxyapatite apatite (n-HAP)	20–50			Earthworms (*Eisenia fetida*)	Soil	1.5 wt% of the soil	Avoidance behavior	Liu et al. (2020)
N-zeolite	20–50			Earthworms (*Eisenia fetida*)	Soil	1.5 wt% of the soil	Avoidance behavior	Liu et al. (2020)

Note: [a]*MLGs* multi-layer graphenes, *QDs* quantum dots, *PEG* polyethylene glycol, *CIT* citrate functionalized wrappage researches demonstrated that nanoparticles can promote the growth and reproduction of some specific functional microbes. No definite rules have been elucidated for the distinct effect of nanoparticles on individual microorganisms. Microorganisms are prone to reveal certain resistance to nanoparticle stress when they appear in a community, such as in soil environment, due to complex interaction among different microbial species and biodiversity. Wu et al. (2020b) indicated that microbial communities with high concentration of dissolved oxygen (DO) had high diversity and good metabolic capacity had strong resistance to ZnO NPs.

So far, there are no consistent results for the effect of nanoparticles on soil microbial communities. Based on the previous researches, the effects were largely related with nanoparticle types, nanoparticle concentration, and exposure time. CeO_2 NPs, Fe_3O_4 NPs, and TiO_2 NPs have no obvious impact on the population size of soil bacterial communities in the concentration range of 500–2000 mg/kg, while ZnO NPs significantly inhibit the total bacterial population even in a relatively less concentration range of 500–750 mg/kg. Moreover, ZnO NPs exhibit a suppression effect on the relative abundances of Bacilli, Alphaproteobacteria, and Gammaproteobacteria at 0.5–2 mg/g. Forstner et al. (2019) observed that carbon nanotubes, reduced GO (rGO), and ammonia-functionalized graphene oxide (aGO) can cause changes in the composition of bacterial communities in the soil at concentrations of 1 mg/kg after 14 days of soil incubation (Forstner et al. 2019). By comparison, nanoparticles showing stronger antimicrobial properties would affect largely soil microbial communities, such as Ag NPs. Bellani et al. (2020) indicated that polyvinylpyrrolidone (PVP)-coated Ag ENMs could obviously inhibit the bacteria, fungi, and actinomycetes in the soil at the concentration of 100 mg/kg. Meanwhile, different concentrations of PVP-AgENMs and 1 mg/kg of Ag_2S NPs also had significant effects on the soil microbial community (Judy et al. 2015). C60 can directly reduce the quantity of microorganisms at 50–500 mg/kg and destroy the structure of microbial community at higher concentrations, e.g., *Nitrospira*, *Planctomyces*, etc. MWCNTs can reduce the activity of microbial enzymes and change the bacterial composition. As shown in Table 3.3, we summarized the effect of representative nanoparticles on soil microbial communities, from which we could clearly observe the difference among different nanoparticles or concentrations.

Besides, exposure time is also a quite important influencing factor for the effect of nanoparticles on soil microbial communities. We previously studied the effect of graphene on the structure, abundance, and function of the soil bacterial community, and observed that the effect was typically time-dependent (Ren et al. 2015). After a short term of exposure (4 days), graphene promoted the biomass of bacterial populations. A significant shift was also observed in the structure of soil bacterial communities. However, as the exposure time extends to 60 days, the respective change became weaker or disappeared in spite of graphene concentrations, suggesting that microbial communities harbor certain recovery ability under the stress of nanoparticles. Up to now, most published articles have paid much attention to the short-term effect, while the response of soil microbial communities to nanoparticle exposure is fairly limited, which may provide more powerful reference for the ecological risk assessment of nanoparticles based on soil microbial communities.

Table 3.3 Effects of representative nanoparticles on soil microbial communities

NPs type	Diameter (nm)	Thickness (length) (nm)	Zeta potential (mV)	Medium	Target microorganisms	Tested concentration (mg/kg)	Toxic effect	References
Ag-GO	47.7			Soil	Microbial biomass, soil bacterial community	100–1000	Promote microbial biomass at 500 mg/kg; increase the relative abundance of *AD3* and *Firmicutes* while inhibit the relative abundance of *Acidobacteria* and *Cyanobacteria* at 1000 mg/kg	Kim et al. (2018)
Au nanorods	10	35	24.8	OECD soil	Soil bacterial community	3.34	Inhibit structural diversity	Nogueira et al. (2012)
CeO_2	<25	<50	35.1 ± 0.7	Soil	Soil bacterial community	500–2000	No obvious impact on population size	You et al. (2018)
$Cu(OH)_2$ nanowire	50	3000–5000	24.1 ± 0.32	Soil	Microbial communities	80–280	Promote microbial diversity (Proteobacteria phylum was mainly affected)	Cota-Ruiz et al. (2020)
Fe_3O_4	50–100	50–100	9.12 ± 0.47	Soil	Soil bacterial community	500–2000	No obvious impact on population size	You et al. (2018)
Fe_3O_4	30		11.6 ± 0.64	Soil	Soil bacterial community	100	Promote relative abundance of *Nocardioides* and *Chitinophaga sancti*; inhibit relative abundance of *Bradyrhizobiaceae* and *Sediminibacterium*	Zhang et al. (2020b)
SiO_2	20			Soil	Soil bacterial community	100	No obvious impact on the richness and diversity	Zhang et al. (2020b)

(continued)

Table 3.3 (continued)

NPs type	Diameter (nm)	Thickness (length) (nm)	Zeta potential (mV)	Medium	Target microorganisms	Tested concentration (mg/kg)	Toxic effect	References
TiO_2	<100		46	OECD soil	Soil bacterial community	5000	Inhibit structural diversity	Nogueira et al. (2012)
TiO_2	21	21	11.6 ± 1.1	Soil	Soil bacterial community	500–2000	No obvious impact on population size	You et al. (2018)
TiO_2	5–10			Soil	Soil bacterial community	100	No obvious impact on the richness and diversity	Zhang et al. (2020b)
TiO_2 mixed with phosphorous fertilizer	26.5			Soil	Microbial biomass	500–750	Inhibit microbial biomass at 750 mg/kg	Waani et al. (2021)
ZnO	<50		−7.63 ± 0.37	Soil	Soil bacterial community	500–2000	Inhibit total bacteria population, the relative abundances of *Bacilli*, *Alphaproteobacteria* and *Gammaproteobacteria* class at 0.5–2 mg/g	You et al. (2018)
C60, rGO, MWCNTs				Soil	Soil bacterial community	50–500	Inhibit the relative abundance of Proteobacteria at 50 and 500 mg/kg	Hao et al. (2018)
GO[1]		~10^2		Soil	Microbial biomass	500–1000	No obvious impact	Chung et al. (2015)
GO	500–2000	0.8		Soil	Soil bacterial community	10–1000	Promote the biomass of the bacterial populations in short term at <100 mg/kg; *Nitrospira*, *Planctomyces* and *Lysobacter* were significantly suppressed at 1000 mg/kg	Ren et al. (2015)

NPs type	Diameter (nm)	Thickness (length) (nm)	Zeta potential (mV)	Medium	Target microorganisms	Tested concentration (mg/kg)	Toxic effect	References
GO	342–532	0.8–1.4		Benzo[a] pyrene contaminated soil	Soil bacterial community	10–100	Inhibit the richness and Shannon diversity	Du et al. (2020a)
aGO (ammonia functionalized)					Soil bacterial community	10^{-6}–1	Significantly affect the composition of bacterial communities (promote 6 while inhibit 3 of OTUs)	Forstner et al. (2019)
rGO					Soil bacterial community	10^{-6}–1	Significantly affect the composition of bacterial communities (promote 7 while inhibit 2 of OTUs)	Forstner et al. (2019)
Graphene		<5		Soil	Microbial biomass and soil bacterial community	1000	Inhibit soil DNA and T-RFLP of bacterial community [2]	Ge et al. (2016)
Graphene[1]	200–10^4	<1		Soil	Soil bacterial community	10–1000	Promote α-diversity at 10–100 mg/kg and contents of *Pseudomonas*; inhibit α-diversity at 1000 mg/kg	Song et al. (2018)
MWCNTs	30–50	~10^4 (length)		Soil	Microbial biomass and soil bacterial community	1000	Inhibit soil DNA and T-RFLP of bacterial community [2]	Ge et al. (2016)

(continued)

Table 3.3 (continued)

NPs type	Diameter (nm)	Thickness (length) (nm)	Zeta potential (mV)	Medium	Target microorganisms	Tested concentration (mg/kg)	Toxic effect	References
MWCNTs[1]	8.7–10	10^4			Soil bacterial community	10^{-6}–1	Significantly affect the composition of bacterial communities (promote 7 while inhibit 5 of OTUs)	Forstner et al. (2019)

Note:

1. The specific surface area of GO is 120.78 m^2/g; Graphene is 1000–1217 m^2/g; MWCNTs is 216 m^2/g

2. T-RFLP is terminal restriction fragment length polymorphism

Effect of Nanoparticles on the Function of Soil Microbial Communities

Compared with the structure of soil microbial communities, the function they are involved in is drawing more attention. Soil enzymes participate in a large quantity of biogeochemical reactions, including synthesis and decomposing of humus, transform of organic compounds, various redox reactions in the soil. Therefore, soil enzyme activities are usually considered as an indicator of specific functional microbiota. Chung et al. (2015) demonstrated that low concentrations of GO (0.5–1 mg/g) can reduce the activity of some enzymes in soil by up to 50%, including xylosidase, 1,4-β-N-acetyl glucosaminidase, and phosphatase. The enzyme activity decreased in a short period of time and also recovered after a period of time. Our previous studies suggested that graphene promoted the enzyme activities of dehydrogenase and fluorescein diacetate esterase after 4 days of exposure, and the promotion effect disappeared after 60 days. These researches reveal that soil harbors a certain self-recovery ability toward the stress of nanoparticles.

Functional microbes play a crucial part in various biological process, and their biomass directly affects functional strength, availability, and reliability of soil microbial communities. Recently the available researches increase gradually about the effect of nanoparticles on functional microbes individually or in soil, but it is difficult to compare the influencing extent of various nanoparticles on some specific functional microbes based on the current researches. Wu et al. (2020a) found that Ag_2S NPs can directly reduce the relative abundance of denitrifying bacteria in the soil. GO NPs can inhibit the biomass of nitrogen-fixing bacteria and iron-reducing bacteria in the soil microbial community. Likewise, Fe_3O_4 NPs can decrease the abundance of nitrogen-fixing bacteria *Bradyrhizobiaceae* and iron redox-related bacteria *Sediminibacterium*. On the contrary, the abundance of bacteria related to carbon cycle in soil increased, e.g., *Nocardioides* and *Chitinophaga sancti*. (Zhang et al. 2020b). Although ZnO NPs showed no significant change on the structure diversity of microbial communities, they can also significantly affect the activity of Proteobacteria at the concentration of 40–120 mg/L.

Besides, some bacteria involved in the nitrogen and sulfur cycles are suffered from adverse reactions, e.g., *Sulfitobacter* and *Thauera* (Wu et al. 2020b). Our previous studies demonstrated that graphene significantly suppressed specific bacterial populations involved in nitrogen biogeochemical cycles, such as *Nitrospira* and *Planctomyces*, while promoted some bacterial populations degrading organic pollutants. As stated above, the current researches mainly focus on the microbial populations involved in biogeochemical cycles of carbon, nitrogen, and iron, whereas there are still limited published reports on environmental functional microbes, such as organic pollutants degrading bacteria and heavy metals transforming bacteria, which are very important for soil decontamination and deserve further study.

Effect of Nanoparticles on Rhizosphere Microbial Communities

In addition to soil indigenous microorganisms, there are also a certain proportion of microbial communities attached to other organisms in the soil, such as plant rhizosphere microbiome, which are considered as the second genome of plants and play an important role in plant growth and development. Rhizosphere microorganisms exist in the form of parasites or symbioses with plants. Upon exposure to nanoparticles, rhizosphere microorganisms might reveal different responses from soil indigenous microorganisms, due to double effects of plant and soil under nanoparticle stress.

Nanoparticles have been reported to affect the rhizosphere microbiome of plants. Rhizosphere microorganisms might absorb part of nanoparticles or immobilize nanoparticles to reduce their bioavailability, protecting the plants from being damaged by the excessively high concentration of nanoparticles. Wang et al. (2021b) demonstrated that corn protected by arbuscular mycorrhizal fungi (AMF) was not affected in growth and nutrient absorption under exposure to 1 mg/kg Ag NPs, and it is also not producing oxidative stress reaction. However, the fungi are subjected to obvious toxic effects. This may indicate that rhizosphere microorganisms are more sensitive to metal nanoparticles or have a stronger ability to absorb metal nanoparticles than plants. AMF can establish a symbiotic relationship with roots of higher plants through colonization. The rGO has been also observed to exhibit little effect on plants but shows harm to fungi (e.g., *Aspergillus niger* and *Aspergillus oryzae*). Moreover, this harm is physical because sharp edges of rGO inhibit fungal hyphae growth. However, the effect of nanoparticles on rhizosphere microorganisms is related to nanoparticle types.

Nanoparticle concentration is also an important influencing factor for assessing the toxicity effect of nanoparticles on rhizosphere microorganisms. Ingle et al. (2017) observed that low concentrations of Ag NPs and Ti NPs promoted the colonization of AMF, while ZnO NPs at 500 mg/kg inhibited this process. However, this process was improved when ZnO NPs and $ZnSO_4$ were mixed to be applied at each concentration of 500 mg/kg. Successful colonization not only means the survival of AMF, but also helps to reduce the negative effects of some nanoparticles (e.g., high concentration of Fe_3O_4 NPs) on soil microorganisms and plants, thus protecting plant roots and soil biodiversity. This means that high concentrations of nanoparticles can poison plant roots and soil microorganisms, while they can promote the colonization of AMF to form a protective effect on root cells and soil microorganisms.

Besides, there are some special plant-microbial systems that are also affected by nanoparticles. The nitrogen-fixing plant-rhizobium system is a typical representative. Mortimer et al. (2020) found that CeO_2 NPs and MWCNTs at concentrations of 0.1 and 10 mg/L respectively in soil could reduce the secretion of root exudates (RE) from soybean roots, which means that the nodulation signal transduction between plants and bacteria is disturbed. Soybean rhizobium is unable to nodule because it cannot receive the signal, which directly affects the nitrogen fixation of soybean. Ag, ZnO, and TiO_2 NPs can also inhibit the nodulation rate and microbial community diversity of *Medicago truncatula* and *Sinorhizobium meliloti* symbiosis system, and plant growth in the system can also be affected (Judy et al. 2015). The plant-rhizosphere microorganism system is an important object to research the special effect mechanism of nanoparticles. Therefore, it is quite necessary to increase the relative researches.

4 Conclusion and Future Perspective

Nanoparticles usually have a limited effect on soil pH unless they are added with a large amount, but they could exert a specific influence on elemental geochemical cycle in soil, affecting the contents of organic matter, nutrient elements, and even microelements. Nanoparticles could penetrate cell walls to enter into the interior plant. Most of the nanoparticles are mainly concentrated in plant roots, especially carbon nanoparticles. It was difficult for carbon nanoparticles to translocate from roots to other organs. Similar to traditional pollutants, nanoparticles exert a hormesis effect on plant growth and development. At low concentrations, nanoparticles can promote plant growth and development through a variety of mechanisms, including enhancing water transfer characteristics in plants, stimulating the uptake of micro- or macro-nutrients in plant tissues, improving the physiological activities of plants themselves, and strengthening their resistance to biotic or abiotic stresses.

However, at higher concentrations, nanoparticles could induce ROS generation in plants, hinder the absorption of macro- or microelements, disturb normal physiological activities, and affect the structure and function of the symbiotic microbiome of plants. These would lead to inhibition in plant growth and development. Compared with phytotoxicity, the researches concerning the impact of nanoparticles on soil fauna and microbial communities are still relatively limited and lack consistent laws. The effects of nanoparticles on soil biota, including soil fauna, plants, and soil microbial communities, are largely dependent on NPs type, their structure and physicochemical properties, NPs concentration, types of soil biota, application method, and exposure duration, environmental conditions, etc. So far, it has not drawn a definite conclusion about the structure-effect or dose-response relationships. Considerable attention is suggested to be focused on the themes as follows in the future.

1. The qualitative characterization and quantitative determination methods of nanoparticles in complex environmental media in the soil ecosystem, including soil media and soil biota. With the combination and development of a series of emerging technologies, such as the isotope labeling method, single-particle inductively coupled plasma-mass spectrometry (SP-ICP-MS), near-infrared fluorescence (NIRF) spectroscopy, surface-enhanced Raman spectroscopic (SERS) mapping technique, and so on, it enables the analyzation of nanoparticles in soil or soil biota, which contributes to elucidate the interaction mechanisms between nanoparticles and soil biota.

2. The standardized assessment methods for ecotoxicological effects of nanoparticles in the soil ecosystem. At present, a variety of materials, experimental methods, and environmental factors are applied and studied in most researches, which are difficult to be compared and summarized to a definite conclusion. The standardized assessment methods will facilitate to explore the structure-effect or dose-response relationships between nanoparticles and soil biota. Besides, the assessment should cover different levels of the soil ecosystem, including molecular, cellular, individual, community, and ecosystem level. Long-term ecotoxicology effects at low dose are needed to be paid more attention in order to be better in conformity with actual environment.
3. The ecotoxicological effects and interaction mechanisms of combined pollution of nanoparticles and traditional pollutants, including heavy metals, organic pollutants, and even biological pollutants. It is universal for the coexistence of nanoparticles and traditional pollutants in the actual soil environment. Nanoparticles usually possess excellent adsorption ability for tradition pollutants due to their specific structure and enormous specific surface area, which probably alter the environmental behavior and ecotoxicity effects of traditional pollutants. Therefore, comprehensive assessment of the ecotoxicological effects of combined pollution will be of practical significance for scientifically evaluating the ecological risk of nanoparticles in the soil environment.

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Chapter 4
Influence of Nanoparticles on the Plant Rhizosphere Microbiome

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1 Introduction

Nanotechnology is a multidimensional face of science that has achieved value in agriculture and many more welfare activities including hydraulics industries and others such as cosmetics, electronics, textiles, and food (Wu et al. 2020; Faizan et al. 2020a, b; Alam et al. 2015). Nanotechnology in agriculture has gained recognition in recent years as a result of technological advancements that have enabled the development of a variety of devices, including nanoparticles (NPs) and nanotubes that are ultimately reported to influence the microbiome of the plant rhizosphere. NPs with unique properties are documented to influence the plant's development, cell structure, physiological, and biochemical processes (Faizan et al. 2021a, b). Besides, numerous chemicals, including metallic NPs, aluminum (Al), titanium (Ti), zinc (Zn), copper (Cu), gold (Au), silver (Ag), iron (Fe), and cobalt (Co), are utilized to adorn NPs which can act as an indirect mean of contaminants' release to the environment (Khot et al. 2012). NPs have specific properties in respect to their minute size (less than 100 nm) with at least in one dimension, which consequences in elevated surface area charges, therefore, they are extra reactive over their

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large amount counterparts (Dimkpa et al. 2019; Faraz et al. 2019). Benefits in farming comprise abridged fertilizer loss; improvement of agricultural efficiency (Rai and Ingle 2012); augmented plants quality and yield (Velasco et al. 2020); and the possibility for pest management (Landa 2021), becoming a substitute to chemical insecticides since they are measured comparatively secure for humans' contrast to synthetic insecticides (Salem et al. 2015). Nanofertilizers are used to slowly release nutrients while diminishing pollution (Seghatoleslami and Forutani 2015). These nanoscale fertilizers are a move toward that creates nutrients accessible to plant leaves, thus raising the competence of plant nutrient uptake (Vishekaii et al. 2019). Zinc oxide NPs have been accounted to lessen the oxidative damage in various crops (Dimkpa et al. 2020; Faizan et al. 2018, 2021c). Zinc oxide NPs abridged malondialdehyde (MDA) content and improved catalase (CAT) and superoxide dismutase (SOD) activities in stressed *Leucaena leucocephala* (Zahedi et al. 2020). Similar results were also reported in *Oryza sativa* (Faizan et al. 2021d) and *Beta vulgaris* (Sun et al. 2020). Due to their small dimension, nanofertilizers have an advanced and quicker translocation between plant parts, which augments nutrient efficiency (Smith 2014). In crop growing, plant yield and effectiveness are enhanced by the employment of pesticides. NPs envelop broad diversity of products, some of which previously are accessible in the market (Nuruzzaman et al. 2016). Scientists demonstrated various methodologies for NPs formulation, characterization, their consequence, and their appliance in plant disease management (Al-Samarrai 2012).

Soil microbial communities have a straight effect on soil eminence through procedures like symbiotic relationships with terrestrial plants, nutrient cycling, and decomposition of organic matter (Kennedy and Smith 1995). Therefore, the defense of soil microbial growth and variety is the most important challenge in agriculture. Numerous carbon nanotubes (CNTs) have recently gained considerable interest due to their potential applications in the management of plant growth. Plus, CNTs play a positive role in the enhancement of plant physiological attributes and biochemical indices as well. According to Tripathi and Sarkar (2014), carbon nanodots over control significantly increased the root growth in wheat. Likewise, the gram plant also showed a positive impact after exposure to carbon nano-onions (Sonkar et al. 2012). It is known that the category, dimension, concentration, and functionalization of CNTs be able to conclude their toxicological and physiological property in dissimilar crops (Tiwari et al. 2014). CNTs have potential agricultural appliances because of their impacts on modifiable plant growth, the aptitude to navigate plant cell walls, and as an average for pesticide submission (Jordan et al. 2020). These can be effective in manipulating the metabolism of cells by stimulating enzymatic and metabolic activity and gene expression, in addition to boosting the photosynthetic performance of leaves via an increase in photosynthetic pigment levels (Rahmani et al. 2020).

2 Source and Impacts of NPs on Soil Properties

The bound of loam to effort as an alive framework, with the surroundings and ground usage restrictions, has been characterized as soil well-being to maintain crop and respiration system effectiveness, improve water and air quality, and crops. Soils are permeable organizations consisting of multifarious prearranged congregations of mineral and natural elements joint in liquid and gaseous points. The behavior and bioavailability of general pollutants such as pesticides, trace metals, and polycyclic aromatic hydrocarbons are highly influenced by soil behavior and characteristics (Labud et al. 2007; Ranjard et al. 2000). The study of the communications among NPs and soil is complex by the elevated unpredictability in properties, sourced by dissimilarity in the ecological situation and soil masterpiece, and by the huge numeral of forms of available NPs. Each year, 11 million tons of metal oxide and metal NPs are expected to be produced in the world, with soil resources determining the final amount (Sun et al. 2014).

These days, nanotechnology is fast attention from industry gratitude to the appearance of novel functions in dissimilar fields like medical, electronics, and agriculture. This rising attention is foremost to higher manufacture of NPs in the business and spaces us in exceptional novel development where the effect might have on the surroundings and livelihood beings wants to be immediately evaluated. Nanoscience is demonstrated as the branch of science that studies nanometric scale matter, bearing in mind its size and uniqueness. However, nanotechnology examines ways of makeover and controlling these properties (Jeevanandam et al. 2018). The term NPs defines the particles whose dimensions are in the nanometer scale for some authors and for others it contains the shortest definition of NPs, which is probably the most instinctive one, taking into contemplation only their size, which is limited conservatively to about 100 nm in any direction (Strambeanu et al. 2015). This minute size produces a broad range of functions in various scientific fields (Tweney 2006).

Nanoparticles affect the majority of soil belongings but there have been no evaluations of their effect on the density performance of soil and the force of collectives. Therefore, we evaluated the impact of NPs on the large density and the restricted density and tensile strength of summative of calcareous loamy soil. The performance of NPs in the environment has involved significant attention in present years due to the dramatic boost in NPs production and consumer use, which has resulted in rising revelation and discharge to the environment. Some researchers have explained the contradictory phenomenon, specifically, the impact of NPs on the environment in common, and on soil properties in particular. Elliott and Zhang (2001) subjected bimetallic NPs to a test area to reveal the decrease of trichloroethene and other chlorinated aliphatic hydrocarbons. The porosity of the soil was not pretentious by the NPs, and the blockage was shown to be insignificant. Fullerene NPs were found to have a modest effect on soil-microbial societies and microbial processes (Nyberg et al. 2008). Multi-walled carbon nanotubes were shown to decrease enzymes activity in the soil and microbial growth (Chung et al. 2011).

Metal oxide NPs were also examined; Ge et al. (2011) studied the effect of TiO_2 and ZnO on soil microbial societies and established that both NPs abridged microbial growth and diversity. Pradhan et al. (2011) examined the impact of copper oxide and silver NPs on leaf microbial putrefaction presentation that experience to these NPs led to a reduction in leaf rotting rate. Furthermore, the decrease in rotting was attended by transformation in the organization of the microbial societies.

3 Effects of NPs on Rhizospheric Microbiome Functionality

The group of microorganisms and their respective genomes living within the sphere of the plants' root are jointly referred to as rhizospheric microbiome (Rajput et al. 2021). They consist of bacteria and fungi, forming the dominant population, and other groups of organisms such as viruses, archaea, and protists, which are also found in other environments beside soils such as aquatic habitat, plants, animals, and humans (Merten et al. 2020). However, the soil microbial community denotes the highest reservoir of biological diversity in the world, as the rhizospheric unit is reported to contain about 10^{11} microbial cell g^{-1} of the roots, accounting for roughly more than 30,000 prokaryotes species (Berendsen et al. 2012). These microbes are known to have either beneficial, commensal, or pathogenic relationships among themselves as well as with their host plants. They are key players in biogeochemical cycles of nutrients such as nitrogen, phosphorus, potassium, carbon, sulfur, etc., and biochemical reactions such as nutrients uptake, antibiotics production, biomass decomposition, biodegradation, maintenance of soil structure, and stimulating stress tolerance in the plants (Rahman et al. 2021; Khan et al. 2021). Thus, plays an important role in the overall determination of fertility and health of soil. Nevertheless, many external factors ranging from farming practices, physical and chemical properties of soils, biotic and abiotic stress, including the use of NPs adversely affect the microbial diversity in the rhizosphere (Brolsma et al. 2017). Subsequently, favor the selective enrichment of certain microbial communities over the others and their associated functions in the rhizosphere.

The prevalence of NPs in the rhizospheric region has been attributed from many sources; including natural mineralization by plants in response to different environmental stress, use of industrial coated NPs-based products such as fertilizers and pesticides in the soils, human activities, sewage or industrial waste products deposited in the soils (Ovais et al. 2018). The use of industrial coated NP products is commonly used in sustainable agricultural practices as a viable technology with a positive impact on soil microbial community, plant growth, yield, and yield quality (Prasad et al. 2017). The efficiency of their application large rests on their sizes, shapes, surface area, composition, and more importantly, the level at which they optimally exert their effects (Khodakovskaya et al. 2012; Zhai et al. 2016; Rastogi et al. 2017). Therefore, depending on their concentrations in the rhizospheric region, the unprecedented utilization and release of NPs may lead to a huge repercussion to the soil microbiomes (Khanna et al. 2021). Nanoparticles can potentially affect microbial functionality and plants in both positive and negative ways (Fig. 4.1). Few studies investigated the positive effects of NP products on microbiome functionality (Shah and Belozerova 2009; Shah et al. 2014). For example, Asadishad et al. (2017) studies revealed that exposing the soil to a fixed size citrate-coated nAu (50 nm) generally increased soil enzymatic activities within 30 days of exposure; the abundance of bacterial groups (Actinobacteria and Proteobacteria) was also considerably increased. Suggesting that exposing the nAu to soils may enhance the enzymatic activities along with microbial communities, thereby affecting the nutrient cycling in the soil.

Contrarily, although the current environmental concentrations of NPs are still under the threshold level of toxicity in most soils, some even argue the idea that NPs (like nZnO and nAg) are not toxic (Mu et al. 2011; Zhou et al. 2015). These, in addition to the limited available literature on the environmental impacts and antimicrobial properties, demanded a thorough investigation in better understanding the physicochemical as well as biotic impacts of NPs in the soils (Kiss et al. 2021). Several reports have revealed negative impacts of NPs on exposure to microbial functionality. For instance, the study conducted by Shen et al. (2015) on neutral soils treated with 1 mg ZnO-NPs and the ecotoxicology impacts on soil microorganism observed a decrease in respiration, ammonification, dehydrogenase (DH), and fluorescence diacetate hydrolase (FDAH) activity within the first to the third month of the study, the proposed mechanisms being the direct contact of Zn-NPs with biologic targets. Similarly, results from Ma et al. (2013) also described the toxic

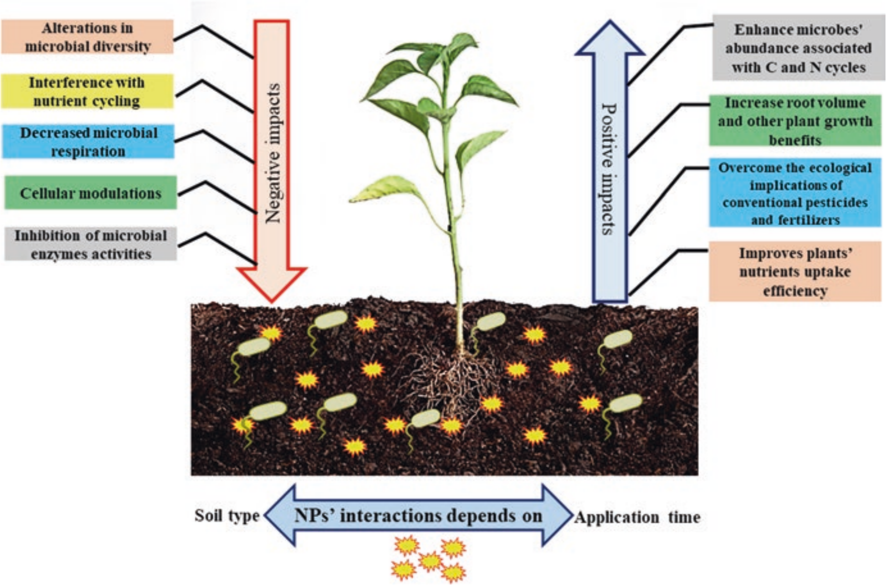

Fig. 4.1 Schematic representation of NPs' interaction with soil microbiome and associated impacts on its functions and plants

nature of ZnO-NPs to the different bacterial systems, leading to the dissociation of ZnO-NPs to zinc ions (Zn+), and generative of reactive oxygen species (ROS), as a result of direct interplay with the biologic target. These were both influenced by environmental conditions (Li et al. 2011). The utilization of nanoscale zero-valent iron (nZVI) has also been reported to have antimicrobial properties (Cullen et al. 2011; Saccà et al. 2014; Fajardo et al. 2019). For instance, Semerád and Cajthaml (2016) reported from their studies a pronounced change in autochthonous bacteria species often exposed to nZVI, which was observed to vary among soil types (2.4 and 2.2) with the phylogenetic changes appear to be more abundant than at the functional level. Hence, suggesting maintenance of the overall functions of soil ecosystem on exposure to nZVI. Generally, living tissues of microorganisms such as cell mitochondria and the cell nucleus often exposed to these nanoparticles can be taken up spontaneously, and subsequently results in the alteration of the cell membrane, mutation of DNA, structural damage to mitochondria, and ultimately, death of the cells (Geiser et al. 2005; Porter et al. 2007; Li et al. 2011).

4 Interactions of Nanoenabled Agrochemicals with Soil Microbiome

Agrochemicals play a crucial part in the economic productivity of agricultural products. When used conventionally, however, they are reported to be degraded or expelled by environmental variables such as wind, sunlight, rain, etc. (Gill and Garg 2014). Also, a considerable fraction of agrochemicals do not reach their intended species, thereby they are applied on a regular basis. Thus, recurrent agrochemical applications not only raise the expense, but also have adverse effects on plants, the environment, and the health of those exposed through the food chain (Vurro et al. 2019). In this context, several techniques have been emerged to resolve this issue and nanotechnology is also one of them. Because of the unique properties of nanomaterials, combining nanotechnology with agro-biotechnology is becoming more frequent in the agricultural sector (Srivastava and Singh 2021). At low concentrations, NMs are reported as potential agents to improve edible plants' yield and quality. Nanomaterials can encapsulate nutrients, coat them with a thin protective nanoscale polymeric coating, or distribute them as nano-emulsions or nanoparticles (Iavicoli et al. 2017). Thus, nano-enabled agrochemicals can either deliver one or more nutrients to plants, hence promoting growth, or they can improve the effectiveness of conventional fertilizers. Also, due to the greater surface area, nano-coatings on fertilizers can hold the substance more firmly on the plant. Thus, nano-enabled agrochemicals are reported to boost the plant-uptake efficiency of nutrients and reduce the adverse impacts of conventional fertilizer applications (Ur Rahim et al. 2021). In recent years, the nanopesticides and nanofertilizers got a great deal of attention due to their numerous advantages over the conventional ones. The basic principle and working of these agrochemicals are discussed in the forthcoming paragraphs.

4.1 Nanopesticides

The nanoformulation of conventional pesticides with polymers or metal nanoparticles is an emerging area in the pesticide industry in and of itself. Any pesticide formulation that implies either very small particles of a pesticide active component or other small, designed structures with effective pesticidal characteristics is referred to as a "nanopesticide" (Kookana et al. 2014; Iavicoli et al. 2017). The controlled and progressive release of active ingredient by modification in the outer shell of the nanocapsule delivers a mild dose over a longer time period and prevents excess run-off of undesirable pesticide, which make it a viable approach for agricultural personnel (Gill and Garg 2014; Sharma et al. 2019). Thus, nano-formulations for pesticides provide benefits due to their improved solubility, mobility, and durability.

4.2 Nanofertilizers

Nanofertilizers are NMs that deliver one or more essential nutrients to plants directly. Also, it has been observed that nanofertilizers improve the performance, availability, or usage of traditional fertilizers (Zulfiqar et al. 2019). Over the last few decades, the global pressure for chemical fertilizers to restore nutrient levels in soils that are regularly used for crop production has expanded considerably (Selim 2020). Contrarily, the most critical elements required by plants, such as nitrogen (N), phosphorus (P), and potassium (K), continue to have low nutrient usage efficiency. Thus, deficits in nutrient delivery to and utilization by plants cause farmers and producers to apply excessive amounts, leading to environmental contamination from emissions, leaching, and run-off (Dimkpa et al. 2019). Owing to this reason, numerous researchers have found that nanofertilizers possess the potential to improve nutrient delivery efficiency to plants. Nanofertilizer is classified into three types based on plants' nutritional requirements: (A) macro- and (B) micronanofertilizer, and (C) nanoparticulate fertilizer (Kumari et al. 2019).

Despite the uncountable advantages of nano-enabled agrochemicals, there are still some gaps and controversies regarding their efficacy and fate in microbiome. The soil is a reservoir of microorganisms, in which the plant selects a certain microbiome, which makes a significant contribution to the plant's growth and health (Trivedi et al. 2020). As a result of the selected microbiome, the plant adapts more quickly to stressors whether abiotic or biotic. Therefore, understanding how nanopesticides and nanofertilizers interact with the microbiome is critical for developing smart nanoagrochemicals that combine efficiency with ecocompatibility to protect soil microbial diversity. There are currently two types of nanomaterials that have resulted in commercially accessible nanoenabled agrochemicals: copper nanoparticles as fungicides and colloidal silver to treat fungal pathogens on seeds, tubers, and vegetative plants (He et al. 2019). The impact of nano-CuO was observed on the soil enzymes activities and composition of microbial community. The applications of TiO_2 and CuO NPs were reported to decrease the soil microbial biomass and enzymatic activities (Xu et al. 2015). In a study, the influence of nanosized CuO on five agricultural was recorded. The exposure of CuO-NPs caused significant reductions in the microbial activities of soil which involved the carbon and nitrogen cycles, respiration, nitrification, and denitrification (Zhao et al. 2020). Likewise, in the study of You et al. (2018), ZnO, TiO_2, CeO_2, and Fe_3O_4 NPs on soil enzymatic activities and bacterial communities of saline-alkali and black soils. The findings revealed an impact on soil enzyme activity, changes in the soil bacterial community, and a risk to biological nitrogen fixation. The content of microorganisms in soil was dramatically reduced when Fe_3O_4 NPs were present in high concentration (Cao et al. 2016). Plate counts of *Azotobacter*, P-solubilizing, and K-solubilizing bacteria were altered by zinc oxide and CeO_2 NPs, and enzymatic activity was inhibited (Chai et al. 2015).

5 Impacts of NPs on Plant-Microbiome Interaction

The plant-microbiome is a complex network of genetic, biochemical, physical, and metabolic interactions. In a natural environment, plants are constantly exposed to diverse microbiota and interact with each other with substantial useful effects to the host plants in nutrients uptake, growth promotion, increased productivity, enhanced biological and chemical reactions, resistance to pathogens, and stress tolerance (Philippot et al. 2013; Busby et al. 2016; Singh et al. 2019; Trivedi et al. 2020). The abundance of microbes in the rhizosphere region is primarily owing to the richness in microbial substrates derived from plant photosynthates and other secondary metabolites like flavonoids, which play a crucial role in maintaining communications among soil microbiomes. Plants may interfere in the manipulation of gene expression of the soil community by secreting quorum sensing compounds (Merten et al. 2020). In analog, it is also claimed that plant microbiome extends the potential function of the host, as the microbiome possesses the ability to impact the expression of plant traits and subsequently improve the physiological state of the plants (Mendes et al. 2013). Therefore, it can be inferred that the plant-microbiome relationship cannot be underestimated, the fact that it represents an interweaving mutualistic association among the components (Rahman et al. 2021). The collective genome of the rhizosphere microbiome is referred to as the plant's second genome. The beneficial impacts of bacterial strains and other consortia of microorganisms on their host are considered cultivar and species (associated to diets, environment, etc.) specific, which in turn limits their applications (Cullen et al. 2020; Rai-Kalal and Jajoo 2021). Hence, understanding the functional aspects of the interplay between microbiomes and their host is crucial for their potent use in agriculture (Ortiz et al.

2015; Singh et al. 2016). The balance of microorganisms in the soil is thus an important aspect of plant physiological development. However, these balances can be impaired by several human activities such as the development of antibiotics, heavy metals exploitation, release of plant protection products (PPP), and high levels of nanoparticles in the soils (Rodriguez et al. 2019).

A large number of NPs-based products are being commercially produced and disposed to the soils as a sink in large quantities. These particles often exposed to the soils can directly result in NPs-microbial or indirectly NPs-plants interactions and revealed the consequences on either the plants or microbial community (Guan et al. 2020). The behavior of these particles and their persistence rests on their chemical nature and soil characteristics. More importantly, NPs-based products like nAg and nZnO possess antimicrobial properties, their presence and persistence in soils can result in the alteration of soil microbiome, thereby distorting key microbial processes like N-fixation, nutrients mineralization, phytoremediation, and plant growth-promoting activities (Thijs et al. 2016; Khan 2020). Several studies on the effects of plant-microbiome interactions and the effects have been reported in the literature as presented in Table 4.1.

6 Future Prospective

It is evident from the current state of knowledge that the use of nanotechnology-derived processes and materials can bring substantial enhancements and improvement in the agriculture and allied sectors. Unfortunately, much R&D has been done in a haphazard and random manner, with little regard for the potential for negative repercussions and impacts. Another issue to be concerned about is the increased nutrition provided by nano-fertilizers, which may encourage intrinsic plant defense and systemic resistance pathways. Thus, if nanotechnology-based approaches are effectively developed and implemented, they will play an important role in achieving and maintaining global food security and safety.

7 Conclusions

Nanotechnology offers enormous potential to improve pesticide delivery and usage by crops. According to key findings on plant exposure to nanoparticles, ENMs can be deleterious at higher doses, while the lower dose applications of NMs under specified conditions will have favorable effects such as improved nutrient delivery, antibacterial and disease suppression, and insecticidal and herbicidal applications. Also, when compared to conventional formulations, one very major advancement connected with NMs is that they can dramatically minimize the number of metals/agrichemicals released into the environment. So, in a nutshell, future research

Table 4.1 Impacts of nanoparticles on plants-microbiome interactions

Nanoparticles (NPs) and concentrations applied	Plants and microbes	Soil microbes	Impacts on plant-microbiome interactions	References
SiO_2 @ 5 mg per plant	Pakchoi (*Brassica chinensis* L.)	Bacteria (*Rhodobacteria* and *Paenibacillus*) and fungus (*Chaetomium*)	Increased number of some bacterial and fungal genera that involved in carbon and nitrogen cycles. Thus, suggesting an alteration in the soil metabolites profiles.	Tian et al. (2020)
CuO @ 50 mg kg^{-1}	Wheat (*Triticum aestivum* L.)	Bacteria (*Caulobacteracaea, Chitinophaga, Paenibaccilus, Peredibacter,* and *Pseudomonas*)	Increased nitrate concentration in the rhizosphere correlated with the gene abundance related to N-fixation and a decrease of gene denitrification abundance. However, the effects on microbial diversity were not clearly explained in the studies.	Guan et al. (2020)

(continued)

Table 4.1 (continued)

Nanoparticles (NPs) and concentrations applied	Plants and microbes	Soil microbes	Impacts on plant-microbiome interactions	References
Ag and TiO_2 @ 100 mg L^{-1}	Early growth of wheat (*Triticum aestivum* L.,) and flax (*Linumusitatissimum*)	Bacteria (*Bacillus* and *Pseudomonas*)	TiO_2 enhanced germination and seedling growth of what, whereas both the NPs increased chlorophyll contents of flax. The bacterial community was not significantly altered; however, the total contents were observed to increase except in positively charged TiO. Hence, suggesting variability of the plants and bacterial communities in response to NPs at varying degree	Gorczyca et al. (2018)
TiO_2 (Conc. Not not specified)	Wheat (*Triticum aestivum* L.)	Fungus (*Arbuscular mycorrhiza*) and prokaryotic	NPs altered the structure of prokaryotic community but the fungal structure remains unaltered. Both the wheat growth and arbuscular mycorrhizal colonization were not negatively affected by different TiO2 concentrations	Moll et al. (2017)

(continued)

Table 4.1 (continued)

Nanoparticles (NPs) and concentrations applied	Plants and microbes	Soil microbes	Impacts on plant-microbiome interactions	References
Fe_3O_4 @ 2000 mg L^{-1}	Common bean (*Phaseolus vulgaris*)	Fungus *(Rhizobium inoculum; Leguminorum CF1 strain*)	Improved symbiotic performance such as nitrogenase activity, nodule leghemoglobin, iron contents, active nodules per plant, nodules dry weight, along with increased root and shoot nitrogen content of the 35-day-old harvested plant. Hence, suggesting a strong relationship between rhizobium and common bean plant due to improved nodulation and N-fixation following application of Fe3O4 NPs	De Souza-Torres et al. (2021)

(continued)

Table 4.1 (continued)

Nanoparticles (NPs) and concentrations applied	Plants and microbes	Soil microbes	Impacts on plant-microbiome interactions	References
ZnO @ 250–1000 mg Zn kg^{-1}	Bean (*Phaseolus vulgaris*)	Bacteria (*Pseudomonad*)	Only NPs at 1000 mg concentrations significantly inhibit shoot growth. Also correlated with root growth inhibition, solubility of Fe, Mn and shoot accumulation of Zn, Fe, and Mn after 7 days. Root ferric reductase activity also often diminished after exposure to NPs. Concluding that soil bacteria could reduce plant accumulation of metals under toxic levels of NPs, thereby negatively affecting uptake of essential elements	Dimkpa et al. (2015)
Hydroxyapatite (nHA) (Conc. not specified)	Soybean (*Glycine max*)	Different general of bacterial and fungal sp. was studied	Treatments with nHA revealed nearly similar results in growth, biomass, total plant phosphorus, and yield. The soil and rhizosphere community also revealed similar results in the nHA and HA, with the minor shifts in the former. Hence, extrapolating that application of nHA may not be considered a viable alternative to traditional Pi fertilizers	McKnight et al. (2020)

(continued)

Table 4.1 (continued)

Nanoparticles (NPs) and concentrations applied	Plants and microbes	Soil microbes	Impacts on plant-microbiome interactions	References
Cu, Ni, and Zn @ 100, 1000, and 10,000 mg kg^{-1}	Radish (*Raphanus sativus*)	Bacteria (*Azotobacter* sp.)	Contamination of the soil with NPs observed to cause deterioration of the biological properties like abundance of bacteria (*Azotobacter* sp.), activity of catalase dehydrogenases, seed germination rate, and the length of radish roots. The Cu ranked first and Zn second, then Zn in order of highest ecotoxicity of the studied pollutants exposed under the same concentration. Their degree of negative impacts on biological activities.	Kolesnikov et al. (2021)

should focus on the possibility of generating different types of nutrient-augmented nanomaterials with a safer and more effective profile.

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Chapter 5
Nanoparticles: Uptake, Translocation, Physiological, Biochemical Effects in Plants and their Molecular Aspects

Tarun Sharma and Neetu Sharma

1 Introduction

In light of the immense applications of nanotechnology and engineered nanoparticles, there is an increased concern pertaining to the short- and long-term effects of such particles in the environment and their persistence and possible harmful effects (Dunphy Guzmán et al. 2006; Azarin et al. 2022; Rajput et al. 2017). Since it is a relatively advanced branch of technology, preventive measures and remediation strategies are not as extensively developed yet. A key process in the development of said measures is studying the effect these NPs have on their immediate environment. The first trophic level visibly affected in nature is the producer level, and this contains microbes and plants. In this chapter, uptake and translocation of various kinds of NPs in plants will be discussed, including the mechanisms by which they enter the internal environment of the plant, how they are transported, and once localized, their effects on the processes at a biochemical and molecular level (Fig. 5.1).

1.1 Nature and Mechanism of Uptake and Translocation

Before addressing the uptake mechanism, NPs entry route must be explored. In the soil or water, or even air, NPs may come from the following sources:

- Natural sources such as dust storms, volcanoes, forest fires, and so on.

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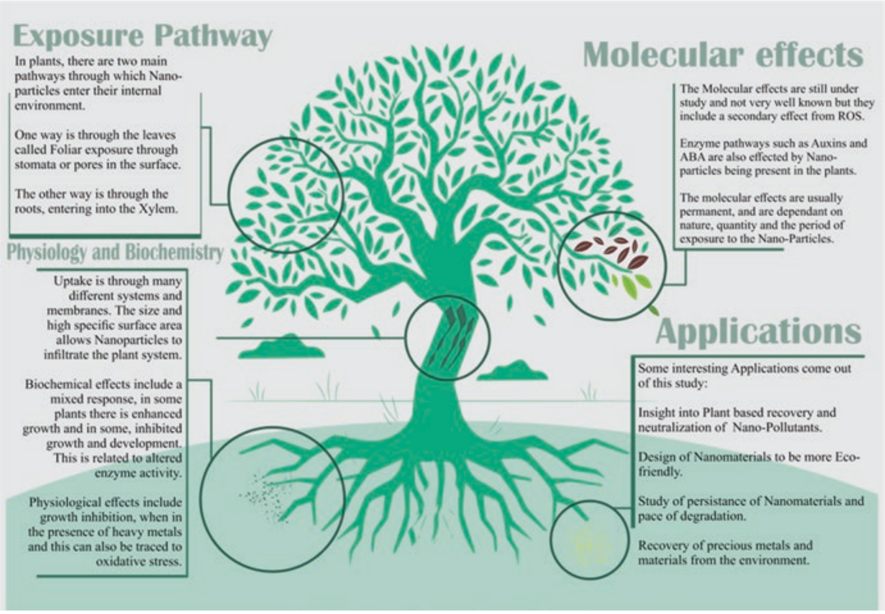

Exposure Pathway

In plants, there are two main pathways through which Nano-particles enter their internal environment.

One way is through the leaves called Foliar exposure through stomata or pores in the surface.

The other way is through the roots, entering into the Xylem.

Physiology and Biochemistry

Uptake is through many different systems and membranes. The size and high specific surface area allows Nanoparticles to infiltrate the plant system.

Biochemical effects include a mixed response, in some plants there is enhanced growth and in some, inhibited growth and development. This is related to altered enzyme activity.

Physiological effects include growth inhibition, when in the presence of heavy metals and this can also be traced to oxidative stress.

Molecular effects

The Molecular effects are still under study and not very well known but they include a secondary effect from ROS.

Enzyme pathways such as Auxins and ABA are also effected by Nano-particles being present in the plants.

The molecular effects are usually permanent, and are dependant on nature, quantity and the period of exposure to the Nano-Particles.

Applications

Some interesting Applications come out of this study:

Insight into Plant based recovery and neutralization of Nano-Pollutants.

Design of Nanomaterials to be more Eco-friendly.

Study of persistance of Nanomaterials and pace of degradation.

Recovery of precious metals and materials from the environment.

Fig. 5.1 Uptake, implications, and applications of nanoparticles in plants. (Dietz and Herth 2011; Ma et al. 2010; Arruda et al. 2015)

- Indirectly from anthropogenic (manmade) sources such as mining, waste disposal, and demolition.
- Sources such as discarded medication, cosmetics, and other consumer products.
- Directly from anthropogenic sources such as engineered nanomaterials and their disposal.
- From aerosol-based products and technology.

Nanoparticles from all of the above-listed sources have been found in plants in various concentrations and places depending on the type of plant studied and its environment (Ranjan et al. 2021a, b). When the particles contact the plant, it is most commonly through the root tissue. A sequential cascade of events takes place through which the particles move from the root tissue into the water transport system to be finally localized, most commonly in the plant leaves (Rajput et al. 2020).

The cell wall, being a polysaccharide network, is mostly porous and non-selective with respect to what it allows through into the cell. Therefore, the passage of NPs through the cell wall is a smooth process and does not need any energy or an underlying mechanism. The particles move first through the plant cell membrane, which is done through the pores in the membrane itself. This suggests that the first parameter which affects uptake and translocation will be particle and pore size wherever it shows variation (Ma et al. 2010; Rico et al. 2011). Before the NPs reach the core of the vascular system, i.e., the stele, they must move passively through the internal membrane (endodermis apoplast), as seen by Judy (2013). After this, the xylem, the central constituent of the water transport system, serves as the major channel through which the NPs reach the various parts of the plant (Aslani et al. 2014).

It must be noted that the NPs do not harmlessly or neutrally pass through the system. They interact with various physical and enzymatic processes, making it such that the complete process of uptake and translocation includes a number of processes. These include signaling, active and passive transport, and passage through numerous membranes (Etxeberria et al. 2009).

Alternatively, NPs may also enter the system through the exposure of the leaf, called foliar exposure. It has been observed happening directly through the stomatal openings in the leaf and the cuticle. However, the latter path shows a lot of variation with respect to the type of plant and age of the leaf. For the stomatal pathway, a study by Kim et al. (2018) demonstrated that nZVIs (nano zerovalent iron) promote the opening of stomata by activating the plasma membrane. It would make the entry of the particle exponentially more likely.

After this, the particles are transported downward through the phloem tissue. An important thing to remember here is that the circulatory system of plants is not circular, and therefore what goes down to the phloem does not come back up through the xylem. A study conducted by Wang et al. (2013) concluded that certain heavy metals could get to the root tissue after foliar exposure in watermelon plants. The passage taken by the particles was through the sieve tubes. Due to the elusive and still being discovered properties of NPs, combined with the elaborate mechanism in plant metabolism, the exact pathways are still a challenge to study and derive with notable precision. It is important to decipher the pathways because that is how we begin to examine localized effects in the plants.

2 Physiological and Biochemical Effects of Nanoparticles in Plants

Nanoparticles are highly reactive, owing to their very small size, high specific surface area, and chemical nature. They tend to behave differently in isolation and dynamic living systems. While positive effects may include increased growth and development, adverse effects can be seen as retardation in growth and development, damaged foliage, and biomass accumulation (Fedorenko et al. 2020; Rajput et al. 2018, 2019). Some examples of observed positive and negative effects are stated below:

- In *Lycopersicon esculentuma* plant, higher seed germination rates were observed when exposed to low concentrations of silicon dioxide (SiO_2) NPs (Siddiqui and Al-Whaibi 2014; Aslani et al. 2014).
- In *Zea mays,* significantly increased growth rates and germination were observed when Si NPs were present (Suriyaprabha et al. 2012).
- Molybdenum NPs having an octahedral shape were causing phytotoxicity in plants (Aubert et al. 2010).

- Carbon nanotubes, one of the most popular NPs in use, were found to cause root elongation and toxicity in tomato, maize, rice, and lettuce plants (Cañas et al. 2008).
- In *Oryza sativa*, silver nanoparticles (Ag NPs) were found to be very damaging, causing pigments concentration, leaf growth development, and so on (Nair and Chung 2014).

It can be concluded that NPs are more likely to cause harmful effects in plants unless specifically engineered. Understanding the underlying physiology and biochemistry helps plan out the process arc of beneficial microbes and design remedial measures for damaged plant systems. In terms of phytotoxicity, very frequent occurrence that is responsible for a lot of damage caused by NPs is their ability to generate reactive oxygen species (ROS). It is very reactive molecules that interact with one or many parts and components of the internal metabolic arc of plants. This interferes with photosynthesis, growth, fruiting, flowering process, water, and food transfer.

2.1 Biochemical Aspect

The toxicity of nanomaterials (NMs) and their negative effects on the growth and development of plants have not been fully elucidated. Several studies reported that higher concentrations of metal and metal oxide NPs are harmful to plants. Hence, the increasing use of NPs in agriculture may have harmful implications on the environment. There is a need for detailed research to understand the complete mechanism of plant NPs interaction as the studies are in their primitive stage. The various types of biochemical implications of NPs on plants are discussed below:

Oxidative stress: In *Salvinia,* it was observed that zinc oxide nanoparticles (ZnO NPs, 25 nm) significantly reduced chlorophyll-a and carotenoid content (Hu et al. 2014). It was also found to minimize peroxidase (POD) activity during short-duration treatment (7 days). There was no reduction in growth rate, but that was attributed to less exposure time. Apart from these, an increase in catalase (CAT) activity is also observed. This was also mirrored in a study on mesquite (Hernandez-Viezcas et al. 2016). Some NPs also have a mild effect, as exemplified by iron nanoparticles (Fe NPs) created from smelting industries. After a significant exposure time in the study on *Physcomitrella patens,* there was a presence of ROS but no apparent membrane damage or reduction in ATP production (Canivet et al. 2015).

In the opposite case, some NPs have positive effects biochemically, catalyzing specific reactions in the plants. Silver NPs have been found to slow down aging in flowers such as *Pelargonium* (Hatami and Ghorbanpour 2014).

Protein production: It is not much known about the effects of NPs on protein production, but two notable cases point to the fact that there might be a lot to discover. In *Eruca sativa,* Ag NPs are demonstrated to affect two important chaperone proteins, the endoplasmic reticulum luminal binding protein and heat shock protein

(Vannini et al. 2013). An interesting conclusion was found in some plant cells where the response of the internal system mistook multi-walled carbon nanotube clusters (MWCN) for viruses. There was the secretion of polysaccharides mimicking an immune response.

2.2 Physiological Aspects

The physiological interactions of NPs were described under mechanical, chemical, enzymatic, biotransformation effects, and binding properties alteration (Dietz and Herth 2011). On an applied scale in plants, the physiological effect can be deduced at the macro or micro levels. The macro-level includes germination and growth, and the micro-level includes metabolite production, enzymatic processes, and long-term effects. Several studies have been on different plants scaling germination and growth against varied quantities of nanoparticles and exposure times. A lot of these studies were conducted in hydroponic systems to reduce the general randomness which is present in soil-based cultivation environments. Studies conducted on Cucumber (Rui et al. 2015) and *Ralphinus* (Corral-Diaz et al. 2014) yielded unexpected results where the presence of NPs had a very mild to no effect on the growth and germination speeds. Even with alteration of exposure and retention times and concentrations, not many significant results were observed. This would lead to the conclusion that with the time element in mind, the effect which is observed may be caused due to the accumulation of other metabolites in the plant, which is brought about by nanoparticles. Therefore, the impact of NPs for these cases and presumably more is indirect rather than direct.

All of this takes a turn when the NPs are metals such as copper and iron. Copper oxide nanoparticles (Cu NPs) have exhibited the ability to reduce biomass, and seed germination times are increased, generally showing a deteriorating effect on rice plants at different concentrations (Shaw and Hossain (2013). Iron nanoparticles show reduced chlorophyll action at toxic concentrations. This is observed in a number of varied species such as wheat, rice, *A. thaliana,* and others. In order to understand the complete physiology and biochemistry of NPs and their impact on plants, one must remember that an immense amount of variation is shown from plant to plant and area to area. Therefore, the only way to have better quality and more data is to develop a paradigm of study so that it does not have to be rewritten from scratch every time for every new NP and every new plant.

3 Molecular Aspects: Long- and Short-term Changes

Nanoparticles in the plant system are very closely linked to the molecular mechanisms, which already run underneath the basic growth and metabolic processes. These include the genetic regulation and execution of protein synthesis, replication, etc. Nanoparticles can affect these processes both directly and indirectly. As of right now, there is not much known about the genetic changes that can come up in plants from exposure to engineered and natural NPs in various concentrations and times. So far, the following key points describe the effects of NPs at a genetic level:

- The key indirect effect is the oxidative stress caused by NPs causing damage to the DNA due to the ROS (reactive oxygen species) generated. This damaged DNA tends to show its effects on growth, stability, and resistance against weather and disease (Britt 1999). This is a relatively slow and subtle change, and not much research has been conducted on this since it is too indirect, and there aren't many ways of linking NPs and causative DNA changes.
- There is a group of cysteine-rich proteins called metallothionins which help in the detoxification of heavy metals. When upregulated, they help in treating toxicity in numerous plant species, and studying them is one way to get insight into the interaction of plant species with heavy metal NPs (Landa et al. 2012).
- Some known pathways affected by NPs include the ethylene, auxin, and abscisic acid pathways responsible for growth, development, maturity, ripening, and aging. Changes in regulation and constituent genes of these pathways can be seen acutely and easily in plants such as root and shoot alteration because of NPs presence.
- A great model organism for the study of genetic and molecular changes in plants in the presence of NPs is *Arabidopsis thaliana.* This is because it has been used extensively before, its entire genome is mapped, and various cytogenetic systems and pathways are well known and understood.

Depending on the plant, there is a variation in how long NPs are retained. There is also a difference such that some NPs are effectively integrated into various processes, and some aren't. This leads to the key difference between changes at the biochemical/physiological level and molecular and genetic levels. The former is usually temporary, from only lasting until exposure of the particle to just the lifetime of the one specific plant. However, there is some evidence of NPs causing changes that alter the genome so that the changes persist even in the next generation of plants with respect to growth rates and senescence.

4 How are Uptake, Translocation, and Presence Measured and Assessed?

Nanoparticles need specialized methods for evaluation and measurement inside the plant system. Unlike living organisms, they cannot be modified to produce detectable proteins in culture, and this is because they cannot be tagged with detectable molecules for the most part. Generally, the techniques used frequently include ultraviolet and visible light spectroscopy, near-infrared spectroscopy, scanning, transmission electron microscopy (SEM, TEM), x-ray diffraction, high-performance liquid chromatography (HPLC), Fourier transform infrared spectrometry, and high-performance liquid chromatography single particle inductively coupled plasma mass spectrometry. Some techniques that have been used with variations for different plants are discussed below:

Case 1
Since the status of the NPs cannot be determined directly, the fringe effects are considered that may be visible on the cells due to these particles. This can be exhibited in Lee et al.'s (2012) study on Ag NPs. It was observed that specific past concentrations of silver slow down the plant's growth rate because it causes toxicity. It was observed that due to interaction with the cell wall of the cells with Ag NPs, there was notable color change when compared with cells that were not exposed to the silver. At the initial low concentrations, silver in the cellular systems caused increased and improved growth, but after a specific concentration, changes in the cell's morphology and inner working caused a decrease or plateau in the growth rates. This happens to be one of the directly detectable interactions based on cellular appearance (Table 5.1).

Case 2
In a study on tobacco by Domokos et al. in 2012, it was observed that selenium nanoparticles (Se NPs) exhibited similar behavior. At a low selenium concentration, the plant shows accelerated growth and development. After specific concentration is reached, the growth gets inhibited. There is some variation demonstrated with the two selenium species in the system: selenite or selenate. The detection method here is that selenium accumulates in the roots in surprising quantities (about 3000 mg/kg). This can be detected easily in sample studies, making it a good marker.

Case 3
In terms of detection behavior, titanium dioxide particles were also found to accumulate in the roots of wheat (Larue et al. 2012). After exposure of the plant to titanium dioxide solutions for about 7 days, clusters of the NPs were detected in the roots. There is a conjecture that particles are related to the cell wall because only particles of a certain size are found in the plants. Also, it must be noted that the result of this study showed no correlation between the presence of said particles and photosynthesis in wheat. Using empirical science, metallic particles can be detected using fine-tuned magnetic techniques for high sensitivity, which is most common for nZVIs and other iron-based particles.

4.1 Insightful Experiments on Plant Uptake of Nanoparticles

The uptake percentage and response toward different NPs are driven by various factors such as exposure pathway, species, age of plants understudy, and size and morphology of NPs. The vascular system of a plant plays an important role in the distribution of NPs into different parts of a plant. On the other hand, particles

Table 5.1 Effects of Ag NPs on a variety of plants

Size (nm)	Concentration	Species	Impact	References
25–70; 7.5–25.0	10–50 ppm	Wheat (*Triticum aestivum* L.)	Caused various types of chromosomal aberations	Abdelsalam et al. (2018)
5–10	0.1–0.5 ppm	White lupin (*Lupinus termis* L.)	Reduction in shoot and root elongation, shoot and root fresh weights, total chlorophyll, and total protein contents	Al-Huqail et al. (2018)
79.0 ± 8.0	0.05–2 ppm	Duckweed (*Lemna minor* L.)	Caused decays on growth rate and fronds per colony; induced oxidative stress	Pereira et al. (2018)
17.2 ± 0.3	1–30 ppm (soybean); 0.1–1 ppm (rice)	Soybean (*Glycine max* L.) Rice (*Oryza sativa* L.)	Significantly reduced plant biomass, increased the MDA and H_2O_2 contents in plant leaves	Li et al. (2017)
20	1000–3000 μM	Pea (*Pisum sativum* L.)	Declined growth, photosynthetic pigments, and chlorophyll fluorescence (Fv/Fm)	Tripathi et al. (2017)
200–800	1 ppm	Fenugreek (*Trigonella foenum-graecum* L.)	Enhancement in plant growth and diosgenin synthesis	Jasim et al. (2017)
47	1–3 mM	Mustard (*Brassica* sp.)	Declined growth of *Brassica* seedlings, induced oxidative stress	Vishwakarma et al. (2017)
35, 73	10 ppm	Cucumber (*Cucumis sativus* L.); Wheat (*Triticum aestivum* L.)	Reduced plant growth, upregulation of genes involved in the ethylene signaling pathway	Wang et al. (2017)
5–50	800 μg/kg	Bean (*Vicia faba* L.)	Declined germination, decreased shoot and root length, retarded the process of nodulation, caused early senescence of root nodules	Abd-Alla et al. (2016)
41	100–5000 ppm	Arabidopsis (*Arabidopsis thaliana* L.)	Reduced root length, leaf expansion, and photosynthetic efficiency, induced ROS accumulation	Sosan et al. (2016)
10	1–10 ppm	Duckweed (*Wolffia globosa* L.)	Caused oxidative damage, higher MDA content and upregulation of SOD activity	Zou et al. (2016)
6, 20	0.5–10 ppm	Common duckmeat (*Spirodela polyrhiza* L.)	Dose-dependent increase in levels of ROS, SOD, peroxidase, and the antioxidant glutathione content	Jiang et al. (2014)

(continued)

Table 5.1 (continued)

Size (nm)	Concentration	Species	Impact	References
20	0.2–1 ppm	Rice (*Oryza sativa* L.)	Significant reduction in root elongation, shoot, and root fresh weights, total chlorophyll, and carotenoid contents	Nair and Chung (2014)
8, 45, 47	2–100 μM	Arabidopsis (*Arabidopsis thaliana* L.)	Induced root growth promotion (RGP) and Cu/Zn superoxide dismutase (CSD2) accumulation	Syu et al. (2014)

absorbed from the soil system via roots are facilitated by xylem and water. They are reported to undergo biotransformation by the action of root exudates (Rico et al. 2011). Owing to their higher surface reactivity, smaller NPs were found to make pores on the surface of roots resulting in increased nutrient uptake (Castiglione et al. 2011). The following case studies give a brief glimpse of the research related to the developmental paradigm for the study of uptake, translocation, and changes observed in plants due to NPs.

Case 1

Jacob et al. (2013) conducted a study pertaining to the uptake and translocation of titanium nanoparticles (TiO_2) in wetland plants. There was an underlying concern that the production of these particles and their release into the environment was increasing radically as titanium and its oxides were being used for various applications in consumer products. The plants which were studied were bean (*Phaseolus vulgaris*), wheat (*Triticum aestivum*), Curly dock, a wetland species (*Rumex crispus*), and the floating plant Canadian waterweed (*Elodea canadensis*). Titanium dioxide was considered as the source of the particles in the plants. Some variation was observed in how all four plants reacted to exposure to the particles. The waterweed was most vulnerable to the effects of the particles since it could absorb them directly from the leaves. Wheat and the dock showed significantly increased quantities of titanium in their roots. On the basis of the aforementioned information, the following points can be concluded:

- Titanium can cycle in the environment through various trophic levels.
- Its presence changes the way plants absorb trace metals from the soil, such as iron, manganese, copper, and so on.
- The quality of the water, amount of organics, and phosphorus can affect the absorption and retention of titanium in the plant.
- From a phytoremediation perspective, it showed that these plants could be used to remove titanium and may be similar heavy metals from the soil by uptake.

Case 2

A study conducted on Ag NPs by Yan et al. in 2019 focused on the phytotoxicity angle and its underlying mechanisms. Silver is also widely used at the nanoscale for numerous applications from technology to healthcare. However, its presence in the environment is largely harmful to plant life. From the very beginning, it was reported that upon exposure to the particles, the plant shows a morphological response, including decrease in growth rate, root growth, leaf surface area, etc. This was observed in cucumber, wheat, Arabidopsis, Spirodela, and rice. At the most basic physiological level, Ag NPs cause oxidative stress in the plant cells, causing metabolic irregularities and interfering with the normal functioning of other systems.

There is evidence pointing toward the fact that the impact runs more profound than the surface changes, this includes visible alteration in cell division and differentiation patterns. In maize, decrease in vacuole size and cell size overall was observed. Severe chromosomal breaks, reduced mitotic index, and disturbed metaphase were observed in onion plants.

The concerns regarding Ag NPs can be summarized in the following points:

- The particles are largely toxic to all plants in varying intensities, and their presence in the biotic environment is an overall negative for agriculture and soil health.
- They are persistent in the food chain and can undergo bio-magnification through the trophic levels; eventually reaching toxic concentrations.
- The changes reach the molecular/genetic level; therefore, the damage may persist even when the environment is cleaned and remediated.
- Some plants have tolerant mechanisms set in place, but some are completely vulnerable to the effects of the particles.

5 Differences in Natural and Manufactured Nanoparticles

The key difference noted here is not the core nature of the NPs but the source. Natural sources include any unintentional release and exposure that may occur from a natural event, including volcanic events, seismic events, and dust storms. They are not very frequent, and the particles appear in a way that makes it easier for plants to naturally adapt to their presence. In an ordinary environment, the occurrence of such events is considered rare. Therefore, the plant's internal system does not consider the presence of the NPs as an immediate and urgent threat. In some cases, the presence of metallic NPs, irrespective of source, catalyzes reactions occurring in the plant and positively affects the plant. This is vastly different for manufactured NPs and those released due to waste disposal, smelting, or other industries. This is for the following reasons:

- Manufactured NPs are generally released in exponentially more significant quantities than naturally occurring particles.
- They are not environmentally neutral or harmless and are more reactive.
- Most, if not all, are toxic even by themselves by sheer virtue of presence.
- The NPs resulting from the disposal of any kind of waste build-up silently in the environment, only coming into the light when they have already caused a significant negative impact.

- Their remediation from the environment is not a simple or straightforward process but is under consideration as an urgent issue since after a certain amount of concentration is reached, remediation approaches non-viability and becomes futile.

As opposed to natural nanoparticles, manufactured Nanoparticles are crucial for the development of Nanotechnology and allied sciences and technology. This implies that instead of curbing and restriction usage, it would be better to regulate and manage better production measures, efficient use and prevention of wastage and misuse. The technology developed through synthetic Nanoparticles has shown a significant amount of potential in various fields therefore bans and restrictions would not be the ideal course to take.

6 Conclusion

The two key perspectives are clear from the above-discussed text, and one is that the adverse effects of NPs must be researched upon more, and methods should be devised to purge the plants of the problem. The first and foremost method is to understand that NPs are an important component of technological development and cannot simply be written off. Therefore, the attention must be shifted to better usage, management, and disposal of particles to avoid buildup in the environment and unexpected exposure to plant populations in closed ecosystems. Prevention is the first step of remediation in plants. The second step begins with the developmental process. In the roster of conditions that new NPs must fulfill before being used for technology, ease of degradability and environmental safety must be treated with actual utility. The other perspective points toward the fact that certain plants can serve as bio-machines capable of removing heavy metals and other NPs from the soil in their natural or genetically modified state. This is a good strategy for higher priority soil remediation of already severely damaged soils and water. It is, however, extremely experimental. Moving one step further, plants can be engineered to collect certain particles from the environment by creating a bioactive workflow capable of harvesting precious or semi-precious metals from the soil in an environmentally neutral or positive way compared to traditional mining. This has widespread applications in minerals, metals, space engineering, transforming, extensive bioremediation, and so on.

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Chapter 6
Mechanism of Nanoparticles-Mediated Alleviating Biotic and Abiotic Stresses in Agricultural Crops: Recent Advances and Future Perspectives

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1 Introduction

Plants are the most vulnerable living entities as they are continually exposed to a variety of environmental changes and many stress factors, either individually or in combination, throughout their life cycles. Since the last decade, crop output has been deteriorated globally due to lack of arable land, water scarcity, ever-changing climate, and low pesticide usage efficiency. Drought, salt, freezing, flooding, UV radiation, and other abiotic stresses on plants are becoming more widely recognized as important agricultural concerns (Wani et al. 2016). All these stresses in combination cause more than 50% yield loss from important agricultural crops (Hirayama and Shinozaki 2010) throughout the globe. As the enhancement of food production in this scenario is becoming a difficult task, and progress in production of abiotic stress-tolerant crop varieties is slow, more research is needed to understand the negative impact of these stresses on plant developmental growth, as well as possible reclaiming strategies using minimal agricultural inputs are required to overcome the effects of such stresses on plants (Wani et al. 2016; Elsakhawy et al. 2018; Zhao et al. 2020). Plants can acclimate to such pressures by introducing molecular, cellular, and physiological changes (Yadav et al. 2020). It has been discovered that numerous enzymatic and non-enzymatic antioxidants that scavenge the damaging

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reactive oxygen species (ROS) are present at a satisfactory amount inside the plant system. Catalase (CAT), glutathione reductase, superoxide dismutase (SOD), and ascorbate peroxidase (APX) constitute enzymatic antioxidants while glutathione and ascorbate are the non-enzymatic antioxidants that work continuously to destroy harmful ROS through shikimate-phenylpropanoid or ascorbate biosynthesis pathways (Khan et al. 2017; Zhao et al. 2020). The ROS molecules such as hydroxyl radical, superoxides, hydrogen peroxides, etc., are basically produced in mitochondria, chloroplasts, and peroxisomes at the time of photosynthesis and cellular respiration under stressful environment (Khan et al. 2017; Tripathy and Oelmüller 2012). Excessive ROS build-up caused by oxidative stress destroys membrane lipids, proteins, and nucleic acids, resulting in abnormal development (Khan et al. 2017). NPs imitate the activity of antioxidative enzymes in plants, making them effective ROS scavengers (Wei and Wang 2013; Khan et al. 2017). Engineered NPs with dimensions of 1–100 nm (Khan and Upadhyaya 2019) possess a very high reactivity and enlarged surface area which have ambiguous devoir in minimizing the harmful and negative effects of diverse environmental stresses on plant system (Elsakhawy et al. 2018; Mittal et al. 2020).

Eric Drexler has gained huge appreciation for popularizing the term “nanotechnology” in the realm of producing tools and technology for precision agriculture (Khan and Upadhyaya 2019). Nanotechnology is the science of using NPs which are molecular aggregates, synthesized at the nanoscale through either physical, chemical, and biological methods (Singh et al. 2016). They interact with plants to improve their developmental growth, increase productivity, and regulate the expression of various genes to overcome unpredictable abiotic stresses (Tan et al. 2017; Khan and Upadhyaya 2019). Due to their tiny size, they have a variety of physicochemical features, including increased reactivity rate in plant cells and tissues (Dubchak et al. 2010). However, plant response to NPs is debatable since it differs depending on plant type and NPs used (Lin and Xing 2007). Besides the positive effects, so many studies have shown several toxicological effects of NPs (Husen and Siddiqi 2014). Excessive use of NPs to plants under stressed condition can alter the process of ROS production resulting in oxidative damage (Chichiriccò and Poma 2015). NPs used in food and agriculture sector may be made up of inorganic, organic, and combined in nature. Inorganic NPs include metal and metal oxides, organic NPs include mainly natural products while combined NPs include clay. NPs can be of different morphological structures like rod shape, pyramid, micro-flower, etc., depending on the purpose of use like food-packaging, nanomedicine, agriculture biotechnology, preparation of biosensors, etc. Silver NPs are mostly commercially used because of their promising antimicrobial activity; while, gold NPs are used as sensor or detector. There is an urgent need for understanding the interaction between plants and NPs for the sake of crop production, nutrient utilization, and crop-health management. The general applications of NPs in the field of agriculture science have been shown in Fig. 6.1.

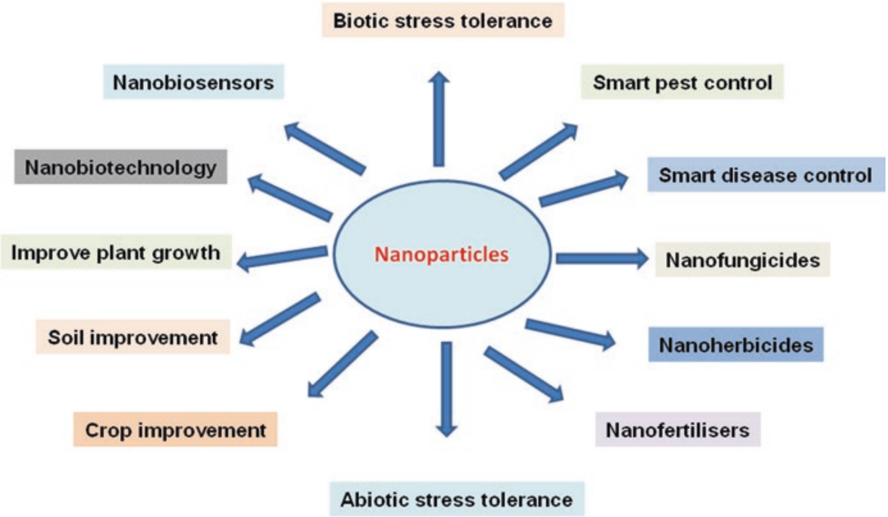

Fig. 6.1 Applications of NPs in agricultural practices

2 Commonly Used NPs and Their Synthesis

NPs are biocompatible, stable, and may be directed to a specific location inside the plant body. Their ability to boost crops and control various stresses is solely determined by their shape, size, and chemical behaviors. Copper (Cu), silver (Ag), gold (Au), and other noble metals having a large absorption range (Marmiroli et al. 2015) are often used as NPs and work on the basis of localized surface plasmon resonance (LSPR). They are synthesized by either top-down or bottom-up processes (Omar et al. 2019; Kumar et al. 2020). In bottom-up approach (also known as sol-gel approach), atoms and molecules are assembled together to form NPs of desired size and shape. In top-down approach, atoms and molecules are separated from the bulk material to get the desired NPs. Nano-sized materials can be prepared by different physical, chemical, biological methods either singly or in combination. NPs that are synthesized using the plant extracts possess a functionalized surface having proteins, ligands, polysaccharides, which are otherwise absent when synthesized by either physical or chemical methods. These components increase the stability of particles and help in the attachment of functional molecules like antibodies, DNA to the NPs. Preparation of metallic NPs through the green synthesis method using plant extract is economic, eco-friendly, and less time-consuming as compared to the chemical synthesis method. Incorporation of the desired metal NPs in starch films reduces the problem of biodegradability and food containment. Nano-fertilizers, nano-sized nutrients, nano-sensors, carbon-based nano-materials, and nano-pesticides have been reported beneficial to agricultural practices by easy environmental detection, pathogen detection, sensing, degrading persistent chemicals, and remediation (Iavicoli et al. 2017).

Magnetic NPs are usually made from iron (Fe), cobalt (Co), magnesium (Mg), and manganese (Mn) either by microemulsions or co-precipitation thermal decomposition preparatory methods (Ashfaq et al. 2013). Graphene, carbon nanotubes (CNTs), carbon nanofibrils (CNFs), fullerenes, and other carbon-based nanostructures have recently been created for agricultural enhancement, crop protection, and environmental clean-up (Omar et al. 2019). CNTs and CNFs have the capacity to translocate from root to shoot inside plants, making them useful in agriculture (Ashfaq et al. 2017). Hybrid NPs on the other hand are synthesized as the conjugates of organic and inorganic nanostructures having lots of utility values in several biological applications. They are efficient in stress management in plant system than the other commonly used NPs as they enhance the biocompatibility of NPs (Qi et al. 2013).

3 Absorption, Translocation, and Accumulation of NPs into Plant System

Absorption of NPs by plant system and genuine interactions with them prominently depend on several factors including plant physiology and physiochemical properties of the used NPs such as their size, charge, shape, functionalization, and stability (Pérez-de-Luque 2017). Above ground plant parts such as stomata, cuticles, trichome, and hydathodes generally act as the sites through which NPs enter into the plant tissues; even the wound regions play the same role (Verma et al. 2019). Enormous scientific reports have mentioned that the uptake of NPs in plant system occurs through root absorption and transported by specialized plant tissues with some modifications, like biotransformation, bioaccumulation, and dissolution through crystal phases (Ali et al. 2021). The size of NPs is considered as the most important parameter as it enables their entrance either through cell wall pores or stomatal openings and even their subsequent transport processes intercellularly inside the plant system. The attachment and absorption of NPs in plant system is believed to rely directly on the existing negative charges on the cell wall surface. In addition, the hydrophobicity present on the plant surfaces has been found to play important role in absorption and translocation of NPs throughout the plant body (Kaphle et al. 2018).

NPs can enter the plant body via lateral roots with the aid of capillary forces and osmotic pressure, or they can enter directly through root epidermal cells (Lin and Xing 2008; Du et al. 2011) and finally translocated to xylem vessels via cortex and pericycle tissues (Dietz and Herth 2011; Miralles et al. 2012). NPs of sizes below 5 nm, under foliar application, are able to penetrate the leaf cuticle and reach the cell cytoplasm (Jeyasubramanian et al. 2016), while the NPs larger than the size of 10 nm enter through leaf stomata, with apoplastic and symplastic pathways for cellular transport (Ali et al. 2021). Through plasmodesmata, NPs can travel from one cell to another cell and are later on internalized in the cytoplasm (Wang et al. 2012).

NPs of size 50–100 nm are translocated via apoplastic routes between the cells. Internalized NPs are conveyed through the vascular transport system via phloem sieve, allowing them to flow bidirectionally and accumulate in varying concentrations in leaves, stems, roots, fruits, and/or other tissues (Ruttkay-Nedecky et al. 2017).

In cytoplasm, the NPs are thought to bind with different cellular organelles and take part in various cellular metabolisms (Zhang and Monteiro-Riviere 2009). The overall mechanism of NP interaction with plant system is based mostly on chemical reactions involving generation of ROS, ionic movement through cell membrane, oxidative damage, and lipid peroxidation. When NPs penetrate plant cells, they react with sulfhydryl and carboxyl groups, causing change in protein function (Das and Das 2019). In order to find out the movement and localization of NPs to various organelles within the plant cell, we need to monitor and track NPs very precisely.

4 Mode of Action of NPs to Counter Harmful Effects of Environmental Stresses

Plants can show minimum effort to withstand acute adverse environment conditions (drought, salinity, chilling, radiation, and metallic stress), but they need a precise perception and transduction of stress stimulus for immediate activation of appropriate defense units against that stress factor before it becomes severe and damage plant's cellular machinery. Activation of defense regiment in plant system primarily involves a temporary elevation of cytoplasmic Ca^{2+}, production of intracellular secondary metabolites such as inositol and polyphosphate, generation of ROS, raise in cellular plant hormones concentration especially of abscisic acid (ABA), and higher increase in mitogen-activated protein kinase (MAPK)-dependent pathways which ultimately trigger the molecular machinery against the particular stress (Baxter et al. 2014; Jalil and Ansari 2019). Calcium ions (Ca^{2+}) act as secondary messengers and play important role in signaling responses under various stresses. Ca^{2+}-binding proteins (CaBPs) are activated by cytosolic Ca^{2+} and stimulate downstream pathways that result in gene expression modifications and results in plants' adaptation to stresses (Khan et al. 2014; Khan et al. 2017).

When plant cells are exposed to various stresses, nitric oxide (NO) has been shown to cause an increase in calcium levels (Khan et al. 2014), implying that calcium stimulates NO generation. NPs act as an efficient Ca^{2+} substitution in CaBPs, resulting in the development of a stress-responsive gene cascade (Khan et al. 2017). NPs show duality in plant system under abiotic stress by enhancing production of ROS and scavenging of ROS simultaneously (Simon et al. 2013; Wei and Wang 2013). If any disturbance occurs between these two processes, it might result in oxidative stress and failure in the signal transduction process. The equilibrium of ROS inside the plant cells is managed by continuous synthesis and scavenging of ROS (Khan et al. 2017). To understand critically the mechanism of stress-signaling and significant response by NPs, in-depth investigations are needed with proteomic and genomic approaches. Furthermore, the application of NPs influences gene expression, cell division, cell elongation, and overall plant growth.

5 Biotic Stress: A Major Problem in Agricultural Crops

Diminution of agricultural productivity mainly depends on the exposure of biotic and abiotic factors. The growth of agricultural crops and plants, seed quality, and crop yield are affected by various biotic stresses. Biotic stresses involve damages primarily caused by living micro-organisms such as viruses, bacteria, fungi, insects, nematodes, etc. Wang et al. (2011) studied a proteomic-based technology in rice crop under biotic stress and found several biomarkers. Potential biomarkers like proteins that are common and unique to each stress can be used for generating the next generation crop plants using molecular breeding and genetic engineering to enhance crop yield and seed quality. Dresselhaus and Hückelhoven (2018) studied the role of metabolites during biotic and abiotic stresses in plants and how these two stresses are inter-related to each other for causing huge losses in the productivity of crops. Several agricultural crops like rice, wheat, maize, cotton, barley, chickpea, and other pulses are damaged every year due to biotic stresses and cause huge losses. Winter crop like wheat is affected by several diseases like powdery mildew, leaf blight, loose smut, rusts, etc.

Among these, a disease known as fusarium head blight caused by the fungi *Fusarium graminearum* and *Fusarium poae* causes huge losses to the wheat crop. Fungal diseases in wheat crop results in a reduction in kernel weight, vigor of seeds, and overall plant yield (Martínez et al. 2020; Dandve et al. 2019). *Fusarium oxysporum* damage different parts of wheat like leaves of seedlings, roots, etc., and results in qualitative and quantitative losses (Banerjee and Mittra 2018). Bocquet et al. (2018) conducted a study on *Septoria tritici* blotch disease of wheat, which is caused by fungus *Zymoseptoria tritici* and concluded that this fungus can cause extensive damage to the wheat crop. Ceresini et al. (2018) reviewed the past and present status of wheat blast disease caused by *Pyricularia graminis tritici* and also studied about its physiology, genetics, and its remedial measures.

5.1 Role of NPs to Deal with Biotic Stress in Crops

Plant pathologists and researchers are looking forward to safeguard food and agricultural products against biotic stress caused by bacteria, fungi, and viruses. Pathogen can be detected using this new technology which is nanoscale in size, have biological sensors with nano-based miniature detection devices. The use of various NPs in the crop plants during biotic stresses has been shown in Table 6.1. Abd-Elsalam (2013) has made efforts to develop a harmless method to manage fungal

Table 6.1 Use of NPs to mitigate biotic stresses in various crop plants

Sr. No.	Nanoparticle(s)	Concentration	Crop species	Causal organism	Reference
1	Chitosan and chitosan-based NPs	0.1–5.0 mg/ml	*Lycopersicon esculentum* (tomato)	*Fusarium andiyazi*	Chun and Chandrasekaran (2019)
2	Cu-chitosan NPs	0.08–0.12%		*Alternaria solani* and *Fusarium oxysporum*	Saharan et al. (2015)
3	Cerium oxide NPs	250 mg/L		*Fusarium oxysporum* f. sp. *lycopersici*	Adisa et al. (2020)
4	MgO NPs	0.05–0.1%		*Ralstonia solanacearum*	Imada et al. (2016)
5	Titanium dioxide NPs	500–800 ppm		*Xanthomonas perforans*	Paret et al. (2013)
6	Silver NPs	100 ppm		*Xanthomonas perforans*	Ocsoy et al. (2013)
7	Silver NPs	100–200 ppm	*Solanum melongena* (eggplant)	*Meloidogyne incognita*	El-Ashry et al. 2021
8	$Cu_3(PO_4)_2 \cdot 3H_2O$ NPs	1000 ml/L	*Citrullus lanatus* (watermelon)	*Fusarium oxysporum* f. sp. *Niveum*	Borgatta et al. (2018)
9	Silica NPs	500 mg/L		*Fusarium oxysporum* f. sp. *Niveum*	Buchman et al. (2019)
10	Silver NPs	2–10 μg/ml	*Triticum aestivum* (wheat)	*Bipolaris sorokiniana*	Mishra et al. (2014)
11	Silver NPs	50 ppm	*Trachyspermum ammi* (Ajwain)	*Meloidogyne incognita*	Danish et al. (2021)
12	Copper NPs	0.02–0.2 g/L	In vitro (1:1 beet moss and sand)	*Meloidogyne incognita*	Mohamed et al. (2019)
13	ZnO NPs	0–500 mg/L	In vitro (mung bean broth agar and in sand)	*Fusarium graminearum*	Dimkpa et al. (2013)

pathogens using nanoplatforms and nanomaterials. Rajeshkumar (2019) studied the antifungal impact of NPs against various fungal plant pathogens. According to him, various nanomaterials can be used to serve the purpose of fighting against fungal pathogens like *Rhizoctonia crocorum* and *Cercospora canescens*. Green methods are used to synthesize nanoparticles, which have antimicrobial activity. For example, gold NPs are synthesized using marine brown seaweed *Turbinaria conoides* and are used as an antibacterial agent against *Bacillus subtilis*, *Klebsiella pneumoniae*, and *Streptococcus* sp., while titanium oxide (TiO)-NPs are synthesized using a bacterial strain of *Planomicrobium* sp. and are used as antibacterial and antifungal agents against gram-positive bacteria like *B. subtilis*, gram-negative bacteria *Klebsiella planticola*, and against fungal cultures such as *Aspergillus niger*. Engineered NPs also had several impacts like plant growth, cell structure, physiological and biochemical functions on plants along with applications (Siddiqui et al. 2015). These engineered NPs also had an effect on photosystems, mechanisms of reactive oxygen species, and several enzymes in crops, which ultimately help in fighting against the biotic stresses.

Another example of nanoparticle used in agriculture is the use of nano-ZnO to inhibit the activity of Fusarium head blight pathogen in wheat crop. Therefore, it is used as a novel seed treatment method as it prevents seed disease, increases seedling growth, and increases activities of antioxidant enzymes such as SOD and CAT (Liu et al. 2020). Rice is often damaged by one of the severe biotic factors, like *Xanthomonas oryzae*, which causes bacterial leaf blight (BLB) disease in rice. Specific use of biogenic silver NPs (AgNPs) has proved beneficial rather than the use of chemical methods to control this disease. These AgNPs were prepared using a naturally isolated *Bacillus cereus* strain SZT1 of bacteria. Aside from combating pathogens, these NPs aim to boost plant biomass, reduce cellular concentrations of ROS, and enhance antioxidant enzyme activity (Ahmed et al. 2020). Alvarez-Carvajal et al. (2020) showed that AgNPs coated with chitosan function effectively in restricting the mycelial growth of *Fusarium oxysporum*, which is responsible for causing wilt by up to more than 70% and also reduce the severity of disease in tomato. Silver NPs can also be synthesized by biological method using endophytic *Pseudomonas poae* strain CO of bacteria. This NP works as an excellent fungicide against *Fusarium graminearum* pathogen. Application of biosynthesized AgNPs also showed inhibition in spore germination, hyphal proliferation, germ tube elongation, and mycotoxin production of various pathogens. Ibrahim et al. (2020) also approved that AgNPs have great potential in defending wheat from fungal attack.

Another example of engineered nanoparticles used during biotic stress is titanium dioxide nanoparticles (TIO_2-NPs), which plays significant role in inactivating various pathogenic bacteria's. TIO_2-NPs are synthesized by hydrothermal treatment using different temperatures ranging from 250 °C or 310 °C. It has photocatalytic activity and inactivates various plant pathogens like *Xanthomonas arboricola*, *Pseudomonas syringae*, and *Erwinia amylovora* (Kőrösi et al. 2020). Therefore, this engineered nanoparticle is very promising with its antimicrobial activity. The innovative use of silicon as nanoparticle in agriculture can not only meet the rising demand of food and agriculture but also help in developing sustainable environment by using agricultural wastes for the production of silicon NPs (Si-NPs) leading to waste management through recycling. Since Si-NPs are mesoporous in nature, it acts as a specific carrier for pesticides and fertilizers also known as nano-pesticides and nano-fertilizers respectively. It also involves in site-targeted delivery of nucleic acid, nutrients and increases crop protection, as well as plant growth and development. It reduces the damages caused by biotic and abiotic stresses in plants (Roychoudhury 2020). Since commercial fungicides are harmful to use due to the rise of microbial resistance nowadays, biological NPs are an alternative management tool used more preferably. Zinc NPs have an antimycotic activity against dark spore-forming pathogens like *Bipolaris sorokiniana*, *Alternaria brassicicola*, etc. (Kriti et al. 2020). It inhibits the spore formation, mycelial growth of fungus.

The interaction between NPs and protein (present in microbe) results in the inflammatory signal because microorganisms consider NPs as foreign material and results in microbial inhibition and reduced mycelial growth, when zinc-based NPs were used (Kriti et al. 2020). Luksiene et al. (2020) reported the importance of ZnO-NP as it has antifungal activity against pathogen *Botrytis cinerea*, infecting strawberry. However, ZnO-NP worked more efficiently in the presence of sunlight as it gets activated by ultraviolet (UV) and visible light, resulting in increased harvest. It therefore can replace conventional fungicide fenhexamid. Chitosan copper NPs (Ch-CuNPs) are known to possess antifungal properties (*Rhizoctonia solani* and *Pythium aphanidermatum*) against several fungal pathogens and can also be synthesized. In addition, NPs promote development in chili seeds by overcoming the low germination rate of sensitive seeds (Vanti et al. 2020). An endophytic fungus isolated from *Solanum nigrum* is used to make myco-NPs. Several plant pathogenic fungi, including *Fusarium graminearum, Fusarium udum, Rhizoctonia solani,* and *Aspergillus niger*, displayed antifungal activity and reduced pathogenic pressure by limiting their radial growth when treated with mycosilver NPs (Akther and Hemalatha 2019).

To combat dangerous phytopathogens, green production of AgNPs utilizing *Azadirachta indica* leaf extract is a preferable option to chemical agents (Haroon et al. 2019). The use of this NP is eco-friendly, safe, and inexpensive.

6 Advances in Abiotic Stress Mitigation by NPs

Fluctuation in the environmental conditions due to irregular rainfall, forest fire, melting of glaciers, faulty agricultural practices, and adverse effects of global warming due to industrial revolution constantly disturbs the metabolic equilibrium and developmental growth of plants (Jalil and Ansari 2019). Consequently, farmers as well as researchers become clueless to maintain sustainability in agriculture by mitigating all those stress factors. Advances in nanotechnology prestigiously offer huge scopes to check the detrimental impacts of various abiotic stress factors including drought, salinity, chilling, heat, metallic, and to some extent radiation on plant system. The use of NPs to mitigate the abiotic stresses in diverse crop plants has been put on view in Table 6.2.

6.1 Drought Stress

Drought is one of the serious abiotic stress factors that occurs regularly in dry locations and reduces agricultural productivity (Tripathi et al. 2017). A number of studies have recently demonstrated that applying silica NPs (SiNPs) at various concentrations increases drought tolerance in sorghums (*Sorghum bicolor* L.) by reducing their shoot to root ratio (Hattori et al. 2005). Varied concentrations of

Table 6.2 NPs for abiotic stresses management in various plant species

Sl. No.	Nanoparticle	Concentration	Plant species	Stress	Application method	Reference
1	TiO_2	0–500 mg/L	*Linum usitatissimum*	Drought	Foliar spray	Aghdam et al. (2016)
2	TiO_2	500–2000 mg/kg	*Triticum aestivum*		Soil amendment	Faraji and Sepehri (2020)
3	ZnO	0–1 g/L	*Glycine max*		Petri dish exposure	Sedghi et al. (2013)
4	y-Fe_2O_3	100–400 mg/plant	*Brassica napus*		Fertigation	Palmqvist et al. (2017)
5	Cu NPs	3.333–5.556 mg/L	*Zea mays*		Seed priming	Van Nyugen et al. (2021)
6	CNTs and graphene	50–200 µg/ml	*Gossypium hirsutum*		Seed priming	Pandey et al. (2019)
7	Chitosan NPs	0–90 ppm	*Hordeum vulgare*		Foliar spray	Behboudi et al. (2018)
8	ZnO	1–5 mg/kg	*Sorghum bicolor*		Soil amendment	Dimkpa et al. (2019)
9	SiO_2	0–100 mg/L	*Crataegus sp.*		Soil amendment	Ashkavand et al. (2015)
10	SiO_2	50–100 mg/L	Strawberry (Fragaria × anansa)	Salinity	Nutrient solution	Avestan et al. (2019)
11	$FeSO_4$	2 g/L	*Helianthus annuus*		Foliar spray	Torabian et al. (2017)
12	Ag NPs	0–10 mM	*Triticum aestivum*		Seed priming	Mohamed et al. (2017)
13	CeO NPs	500 mg/L	*Gossypium hirsutum*		Seed priming	An et al. (2020)
14	SiO_2	25 mM	*Lycopersicum esculentum*		Seed priming	Haghighi et al. (2012)
15	Ag NPs	25–100 mg/L	*Triticum aestivum*	Temperature	Soil amendment	Iqbal et al. (2019)
16	Se	10 mg/L	*Sorghum bicolor*		Foliar spray	Djanaguiraman et al. (2018)
17	TiO_2	5 mg/L	*Cicer arietinum*		Foliar spray	Mohammadi et al. (2014)
18	Al_2O_3	50 ppm	*Glycine max*	Flooding	Nutrient solution	Mustafa and Komatsu (2016)
19	SiO_2	10 µM	*Triticum aestivum*	UV-irradiation	Nutrient solution	Tripathi et al. (2017)

SiNPs cause physiological and biochemical reactions in hawthorns (*Crataegus* sp.) at different levels of drought stress (Ashkavand et al. 2015). Under water stress, SiNPs have also been shown to boost the activities of catalase (CAT) and peroxidase (POD) in the leaves of faba bean (Kalteh et al. 2018) and tomato (Siddiqui and Al-Whaibi 2014). Furthermore, SiNPs have been shown to have an influence on xylem humidity, water translocation, and turgor pressure, resulting in an increase in leaf relative water content and water usage efficiency in plants. Application of sodium silicate at low concentration (1.0 mM) has been found in mitigation of the harmful ramifications of moisture stress as well as membrane lipid peroxidation in wheat (Pei et al. 2010). In addition, foliar application (0.02%) of TiO_2-NPs have been reported to give promising results on certain agronomic traits like plant height, seed number, ear weight, ear number, thousand-seed weight, starch and gluten content in grains, yield, biomass, and harvest index of various existing wheat cultivars under limited water condition (Jaberzadeh et al. 2013).

Similarly, applications of TiO_2-NPs were studied in spinach (Lei et al. 2007) and Canola (Mahmoodzadeh et al. 2013) plants to mitigate the effect of drought stress by activating the antioxidant enzymes (SOD, CAT) machinery. Exogenous application of TiO_2-NPs at lower dose has been observed to increase photosynthetic rate and nitrogen metabolism in spinach (Yang et al. 2006), linseed (Aghdam et al. 2016), and sugar beet (Borišev et al. 2016). Shallan et al. (2016) looked into the impacts of nano-TiO_2 and nano-SiO_2 on cotton production in drought-stricken conditions. They discovered that pre-treating cotton plants with nano-TiO_2 and nano-SiO_2 increased the content of plant pigments, total soluble sugars, proline content, total soluble proteins, total antioxidant capacity, and antioxidant enzyme activities under prolonged drought stress. Sedghi et al. (2013) showed that ZnONPs, which have the ability to boost seed germination percentage and rate, successfully lowered the fresh and dry weight of seeds, promoting drought tolerance in soybeans (*Glycine max*).

Taran et al. (2017) reported enhancement of ability to withstand drought by increasing enzymatic activities of SOD and CAT due to nano-zinc application in wheat (*Triticum aestivum*). Davar et al. (2014) exhibited how foliar application of iron NPs (FeNPs) promoted tolerance against drought stress in safflower cultivars. Advances in the application of AgNPs to decrease the deleterious effects of drought stress on lentils were also praised (*Lens culinaris* Medic). Hojjat and Ganjali (2016) found that judicious application of AgNPs can help lentil seeds germination, root length, and dry weight by alleviating drought stress, moderating loss of plant growth, and enhancing germination rate, root length, and dry weight.

6.2 *Salinity Stress*

Around 20% of arable land throughout the world has perished of salinity. Salinity or salt stress is the most critical environmental issue for the plant species belonging to the lycophyte category (Negrão et al. 2017; Khan and Upadhyaya 2019). In the arid, semiarid, and coastal environments, salinity stress may be triggered by the build-up of chloride (Cl^-), sulfate (SO_4^{2-}), sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) ions (Singh and Husen 2020). It reduces agricultural output by interfering with a variety of physiological and biochemical processes involved in plant growth. The salinity stress caused by improper use of agrochemicals like pesticides, insecticides, etc., affects the soil's fertility, leading to imbalance of osmotic potential and nutritional components of soil, which become toxic to plants growth and development (Khan and Upadhyaya 2019). Furthermore, synthetic chemicals used in agricultural practices badly impact photosynthesis, protein synthesis, lipid metabolism, and other vital processes (Parida and Das 2005). In this context, the use of nanofertilizers may be a viable option for mitigating these challenges and reclaiming environmental sustainability.

Kalteh et al. (2014) found that applying SiNPs to basil (*Ocimum basilicum*) increased its chlorophyll content and proline levels significantly. Many studies also revealed that application of SiO_2 NPs had the potential to increase the amount of chlorophyll, proline accumulation, and the activities of antioxidant enzyme in plant system under salt stress (Gao et al. 2006; Haghighi et al. 2012; Kalteh et al. 2018). SiO_2 NPs encourage seed germination and improve yield-related features in lentil when salinity stress is prevalent. Furthermore, SiNPs are thought to promote osmotic potential and plant development by reducing Na^+ toxicity under severe salt stress (Khan and Upadhyaya 2019). By altering the characteristics of the salt-stressed root plasma membrane, multi-walled carbon nanotubes exposure on broccoli under salinity stress has been shown to boost net CO_2 assimilation and aquaporin transduction (Martínez-Ballesta et al. 2016).

Rossi et al. (2016) have shown that the application of CeO_2 NPs significantly mitigated detrimental impacts on biomass production and activities of chloroplast in *Brassica napus* L. when subjected to grow under saline water. The limited solubility of CuO-NPs in alkaline soil may explain why CuO and ZnO-NPs boosted wheat growth and yield (Fathi et al. 2017). Hussein and Abou-Baker (2018) carried out a pot experiment to understand the effects of nano-zinc fertilizer on cotton growth, yield, and mineral status under salt stress. They revealed that irrigation with seawater reduced leaf dry weight and boll production, but foliar application of nano-zinc fertilizer at the optimal dose alleviated the negative effects of salinity and enhanced the yield parameters. To investigate the expression rate of salt stress genes, Almutairi (2016) implemented semiquantitative RT-PCR. He discovered that Ag-NPs caused up-regulation of four genes, including *AREB*, *MAPK2*, *P5CS*, and *CRK1*, as well as down-regulation of three other genes, including *TAS14*, *DDF2*, and *ZFHD1*. Such a pattern of expression revealed the involvement of Ag-NPs and their response to stress conditions, suggesting that they have the ability to improve plant tolerance to salt stress.

6.3 Heavy Metal Stress

Heavy metal (HM) pollution is becoming so crucial for retarded plant growth and severe yield loss throughout the globe (Chibuike and Obiora 2014; Khan et al. 2017). Under HM stress, plants lose their potential to withstand in a challenging environment. Severe metallic stress influences rapid ROS production, eventually promotes oxidative damage by disturbing cellular structure as well as membrane integrity along with degradation of cellular proteins (Sharma et al. 2012). Plants try to fight back the negative effects of heavy metal shock by developing their defense system at the cellular level. Plants undergo shock when heavy metals breach the cell wall and enter the cell. Infected plant parts respond quickly to HMs by accumulating biomolecules and nutrients, which activate the antioxidant enzyme machinery. Nanotechnology in this scenario has been recognized as one of the promising approaches for decreasing phytotoxicity caused by heavy metals (Tripathi et al. 2015; Gunjan and Zaidi 2014). Exposure to TiO_2 NPs limited cadmium toxicity and increases photosynthetic rate in soybean (Singh and Lee 2016). Foliar treatment of ZnO-NPs to *Leucaena leucocephala* has been reported to enhance total soluble protein and photosynthetic pigment while decreasing membrane lipid peroxidation (Venkatachalam et al. 2017). NPs are becoming more important in the cost-effective rehabilitation of heavy metal-contaminated soils. NPs alleviated metal-induced toxicities during phytoremediation, according to Martínez-Fernández et al. (2017). Many studies have shown, however, that using NPs for crop improvement and phytoremediation has both good and negative effects on the agri-ecosystem.

6.4 UV-Irradiation

Plants exposed to radiation such as UV-B (frequency range: 280–315 nm) acquire an elevated amount of ROS in their cells, which directly or indirectly affects cell functions such as DNA damage, damage to chloroplast structure, disturbs cell functions, etc. (Chen et al. 2011; Wang et al. 2012; Hideg et al. 2013). Plants have evolved to accumulate phenolic chemicals, such as flavonoids and flavones, which absorb harmful UV rays, as well as enzymatic and non-enzymatic antioxidant defense mechanisms (Shen et al. 2010). Inclusion of NPs in the growth medium, on the other hand, may exacerbate detrimental effects of UV exposure.

For example, Regier et al. (2015) found that while CuO-NPs applied alone had no detrimental impacts when combined with UV light, they had a substantial negative influence on many physiological and morphological characteristics of *Elodea nuttallii*. Similarly, in wheat, subjected to a combination of cadmium telluride quantum dots (CdTe-QDs) and UV radiation, Chen et al. (2014) found reduced chlorophyll content, antioxidant enzyme activity, and enhanced DNA damage. When exposed to UV light, Lei et al. (2008) found that nano-anatase TiO_2-treated spinach increased photosynthesis, electron transfer, photoreduction activity of photosystem

II, oxygen evolution, and photophosphorylation (PSP) in chloroplast. Under UV-B exposure, nano-anatase exposure resulted in a large drop in superoxide radicals (O_2^-), H_2O_2, and MDA build-up, as well as a significant rise in antioxidant enzymes levels, indicating a prominent reduction in oxidative stress in plant cells (Lei et al. 2008).

6.5 Chilling Stress

Chilling or low-temperature stress is generally characterized by the occurrence of frost injuries in plant cells due to the accumulation of ice crystals within the tissues (Hasanuzzaman et al. 2013) under the exposure of very low temperature (0–15 °C). It negatively impacts on plant health by triggering loss of fluid and electrolyte leakage from the cellular membranes and consequently poor seed germination, stunted growth as well as reduced productivity (Singh and Husen 2020). Although vulnerability to cold stress depends on the degree of tolerance in various species (Heidarvand et al. 2011), plants suffering from low-temperature condition show disrupted photosynthesis by lowering down the chlorophyll content, transpiration rate, and degradation of Rubisco enzyme and its activity (Liu et al. 2012). In this context, many research studies showed that the use of NPs significantly increased production of Rubisco (Khan and Upadhyaya 2019), light immersion by chloroplast organelle (Ze et al. 2011), and inhibition in the generation of ROS (Giraldo et al. 2014). After application of TiO_2 NPs, the activities of antioxidant enzymes have increased in plants (Mohammadi et al. 2016). The use of nano-TiO_2 as a viable technique to reducing the detrimental effects of chilling stress has been recognized significantly. Application of NPs thus, causing suppression of lipid peroxidation, chlorophyll degradation, and synthesis of H_2O_2 under chilling stress, has been well-popularized in managing plant growth and health under various stresses (Kohan-Baghkheirati and Geisler-Lee 2015; Khan and Upadhyaya 2019; Singh and Husen 2020).

6.6 Heat Stress

Tending to temperature rise above the threshold limit for a long period of time often results in irreclaimable damage to growth and biological yield of crop plants (Wahid 2007). High-temperature stress increases production of ROS which leads to oxidative stress, and ultimately membrane lipid degradation as well as membrane ion leakage (Savicka and Škute 2010; Karuppanapandian et al. 2011; Aref et al. 2016). It also influences the reduction in photosynthetic rate as well as chlorophyll content (Khan and Upadhyaya 2019). In this regard, heat shock proteins (HSPs) have been identified as the key molecular chaperons to function in thermo-tolerance by plants (Singh and Husen 2020). Khodakovskaya et al. (2011) reported a significant contribution of multiwall carbon nanotubes (MWCNTs) in the upregulation of stress-responsive genes like *HSP90* in both leaves and roots of tomato. Additionally, when NPs such as CeO_2NP were exposed to maize, it resulted in the generation of hydrogen peroxide and also upregulated *HSP70* gene (Zhao et al. 2012). Treatment with TiO_2NPs also found to improve the mechanism of stomatal opening in tomato leaves under heat stress (Qi et al. 2013). Application of SeNPs at the nanoscale has been observed to mitigate the detrimental effect of heat stress in tomato (Haghighi et al. 2014) as well as sorghum (Djanaguiraman et al. 2018) by increasing the level of hydration ability, chlorophyll content, and various antioxidative features.

7 Conclusion

Nanotechnology is undoubtedly an essential element of several fields of agriculture. NPs reveal extremely low levels and have a kind and dose-dependent effect on plants. The scientific community is concerned about how to combat the loss of agricultural output caused by biotic and abiotic stresses. Several NPs are being investigated to determine their involvement in protecting plants from various environmental challenges, as well as their roles in promoting plant growth, crop production, and modifying plant processes. NPs have been demonstrated to be a more efficient and effective option for the production of nano-fertilizers than conventional fertilizers. Smaller NPs provide for easier penetration and control of water channels, which aid seed germination and plant growth; moreover, increased surface area allows for greater adsorption and controlled delivery of chemicals.

In contrast, the production of ROS is also described for NPs. The increased ROS level by NPs could be related to a stress signal amplification that can activate the defensive mechanism of the plant more efficiently. The uses of NPs approach have high potential to minimize the use of toxic chemicals as well as pesticides, fungicides, and insecticides on plants to combat environmental stresses and thus can lower the level of pollution of contaminants in air, groundwater, and in soil. Further research at multiple levels, including plant molecular and cellular levels, is needed for the function of nanomaterial to alleviate the damage caused by various environmental stresses.

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Chapter 7
Deciphering the Enigmatic Praxis of Nano-fertilizers in Agro-food Industrial Landscape

Richu Singla and Honey Goel

1 Introduction

Fertilizers, also referred to as plant feeders, have been employed for the past few decades in agriculture to assist the farmer community by fulfilling the requisite nutrition, vital for the evolution and expansion of plants. However, because of the burden of ever-expanding global population, which is expected to reach 9.6 billion by 2050, there is imperative prerequisite for the adoption of potent agricultural practices that would succour in accomplishing the world's right to food and alleviation of poverty and hunger. To meet such expectations, there is tremendous requirement for the implementation of good agricultural practices such as use of nano-fertilizers, which improve not only the crop yield but also the quality and shelf life. Further, traditional fertilizer practices are not only enhancing the cost burden but are also posing deleterious impact on the human as well as environmental health, apart from reducing the soil fertility, crop yield and overall development.

With the dawn of nanotechnology, it has presaged huge sway in all the realms of society including environment, healthcare, energy and electronics. Nowadays, nanotechnological practices (such as encapsulation and delivery of substances at targeted sites, enhancing the organoleptic properties, introduction of antibacterial nanoparticle coatings onto the food, enhancement of food shelf life, sensing contamination, improved food storage, tracking, tracing and brand protection) have been swamping the agro-food industry by enriching its nutraceutical potential,

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production yield, quality and safety levels to a superior level with the judicious application of fertilizers/manures, pesticides/insecticides, herbicides and plant growth factors.

2 Nano-fertilizers

Nano-fertilizers (NFs) facilitate the potential means to augment the crop productivity via delivering the nutrients to crops (in the dimensions of 1–100 nm) at their targeted site of application with controlled rate of release, thereby minimizing the illicit exposure of the fertilizers to the non-targeted areas. Further, the application of nano-fertilizers can also be harnessed to release the bulk materials together with nanoscale formations in order to develop new improved, potential fertilizers for improving the yield and nutritional value. Literature studies have shown that agriculture crops nano-enabled with fertilizers were proved to be significant in the accretion of nutrient use efficiency (NUE) by crops (Gogos et al. 2012; Anjunatha et al. 2016; Singh et al. 2021; Lowry et al. 2019; Bandala and Berli 2019). Therefore, apart from enhancing the crop productivity, the primary goal in the field of fertilizer research is also to prevent or minimize the nutritional loss for better crop development (Chhipa 2017). Nevertheless, specially designed nanostructures, which are generally expected to harmonize the nutritional needs of the crops, also allow the release of nutrients in a controlled fashion. Further, it is a matter of the fact that reducing the size of nanoparticles by physical or chemical means results in the enhancement of surface mass ratio of fertilizers. This strategy plays a critical role in the better absorption of nutrients from root which in turn allows the slow, targeted and efficient release of nutrients from NFs. Moreover, implementation of such NF's practices aids in the reduction of dosage quantity, cost of its application and nutrient losses, thus improving NUE by 20–30% compared to conventional approaches of fertilizer's use (Kah et al. 2018).

3 Manufacturing of NFs

NFs are primarily prepared from conventional fertilizers or extracts obtained from diverse plants or plant parts by coating/encapsulating them with nanomaterials regulating the release of nutrients in a controlled manner, thereby ensuring the productivity, fertility of the soil and agricultural product quality (Zulfiqar et al. 2019). Further, the physicochemical characteristics of nanomaterials permit superior encapsulation of the nutrients into nanosized form which can be released in a precise manner to expand the efficiency of crop plants with minimum impact to the environment. Furthermore, the interaction of nanomaterials with fertilizers improves absorption of nutrients and bolsters bioavailability of nutrients (due to the definite surface area, mini size and extra reactivity) and NUE, thereby preventing leaching, volatilization and environmental hazards such as soil fertility as well as safety of workers (Solanki et al. 2015; Chen and Wei 2018; Linquist et al. 2013). The manufacturing of nutrients/NFs into the nano-form can be done in three different ways (Iqbal 2019).

3.1 Entrapment or Encapsulation Within the Nanomaterials

The praxis of encasing a constituent within another material to produce particles with diameters of a few nanometres to a few micrometres is referred to as encapsulation. The absolute aim of encapsulation is to thwart the nonspecific outcomes by some nutrients when they come in contact with soil components and to prevent the instability of such nutrients in soil for prolonged period of time, thereby reducing their overall efficacy (Bratovcic and Suljagic 2019). Diverse forms of polymers have been employed for encapsulation for both NFs and nanopesticides which are usually of natural origin such as proteins (e.g. chicken egg albumin, zein, casein, α-lactalbumin, β-lactoglobulin, collagen, gelatin) and polysaccharides (e.g. alginate, carrageenan, xanthan gum, chitosan, modified starch) (Pestovsky and Martinez-Antonio 2017; Sabliov et al. 2015). The process of nanoencapsulation has also been exploited for hydrophobic NF or pesticide candidates (having poor or limited water solubility profile) in order to ensure better stability, improved dispersability in aqueous media and controlled release of the active compound. Further, nanoencapsulation improves pest control efficiency or nutrient delivery and restrains the amounts of dose/treatment in crops and human exposure (de Oliveira et al. 2015; Grillo et al. 2016; Nuruzzaman et al. 2016).

Literature studies have revealed the encapsulation of active agents by microspheres of starch on a matrix having nanopores which verified its flexibility precisely in distribution of the active agents to their target (Larue et al. 2012b). These nanocapsules or microspheres become attached to the heir of bees alike to pollens and keep parasites at bay owing to the controlled release of active agents in a gradual manner. Thus, dissemination and application of nanoencapsulation lead to the least possible usage of active agents and presented extreme defence to bees against parasites. Similarly, nanogels were also fabricated to assist the precise release of pheromones from insects for protection against diversified pests. Further, nanoencapsulation has also yielded favourable effects for improving the therapeutic efficacy of NFs with a substantial decline in the dose of energetic components (Larue et al. 2012a). In order to spot the pathogens and to extend the shelf life of packed foods, nano-biosensors have displayed promising outcomes. Although the extensive and multidimensional applications of nanomaterials in food production and preservation are still evolving, in the current scenario, it seems a far distant dream to fulfil the objectives of global food and nutritional security without the assistance of nanomaterial-based technologies in agro-food industrial sector.

3.2 Coating with a Layer of Nanomaterials

Nanoscale coatings comprise traditional fertilizers coated or loaded with nanoparticles, whereas nanomaterial coatings (also termed as nanomembranes) and porous NFs, respectively, help in slowing down the release of nutrients and include a network of capillary channels that delay nutrient solubility. Various biological microorganisms such as bacteria or fungi degrade these coatings composed of biodegradable polymers or synthetic polymeric materials, consequently permitting the discharge of nutrients and its fixation into the soil. These are generally termed as "controlled release fertilizers" (CRFs), and are available commercially for application to ornamental gardens or lawns for the last two decades in order to enhance the nutrient efficiency of fertilizers. In CRFs, the thickness of the polymer coating and the mix of nutrients that are coated govern the ejection rate of the fertilizer nutrients to the soil for the complete absorption by the plant. Such smart coating nanotechnology applications which allow greater control of the plant over the nutrient release rate have also been touted as "intelligent NFs" (Crawshaw 2010). Further, the large surface coatings of nanopolymers over the biofertilizers improve the distribution of constituent nutrients and act as reservoir for constant supply of plant nutrients. Furthermore, CRFs exhibit great solubility in comparison to slow release fertilizers, but they are covered with such type of components that significantly minimizes the acquaintance of active ingredient resulting in precise dissemination of nutrients.

3.3 Formation of Nano-emulsions

Application of herbicide- or pesticide-based nano-emulsions has been implemented with the aim of providing potential advantages over other conventional techniques, such as robust adhesion to surfaces, better permeability and wide-ranging applicability (Feng et al. 2018). Investigations employing hydrophobic silica NPs to the water-in-oil (w/o) emulsion reported enhancement in the distribution of the product, as well as an improvement in shelf life by reducing desiccation (Kaushik and Djiwanti 2017).

The overall efficiency of NFs is governed by three primary factors, namely, intrinsic (e.g. method of preparation of nano-formulation, particle size and surface coating), extrinsic (e.g. soil depth, soil pH, soil texture, temperature, organic matter and microbial activity) and route of exposure, which affect the overall performance of NFs (Zulfiqar et al. 2019; Solanki et al. 2015; Ma et al. 2018; El-Ramady et al. 2018). Moreover, the exposure route or mode of administration through plant roots or leaves (foliar) also plays a noteworthy role in the absorption, behaviour and bioavailability of NFs. Figure 7.1 describes the methods of preparation of NFs along with factors affecting the potential of NFs.

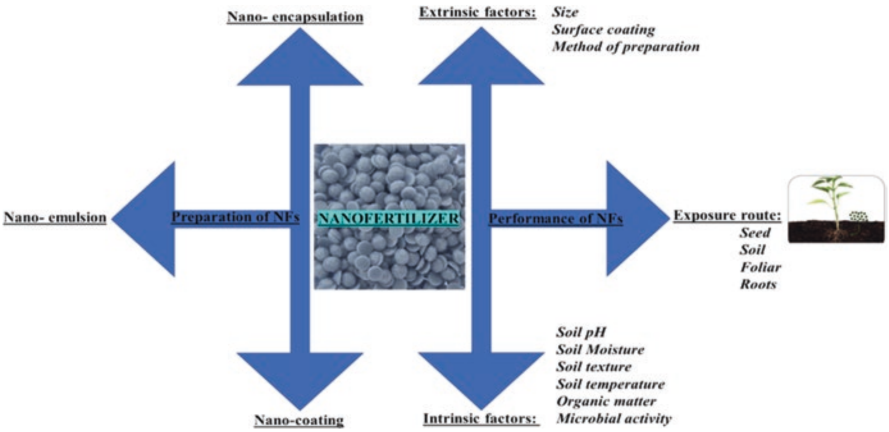

Fig. 7.1 Preparation methods and factors affecting the potential of NFs

4 Classification of NFs

The prime focus of nanotechnological tools in agro-food sector is to revitalize food production with ever-increasing population demand for food, with higher nutritional quotient, quality attributes and safety profile. Therefore, precise release of herbicides, pesticides and plant growth factors can be realized through utilization of nanocarriers as fertilizers which could serve as significant means to improve crop productivity.

Although the application of NFs is still in its infancy (Pulizzi 2019), their usage seems economically more rational as they limit the transportation requirement and application cost. Further, their miniature quantities of NFs used in the soil diminish the risk of loading undesirable salts in comparison to conventional fertilizers. Besides this, in current agriculture, NFs can be merely designed on the basis of nutritional requirements of target sites (León-Silva et al. 2018; Zulfiqar et al. 2019).

On the basis of specific nutritional requirements of plants and properties of nanomaterials employed, NFs can be categorized, namely, as macronutrient NFs, micronutrient NFs, nanoparticulate fertilizers and plant growth stimulating NFs. Apart from the safety and eco-friendly nature of nutrient loaded nanomaterials, these fertilizers coated/encapsulated in the nanocarriers can control the release of nutrients in a precise manner as well as be employed for many other applications, including pesticides, food and drug delivery (Chopra et al. 2014; Kumar et al. 2016; Sotelo-Boyas et al. 2017; Bernela et al. 2018). Figure 7.2 depicts the classification of NFs in accordance with the nutritional requirement of the plants.

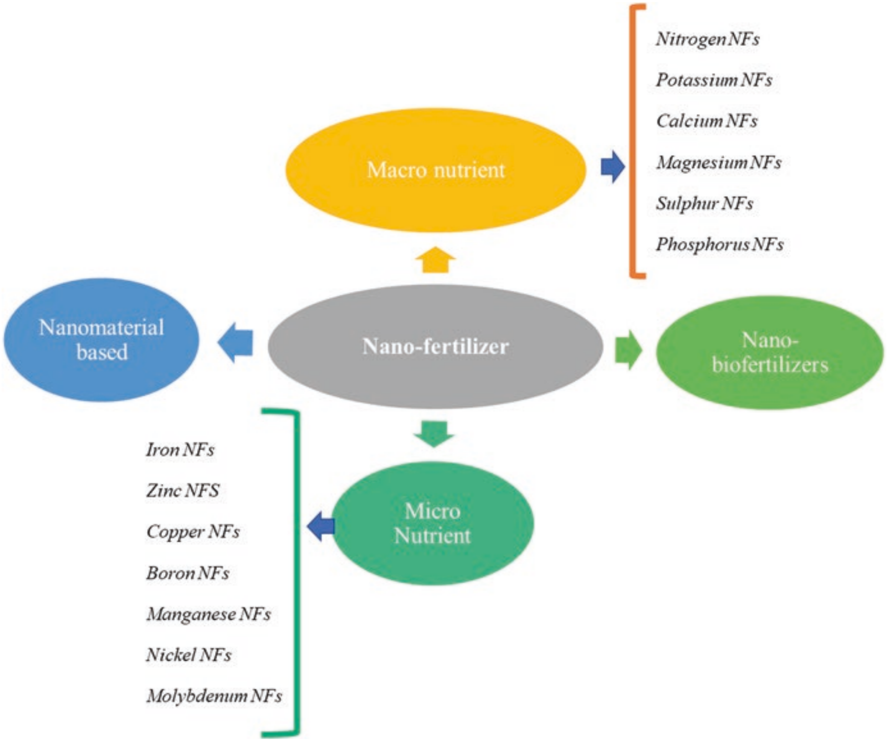

Fig. 7.2 Classification of NFs on the basis of nutrient requirements and nanomaterial properties

4.1 Macronutrient NFs

For plant nutrition, sufficient amount of macro- and micronutrients are indispensable, including oxygen, carbon, hydrogen, phosphorus, nitrogen, calcium, potassium, sulphur and magnesium. Among these, the three (oxygen, carbon, hydrogen) are structural elements and excerpted from the existing environment, while the remaining macronutrients are acquired from soil. Though all the macronutrients are imperative, few prime macronutrients are consumed in higher quantities in comparison to secondary ones. These essential macronutrients (nitrogen, phosphorus, potassium) are considered fertilizer vitals or labelled as “N-P-K” since many years as other macronutrients are considered as secondary.

Nitrogen NFs

Nitrogen is the first and foremost element considered as critical nutrient for plant growth worldwide for its vital role in metabolism and protein synthesis. In contrast to this, the nitrogen use efficiency in agronomical sector still remains <50% owing to loss of excessive nitrogen through denitrification, volatilization and leaching, thereby resulting in nitrogen overuse to accomplish the targeted crop yields and posing great concerns fiscally or ecologically at the global level (Mejias et al. 2021).

Primarily, nitrogen is applied as granulated fertilizers, which usually consequences in substantial losses through surface run-off/leaching, ammonia volatilization and nitrogen oxide emissions. Further, the pervasive practice of conventional nitrogenous fertilizers, such as urea (CH_4N_2O), has alarmed environmental concerns worldwide. The indefatigable efforts for advanced solutions have resulted in the synthesis of novel nanomaterials, ensuing in the growth of potent tools for the progress of innovative technological products. Therefore, nitrogen NFs have been designed to elevate nitrogen absorption by refining the efficiency of nitrogen distribution to plants and dropping its damages to the atmosphere. Further, the evidence on the efficacy of nitrogen NFs in agricultural crops is evolving, and the approaches that can be implemented to circumvent nitrogen losses are yet to be fully elucidated. New scenarios with environmental constraints offer ample opportunities for the application of nitrogen NFs. Hence, more innovative solutions such as NFs, to improve nitrogen use efficiency, to reduce leaching into the environment and for future considerations for agricultural crops, are considered obligatory that can achieve sustained release of nitrogen during crop production. Several studies have advocated the role of nitrogen NFs to obtain high production yield in contrast to conventional mineral urea while minimizing the shortcomings of conventional ones (Milani et al. 2012). The first studies concerning nitrogen NFs were investigated on urea, and use of nano-hydroxyapatite (nHAP) in fertilizer suggestions by Kottegoda et al. (2011) unbolted the pandora box for employing nitrogen carrying nanomaterials in agro-food sector. In this study, a nanohybrid structure based on nHAP encapsulated urea molecules was developed which exhibited significant sustained release of nitrogen from the NFs in contrast to conventional urea (Kottegoda et al. 2011). In another investigation, nHAP encapsulated urea molecules displayed significant impact on both germination of seedlings and early growth of plantlets of *Vigna radiata*, apart from better stability over the time for slower nitrogen release (Subbaiya et al. 2012).

Manikandan and Subramanian fabricated intercalated nitrogen NF formulation and found a consistent rise in growth, yield, quality and uptake of nutrients in maize crop with respect to traditional urea (Manikandan and Subramanian 2016). Further, it has been observed that nanocarriers such as zeolites, chitosan or clay can manage with plant's mandate and release of the nourishment at a retarded rate and ensure better plant uptake and prudent use of nitrogen (Panpatte et al. 2016; Aziz et al. 2016). Because of other parameters such as increase in surface area and capability to harmonize the proclamation of nitrogen, nanozeolites along with its combinations have been broadly exploited for the manipulation of NFs. Furthermore, zeolite-based nitrogen NF not only indicated higher accumulation of nitrogen in plants but also exerted positive effect on intrinsic factors such as soil pH, moisture and availability of nitrogen as compared to conventional fertilizers (Rajonee et al. 2016).

Phosphorus NFs

Phosphorus is another utmost vivacious nutrient for ideal plant growth, apart from its role in root growth and flowering stage. Some of the additional sources of phosphorus fertilizers include bone meal and industrial wastes like Thomas slag or basic slag. Phosphorus is essential for energy storage and energy transfer molecules such as ATP (adenosine triphosphate), ADP (adenosine diphosphate), phospholipids, photosynthesis execution and organic compound formation. It exhibits dynamic role in photosynthesis, respiration and the biosynthesis of DNA (Soliman et al. 2016). It also aids in the plant's ability to survive in unfriendly climatic situations such as resistance to diseases. Although the amount of phosphorus in soils may be much higher than the one desired for plant growth, several factors can limit its availability to plant (Sohrt et al. 2017), such as formation of its complexes with iron, aluminium hydroxides and calcium in the soil or its immobilization with dirt particles in the soil that restricts its availability (Bindraban et al. 2020). It is also a matter of fact that phosphorus in synthetic fertilizers is poorly available and only 10–20% of it is taken up by plants, whereas phosphorus in excess deteriorates the condition by altering the microbial biomass and its proportions with nitrogen and carbon (Fan et al. 2018).

Depending on their solubility profile, phosphorus fertilizers can be categorized into three types: (a) water soluble such as *ammoniated superphosphates* and *monobasic calcium phosphate*; (b) citric soluble, e.g. *Thomas slag*, *dicalcium phosphate*, basic *slag*, *defluorinated phosphate* and *fused magnesium phosphate*; and (3) sparingly soluble phosphate such as *tricalcium phosphates* (Diatta et al. 2018).

Literature studies have proposed the potential application of NFs or release-retarding materials like zeolites to augment the NUE of phosphorus that NFs can steadily distribute phosphorus for 40–50 days subsequent to their administration; on the other hand, traditional phosphorus fertilizers distribute all the components within 8–10 days after their application (Liu and Lal 2015).

Nanotechnological approaches such as nHAP-based NFs respectively resulted in 32.6% growth rate and 20.4% seed yield in soybean plants in contrast to other synthetic phosphorus fertilizers (Liu and Lal 2014). Soliman et al. observed the implementation of hydroxyapatite (HAP) nanocarriers for the delivery of phosphorus which resulted in significant improvement in the growth, chemical contents and anticancer properties of leaves of *Adansonia digitata* plants compared to different sources of phosphorus fertilizers (Soliman et al. 2016). Another study indicated several fold enhancements in fresh and dry biomass, amplified fruit yield, enriched quality and also improved NUE (Patra et al. 2013). Further, the usage of surface-modified zeolites has also been pronounced to endorse the phosphorus use efficiency (Preetha and Balakrishnan 2017). The encapsulation of phosphorus in biodegradable nanocarriers was studied for its activity, and it was found that phosphorus gets absorbed directly through leaves, which eliminates the necessity of binding phosphorus to the soil, so that excess phosphorus should not be accumulated in soil which does not benefit the crop production and yield (Husted 2018). Additionally, polysaccharides such as sodium alginate, carrageenan and carboxymethyl cellulose along with lignin have also been employed to coat water-soluble granular fertilizers in different mass ratios, which effectively controlled the phosphorus release in a sustained manner (Fertahi et al. 2020). Further, Dwivedi et al. have also suggested the role of zeolites as a carrier for improving the solubility and accessibility of phosphorus (Dwivedi et al. 2016). Thus, phosphorus NFs may possibly serve as an appropriate choice for smart agriculture practices, as it maximizes NUE as well as reduces the leaching of phosphorus into groundwater, thereby assisting in improving the crop yield.

Potassium NFs

The third prime macronutrient after nitrogen and phosphorus is potassium, as it exhibits a vigorous monitoring role in the biochemical procedures of plants (such as water uptake, reproduction, photosynthesis, synthesis of protein, activation of enzyme, stomata regulation, water intake, transport of the plant's reserve substances, augmentation of capacity, prompting of the absorption of nitrates, strengthening of cell tissue, encouragement of flowering, synthesis of carbohydrates or enzymes, etc.) which are indispensable for quality assurance, excellent appearance and substantial crop harvesting. Potassium deficiency hugely impacts the growth of root and shoot, the number of seeds inside fruits, size, shape, colour, taste, plant immunity towards diseases, resistance changes in temperature/wind, overall growth and the final crop yield (Preetha and Balakrishnan 2017). Plants with an acceptable level of potassium have been reported to be more resistant to abiotic stresses such as water stress and variable temperatures (Sohair et al. 2018; Wang et al. 2013; Taha et al. 2020). It has been observed that maximum use efficiency of potassium NFs typically ranges between 30 and 50% (Battaglia et al. 2018), which designates that about 50–70% of applied potassium NFs can be vanished, thus instigating considerable commercial losses and damaging effects on soil health and water quality (Czymmek et al. 2020). On the other hand, potassium NF formulation ensures slow potassium release rate as well as losses in soil and thus maintains uninterrupted supply of potassium to crops for a prolonged period (Kubavat et al. 2020).

Similarly, the use of potassium NFs for foliar administration pointedly enriched the growth, number of leaves, product quality, disease and pest resistance and drought tolerance in *Cucurbita pepo* (Gerdini 2016). Therefore, it can be postulated that potassium NFs exhibit the potential to protect soil strength and water quality improvement by dropping potassium losses into soil owing to leaching and thereby helping to enhance physiological and yield traits. Potassium NFs and potassium loaded zeolites were able to enhance the leaf area, grain yield, biological yield, harvest index, potassium concentration and chlorophyll (chl) content, respectively, in *Ocimum basilicum* (Ghahremani et al. 2014) and hot pepper (*Capsicum annuum* L.) (Li et al. 2013). In contrast to conventional fertilizers, potassium NFs delivered higher potassium content in the plants when treated at similar concentrations (Rajonee et al. 2016). In another study, *Lithovit* NF particles existed as a tinny layer on the surface of leaves and penetrated inside after getting mixed with dew droplets at night. It has been observed that these NF particles also promote the supply of carbon dioxide which further led to enhanced photosynthesis and ultimately improve the plant growth or productivity (Attia et al. 2016). It is also pertinent to note here that potassium NF application at the level of 150+150 ppm caused significant rise in the nutrient level of shoots and seeds in peanut plants compared to other treatments (Afify et al. 2019).

Magnesium NFs

Magnesium, a pulsating secondary element after N-P-K for plant growth, composes the central part of the chl molecule and acts as an enzyme activator crucial for photosynthesis. Unfortunately, magnesium has been an undervalued secondary nutrient (also referred to as *The Forgotten Element*) as its deficiency is rarely identified in crops (Cakmak and Yazici 2010). Magnesium NUE is quite low, as it escapes from the soil through leaching mobilization, and prejudiced use of nourishment. Further, its uptake gets affected in the occurrence of cations such as NH_4, Ca^{2+} and K^+ (Gransee and Führs 2013).

Delfani et al. evaluated magnesium and iron nanocarriers for foliar administration in black-eyed pea which exhibited noteworthy effect on yield, leaf iron content, stem magnesium content, stability of plasma membrane and chl pigments noticed for the combination of these two elements (Delfani et al. 2014). Further, it is a well-documented fact that N-P-K are the primary macronutrients; however, their excessive use may lead to disparity of other macro-/micronutrients and unwarranted usage of nitrogen or potassium and phosphorus respectively leading to deficiency of magnesium and disproportion of zinc. Furthermore, pretreatment of tomato roots with magnesium oxide NFs significantly inhibited development of bacterial wilt in tomato roots against *Ralstonia solanacearum* (Imada et al. 2016) and also played a pivotal role as antibacterial agent against *Ralstonia solanacearum* besides additional benefits such as nontoxicity and ease of availability (Cai et al. 2018). $Mg(OH)_2$ nanocrystals have also been exploited for their efficiency in seed germination and plant growth promotion on *Zea mays* which resulted in 100% seed germination and enhanced growth with high magnesium content (Shinde et al. 2018).

Sulphur NFs

Sulphur plays a significant role in plant growth, because it participates in chl formation and upsurges nitrogen efficiency along with plant defence against several diseases. Some of the common sources of sulphur include elemental sulphur (S_8) and sulphates (SO_4^2). Elemental sulphur (S_8) exhibit much higher sulphur concentrations (>90%) with larger particle size; however, it cannot be directly absorbed by the plants, until it is biologically oxidized by soil microorganisms. On the other hand, SO_4^{2-}salts undergo rapid absorption by plants, but it unveils low sulphur concentrations as well as SO_4^{2-} leaching, thereby resulting in significant loss which further leads to environmental toxicity (as the leftover is not sufficient amount required by the crop) (Valle et al. 2019). Therefore, oxidation rate of sulphur can be significantly amplified by reducing the particle size (Germida and Janzen 1993). Thus, to serve this purpose, the necessity of sulphur NFs becomes obligatory and a valuable approach.

Alipour et al. stated insignificant effect of sulphur NFs on different parameters of *Ocimum basilicum* after salt stress (Alipour 2016). Additionally, in a study, green synthesis of sulphur NPs was carried out employing leafy extract of *Ocimum basilicum*, subsequently applied to the seeds of *Helianthus annuus* and irrigated with $MnSO_4$ resulting in low manganese uptake, improved sulphur uptake, eradication of physiological drought and elevated water content of plantlets, which substantiates the efficiency of sulphur NFs (Ragab and Saad-Allah 2020). Besides this, sulphate and chitosan NPs-based N-P-K NFs revealed auspicious results as macronutrient fertilizers in agriculture (Dhlamini et al. 2020; Ha et al. 2019). Silver nanocarriers (Ag-NCs) having size <20 nm exhibit antibacterial properties by attaching to the sulphur-containing amino acids of the bacterial cell membrane which imparts greater permeability and are primarily responsible for its cell death (Slavin et al. 2017; Roy et al. 2019; Guilger Casagrande and Lima 2019). Furthermore, such nanocarriers also react with the phosphorus moiety of the DNA and inhibit its replication and metabolic processes, thereby disrupting cell functions (Liao et al. 2019).

Calcium NFs

Calcium plays a pivotal role in plant activities such as stabilization of cell wall, formation of seed, transportation of minerals in soil and counter-balancing of toxic substances. Foliar application of calcium in fruits with low efficiency did not enhance its concentration in fruits owing to limitations of calcium uptake or penetration in fruits, composition and occurrence of cuticle and lesser translocation of calcium in the phloem (Wojcik 2001; Conway et al. 2001; Mengel 2001; Danner et al. 2015).

Calcium NFs even at smaller calcium concentrations significantly reduced the cracking of fruit in comparison to higher concentrations of calcium chloride ($CaCl_2$). However, the foliar application of calcium did not show any significant changes on crop production, fruit yield and quality (Davarpanah et al. 2018). In contrast to this, calcium NFs sprayed on the apple fruit before harvesting significantly improved the fruit quality and quantity in comparison to spraying with $CaCl_2$ (Ranjbar et al. 2019). Further, foliar application of calcium carbonate in its nano-form resulted in 15 days prior to flowering along with increase in the number of flowers to >50% in *lisianthus* (Seydmohammadi et al. 2020).

Both crystalline and nanocrystalline forms of calcium phosphate (CaP) compounds exist in biological system as well as in the environment as mineral deposits (Dorozhkin and Epple 2002). CaP compounds constitute inorganic elements of biological tissues of living systems in the hydroxyapatite form, to maintain the stability, hardness and functioning of bone, teeth and tendons. CaP, in various crystal forms and their unusual property of hosting a variety of cations (K, Mg and Zn), makes it conceivable for broad applications (Epple 2018). Further, calcium peroxide NCs are capable of eliminating pollutants from soils, speeding up the response rates by augmenting the aspect percentage of responsive surfaces and rendering them applicable for nano-remediation (Khodaveisi et al. 2011). In an investigation, Supapron et al. reported slower release of calcium and magnesium from zeolites, thereby improving its content in soil (Supapron et al. 2007). Various other studies have also shown generation of oxygen during deprivation of NCs from contaminants which expedite an aerobic environment essential for bioremediation (Mueller and Nowack 2010; Sarkar et al. 2019).

Therefore, the application of NFs with all the primary (N, P, K) and secondary macronutrients (Mg, S, Ca) may improve the NUE, when administered at lower doses, and reduced their bulk requirements which escalates environment risk as verified by several investigators on a variety of macronutrient NFs as agricultural involvements (Chhipa 2017; Ditta and Arshad 2016).

Ramírez-Rodríguez et al. attempted the application of multi-nutrient NFs based on nitrogen and potassium ions-doped (CaP) NCs for the release of nutrients in controlled manner in order to devise smart agricultural practices (Ramírez-Rodríguez et al. 2020a). It was observed that NCs exhibited improvement in yield after using 40% lesser amount of nitrogen by weight for wheat plants in comparison to conventional methods. Further, urea-doped CaP NCs on *Triticum durum* plants also displayed superior prospect of nitrogen administration to plants in an extra safe and effective method (Ramírez Rodríguez et al. 2020b). Furthermore, sulphate-supplemented or chitosan-based N-P-K NFs have also indicated encouraging outcomes as macronutrient fertilizers on sustainable agricultural activities (Dhlamini et al. 2020; Ha et al. 2019). Table 7.1 summarizes the effect of different macronutrient-based NFs to improve the NUE and all other important parameters for different plants.

4.2 Micronutrient NFs

Secondary nutrients or micronutrients (e.g. iron, copper, zinc, boron, manganese, nickel, molybdenum, chlorine and selenium) are required in minor quantities, but are very much essential for crop nutrition and growth similar to primary macronutrients (e.g. nitrogen, phosphorus, potassium, calcium, sulphur and magnesium). The deficiency of micronutrients not only affects the crop yield but also results in low absorption of other macronutrients and causes structural problems. Although N, P and K serve as prime nutrients for crop production, their immoderations may also cause misbalancing of the micronutrients; for example, excess of nitrogen and potassium leads to deficiency of magnesium, whereas surplus of phosphorus causes imbalance of zinc.

Therefore, it is mandatory to combine the secondary micronutrients with primary nutrients (NPK), in appropriate dosage regimens and should be administered

Table 7.1 Effect of various macronutrient-based NFs on diverse crops/plants

Macronutrient/ NFs	Technique used	Concentration (mg/L)	Plant/crop	Results obtained	References
NPK	Foliar	100	*Solanum lycopersicum*	Enhanced growth rate and yield	Panda et al. (2020)
	Foliar	10–100	*Oryza sativa*	Boosted rice grain yield by >49%	Dimkpa and Bindraban (2018)
P	Soil	NA	*Oryza sativa*	Greater physiological efficiency of shoots and roots and photosynthetic rate	Miranda-Villagómez et al. (2019)
K	Foliar	NA	*Triticum aestivum*	Improved dry matter yield in saffron	Amirnia et al. (2014)
MgO	Pretreatment of roots	0.007–0.01	*Solanum lycopersicum*	Diminished bacterial wilt disease caused by *Ralstonia solanacearum*	Imada et al. (2016)
$Ca(NO_3)_2$	Foliar	NA	*Vigna mungo*	Upsurge biomass of shoot along with nutrient content	Yugandhar and Savithramma (2013)
N	Soil	NA	*Pennisetum americanum*	Augmented N and P metabolizing soil microorganisms and improved biomass production	Thomas et al. (2016)
CaCO3	Seed treatment	NA	*Vigna mungo*	Enhanced growth root and shoot along with biomass production	Yugandhar and Savithramma (2013)
S	Soil	50–300	*Melia azedarach*	Improved shoot and root growth by 133% and 220%, respectively	Salem et al. (2016)
		150	*Arachis hypogaea*	Upsurge in nutrient content of shoot and root	Chhipa (2017)

(continued)

Table 7.1 (continued)

Macronutrient/NFs	Technique used	Concentration (mg/L)	Plant/crop	Results obtained	References
Ca	Post-transplanting	500, 1000, 2000, 3000 and 500, 750, 1000	*Solanum lycopersicum*	Significantly lessened the detrimental effects of salinity, increased the diameter of stem and flower number	Zulfiqar et al. (2019)
	Seed	2.5	*Vigna unguiculata*	Raised magnesium content in stem, chl content and stability of plasma membrane	Chhipa (2017)
	Sand	160	*Arachis hypogaea*	Ca in stems, protein and soluble sugar upgraded	Bandala and Berli (2019)
Mg	Seed	2.5	*Vigna unguiculata*	More stable plasma membrane, improved chl, Mg content in stem and increased seed production	Chhipa (2017)
	Foliar	0.5	*Vigna unguiculata*	Photosynthesis improved, growth as well as yield	Dimkpa and Bindraban (2018)
K	Foliar	150	*Arachis hypogaea*	Significant rise in nutrient content of shoots and seeds	Afify et al. (2019)
NPK	Foliar	NA	*Solanum tuberosum*	Increased production and quality	Abd El-Azeim et al. (2020)

to crops in order to manage the deficiencies. These nutrients act contrarily in soils; few of them may exist in sufficient amount, but may not be accessible for absorption by plant (e.g. iron and manganese). On the other hand, boron may offer some difficulty to accrue, particularly in sandy soils due to its crusade (Sharma et al. 2017).

Iron NFs

Iron is an imperative cofactor for enzymes which deals with biological processes in plants (Tarafdar and Raliya 2013), and it is present in the soil in high amounts (Talaei 1998), but remains unavailable for the plants, owing to its insoluble form. Therefore, NFs are the sole alternatives for making the iron available for plants (Armin et al. 2014).

Hu et al. demonstrated the influence of diverse concentrations of iron oxide NFs and ferric ions on the physiological variations in *Citrus maxima* plants. Although the study revealed insignificant effect at very low concentrations, not much influence was reported by plants even at very high concentrations (Hu et al. 2017). In an investigation, the foliar application of *Vigna unguiculata* with iron NPs at 500 mg/L significantly enhanced the number of pods per plant by 47%, weight of seeds by 7%, iron content in leaves by 34% and chl content by 10% (Delfani et al. 2014).

In an additional study by Askary et al., the application of iron oxide NFs in plants treated with various concentrations caused a significant rise in growth parameters such as chl and total protein contents (Askary et al. 2017). Further, the evaluation of γ-iron oxide NFs (20–100 mg/L) in watermelon and *Zea mays* increased the chlorine content (Hu et al. 2018). Lower concentrations (0–0.75 g/L) of ferrous oxide NPs were reported to enhance the chlorine content and the levels of lipids and proteins, whereas reduction in these parameters was achieved at higher concentrations (0.75–1.0 g/L) in soybean plants (Sheykhbaglou et al. 2018). Another report which evaluated the effects of nanoscale zerovalent iron on a terrestrial crop, *Medicago sativa* (alfalfa), exhibited higher content of chl in 20-day-old seedlings, while the lignin and carbohydrate contents decreased slightly (Kim et al. 2019). The application of cornelian cherry fruit extract-synthesized ferrous oxide NFs unveiled significant root and shoot biomass encouragement (Rostamizadeh et al. 2020). Further, magnesium and iron oxide NPs have also displayed high photosynthesis proficiency of black-eyed pea (Delfani et al. 2014). Moaveni et al. showed the foliar administration of Mg and FeO NFs on sour tea, which produced alterations in physiological traits and mucilage yield and assisted in improving its physiological properties (Moaveni et al. 2020).

Zinc NFs

Zinc plays a dynamic role in plant growth which acts as a cofactor for several plant enzymes such as isomerases, aldolases, dehydrogenases, transphosphorylases and RNA and DNA polymerases (Hassan et al. 2020; Chaudhuri and Malodia 2017). This element protects the plants against several pathogens (Cabot et al. 2019) and is involved in cell division, tryptophan synthesis, photosynthesis and protein synthesis and also maintaining the membrane structure and potential (Chaudhuri and Malodia 2017). Apart from the limitations of zinc fertilizers in soil fixation, zinc NFs have shown great potential for improvement of crop production yield and quality (Wang et al. 2016). Therefore, appropriate amounts of zinc are essential for different plants for better quality and improved yield. Zinc NFs can be applied to plants using various simple and cost-effective techniques such as direct mixing in soil, foliar spray and seed priming (Narendhran et al. 2016; Sharifi et al. 2016; Khanm et al. 2018; Munir et al. 2018). Davarpanah et al. premeditated the effect of low as well as diverse concentrations of zinc NFs (636 mg) or boron NFs (at 34 mg) on pomegranate and found improvement in the fruit quality along with great yield (Davarpanah et al. 2016). In another study by Moghaddasi et al., the shoot growth and fruit yield were augmented in cucumber seedlings grown in zinc NFs containing nutrient solution in comparison to conventional zinc sulphate fertilizer (Moghaddasi et al. 2013). Also, zinc NFs were designed for the improvement of yield in pearl millet (*Pennisetum glaucum* L.), and it was observed that the development and production of the crop were boosted significantly (Tarafdar et al. 2014).

Zinc oxide NFs at low concentrations (≤100 mg/Kg) mixed with soil resulted in enhanced zinc uptake by cucumber plants, in contrast to higher concentrations (1000 mg/kg) which caused inhibition of plant growth (Moghaddasi et al. 2017). Furthermore, the foliar application of zinc oxide NPs on *lisianthus* enhanced anthocyanin and chl content with an improved number of leaf, branches and flowers (Seydmohammadi et al. 2020). Recently, Abbasifar et al. utilized foliar application of green-synthesized zinc NFs (at a dose of 4000 ppm) as well as copper NFs (at a dose of 2000 ppm), respectively, for basil plants. It was found that copper NPs significantly affected chl content of basil leaves along with maximum flavonoid and phenolic content and highest antioxidant activity with zinc NFs only (Abbasifar et al. 2020). Shebl et al. manufactured zinc, manganese and iron nano-oxide NFs for foliar application employing green chemistry technique with particle size around 20–60 nm and applied on squash plants. The results exhibited that the spraying of MnO NFs on the plants resulted in maximum development of root, shoot, leaf area, fruits, yield and the content of photosynthetic material. The content of organic matter such as protein, lipids and energy was reported highest in squash fruits sprayed with ferrous oxide NFs (Shebl et al. 2019). Iron and Mn NFs were biosynthesized via a rapid and simple technique using microorganism's supernatant containing auxin complex and evaluated as plant NFs. The synthesized NFs revealed to be apposite as micronutrient fertilizers for crop production. Among these, bimetallic manganese oxide/ferrous oxide NFs from bacterial supernatant exhibited the finest outcome on plant growth, especially in germination rates, root growth and fresh weight in maize plantlets giving an idea for using these as micronutrient NFs (de França Bettencourt et al. 2020).

Copper NFs

Copper can be considered as a crucial constituent for several important physiological functions, including respiration, cellular transportation, antioxidative activity, protein trafficking, photosynthesis, hormone signalling of plants (Priyanka et al. 2019) and cofactor of antioxidants such as ascorbate oxidase and superoxide dismutase (Rai et al. 2018). The deficiency of copper leads to various problems such as necrosis; stunted growth; low seed, grain and fruit number; and low crop production. Organic matter in soil impacts the accessibility of copper; therefore, the soil application of copper NFs may prove advantageous owing to their large surface area, high solubility and reactivity (Hong et al. 2015). The administration of copper ions in minor amounts has been suggested for serving the purpose of microelement and stimulating plant growth (Rajput et al. 2018). In recent studies, the field application of copper oxide NFs enhanced the propagation and root growth of soybeans and chickpeas (*Cicer arietinum* L.) (Adhikari et al. 2012). Likewise, the nanocrystalline powders of copper, cobalt and francium (at concentrations of 40–60 nm) had 65%, 80% and 80% sprouting rates of soybean-treated seeds (Ngo et al. 2014). Similarly, diverse concentrations of copper NPs augmented the development and yield of wheat due to expansions in leaf area, chl pigments, number of grains/spike and grain mass; however, enhanced flavonoid content, sulphur acclimatization and proline and glutathione content in *Arabidopsis thaliana* were observed after applying copper NPs with dose of 5 mg L^{-1} (Nair and Chung 2014).

The application of biosynthesized (using *Citrus medica* L. fruit extract) copper NPs (at doses ~20 μg/ml) improved the mitotic index in actively dividing cells of onion (*Allium cepa*) (Nagaonkar et al. 2015). Improvement in stress tolerance in wheat was achieved with the employment of copper nanoparticles as indicated by improved levels of proteins intricated in starch degradation and glycolysis, superoxide dismutase activity, sugar content and Cu content in copper nanoparticle-treated seeds (Yasmeen et al. 2017). A substantial increase in root length, height and fresh and dry weights of pigeon pea (*Cajanus cajan* L.) seedlings was noticed when treated with biogenic copper nanoparticles having 20 nm size (Shende et al. 2017). Encapsulation of copper nanoparticles in CSPVA hydrogels improved the yield, nutraceutical properties and total antioxidant capacity and showed higher lycopene content (Hernandez et al. 2017). Treatment of tomato plants with copper nanoparticles has been reported to produce fruits with more firmness along with enhancement in vitamin C, lycopene contents, antioxidant capacity and activity of superoxide dismutase and catalase (López-Vargas et al. 2018). Foliar spray of copper-chitosan nanoparticles or in combination with seed coating has boosted the yield and growth profile of finger millet plants as well as enhanced defence enzymes resulting in the suppression of blast disease (Sathiyabama and Manikandan 2018). Seed priming of *Helianthus annuus* with copper nanoparticles led to higher content of proteins and oil in seeds (Polishchuk et al. 2013).

Various metals such as copper and silver have been employed for regulating morbific microorganisms owing to their potent antimicrobial properties. Lately, some of the metal nanoparticles, viz. aluminium, copper, gold, magnesium, silver, titanium and zinc, have been revealed to have promising antimicrobial activity and exhibited inhibition of microbial growth through diverse mechanisms (Sánchez-López et al. 2020). The rare crystalline structure which exhibits great surface area enables copper oxide nanoparticles to be an effective antimicrobial agent (Mahmoodi et al. 2018). Further, the high concentrations of copper oxide nanoparticles are essential for their superior antibacterial action (Concha-Guerrero et al. 2014). Furthermore, copper oxide nanoparticles have been also reported to have antimicrobial activity against pathogenic bacteria such as *S. flexneri*, *E. coli*, *S. typhimurium* and *E. faecalis* (Ahamed et al. 2014). In another study, Amiri et al. also conducted an agar diffusion test to evaluate the antimicrobial efficacy of copper oxide nanoparticles against *Streptococcus* mutants and *Lactobacilli* and produced effective results against both the bacterial species (Amiri et al. 2017). Copper oxide NPs, biosynthesized by using papaya leaf extracts, resulted in outstanding antibacterial activity against *R. solanacearum*, a soil-borne pathogen (Chen et al. 2019). Moreover, copper oxide NPs damaged the cell wall of the micro bacteria resulting in leakage of the inner cellular components. It has also been reported to generate toxic hydroxyl radicals which lead to the expiry of the bacteria (Taran et al. 2017). Copper oxide nanoparticles biosynthesized by the actinomycetes and improved antagonistic activity for bacteria were conveyed against some bacterial pathogens (Nabila and Kannabiran 2018). Likewise, Qamar et al. manufactured copper oxide nanoparticles from *Momordica charantia* plants with enhanced antimicrobial activity against various bacterial pathogens such as *Bacillus cereus*, *Corynebacterium xerosis* and *Streptococcus viridians* (Qamar et al. 2020). Some studies have shown the great antimicrobial potential of copper nanoparticles against some bacterial species such as *Escherichia coli*, *Pseudomonas aeruginosa*, *Micrococcus luteus*, *Staphylococcus aureus* and *Klebsiella pneumoniae* and several fungal species such as *Candida albicans*, *Aspergillus flavus* and *Aspergillus niger* (Ramyadevi et al. 2012).

Boron NFs

Boron is also a key element for the development and enlargement of plants, as it involves biosynthesis of the cell wall and its lignifications (Wimmer et al. 2019). It also plays a substantial role in the elongation of pollen grains and tubes, formation of cellular walls, transfer of photosynthetic organisms from leaves to active sites and proliferation in flowers and fruit yields (Davarpanah et al. 2016; Ahmad et al. 2009). Further, it is also indispensable for the development of bark, the transmission of some active hormones that affect the growth of the stem and root levels, germination of pollen, flowering and increasing the level of carbohydrates and transfer to active areas of growth during the reproductive stages. The flowering stage requires its continuous supply, while it should be present in sufficient amount for effective nodulation and nitrogen fixation in legumes (Shil et al. 2007). Boron deficiency can be lessened with the help of fertilizers, but the harmful effect of recurrent fertilizer application disturbs soil fertility and results in environmental pollution. In this viewpoint, nanotechnology has been proposed as an alternative technique, which can be effectively used for boron acquisition (Shireen et al. 2018). Literature studies have implicated the role of boron NFs in improving plant growth and yield. Ibrahim and Al Farttoosi sprayed 0, 90 and 180 mg/L of boron NPs, in which 90 mg/L of boron NPs reported greater plant pod number and seed yield when correlated to conformist fertilizer on mung bean crops (*Vigna radiata*) (Ibrahim and Al Farttoosi 2019). Likewise, nano-boron (20 ppm) and nano-zinc sprayed (at 200 ppm) respectively on olive trees plants produced more fruits with improved oil content in seeds (Genaidy et al. 2020). Similarly, another study stated a larger number of fruits and a higher productivity yield in pomegranate (*Punica granatum*) after the application of boron NFs (at the rate of 34 mg boron per tree) (Davarpanah et al. 2016). Taherian et al. applied boron NFs to alfalfa (*Medicago sativa*) crop under calcareous conditions and harvested maximum yield with suitable forage quality. If concluded, boron NFs can massively improve the quality and yield of crops (Taherian et al. 2019).

Manganese NFs

Manganese possesses a dominant role in many physiological processes by acting as a cofactor of many enzymes; acts as an essential micronutrient in nitrogen metabolism, photosynthesis and the biosynthesis of fatty acids, ATP and proteins; and aids plants to manage different stresses (Palmqvist et al. 2017). Although previous reports have uncovered that the administration of manganese considerably advances the growth and yield of wheat, maize, sugarcane, soybean and common beans, higher doses of manganese may prove fatal to different plants (Fageria 2001; Dimkpa and Bindraban 2016). Manganese NFs can augment the root and shoot growth in mung bean (*Vigna radiata*) by 52% and 38%, respectively, in comparison to manganese sulphate salt, a conventional manganese fertilizer. Maximum growth increment was achieved by using manganese nanoparticles at 0.05 mg/L, and the increased effect was noted in shoot length by 10%, in root length by 2%, in fresh biomass by 8%, in a number of rootlets by 28% and in dry biomass by 100% with respect to manganese sulphate salt (Pradhan et al. 2013). Manganese treatments also boosted the yield of eggplant (*Solanum melongena* L.) by 22% (Elmer and White 2016) and pointedly amplified the root length of lettuce (*Lactuca sativa* L.) (Liu et al. 2016). Manganese NFs (0.1, 0.5, 1 mg/L), when evaluated as a nano-priming agent to improve salinity stress (100 mM NaCl during germination) in *Capsicum annuum* L., have been found to significantly improve the root growth in salt-stressed as well as non-salt seedlings (Ye et al. 2020). However, no prominent effect of manganese NFs on the root length of *Sinapis alba* (white mustard), the germination of seed in lettuce and yield of watermelon (*Citrullus lanatus*) was observed (Landa et al. 2016). At the physiological level, manganese nanoparticles clasp with the chl-binding protein (CP43) of photosystem II, and ultimately enhance the activity of the electron transport chain, affecting the overall efficiency of photosynthesis. Consequently, plants fertilized with manganese nanoparticles have shown a higher rate of nitrogen acclimatization and absorption in contrast to conformist substance applications (Pradhan et al. 2013).

Nickel NFs

Although nickel has been known as a trace element, its uptake is quite imperative for different enzyme activities, for maintenance of cellular redox condition, and several other activities responsible for development such as physiological, biochemical and growth responses (Yusuf et al. 2011). Nickel is required by the urease enzyme which absorbs urea nitrogen into ammonia inside the plant. It also controls absorption of minerals, enzymatic action and several other metabolic progressions of plant. Nickel deficiency induces urea toxicity in which urea gets accumulated inside the tissues which lead to necrotic regions on the leaf tips. Besides this, nickel also possesses systemic fungicidal activity for the management of cereal nuts. Besides this, they also contribute in increasing crop yields (Mahapatra et al. 2022). Nickel NFs of 5 nm at low concentrations of 0.01 and 0.1 mg/L exhibited no effect or stimulated growth in 10-day wheat seedlings although a little surge was noticed in the content of chl after the application of 0.01 mg/L (Zotikova et al. 2018). Biosynthesized nickel NFs' antimicrobial activities were also evaluated and enumerated against a host of pathogenic bacteria such as *Bacillus subtilis*, *Escherichia coli*, *Klebsiella pneumonia*, *Staphylococcus epidermidis* and *Salmonella typhi* and fungi such as *Aspergillus clavatus*, *Aspergillus fumigatus*, *Aspergillus niger*, *Candida albicans* and *Candida tropicalis* (Ameen et al. 2021).

There are a few investigations about the synthesis of nickel NFs from bacteria and fungus. Inoculated microbial strains in the broth along with 1 mM nickel sulphate after 2 days resulted in nickel NPs blend based on the production of subordinate metabolites and proteins, which could diminish the metal campuses to particular metals (Horeyalla et al. 2017). Nickel ferrite nanoparticles have displayed potent fungicidal activity against plant fungi and assist in management of plant disease by improvement in crop growth. These nanoparticles have obtained remarkable results in both plant protection and growth of the plant (Sharma et al. 2017). Such NPs have been appropriately assessed and verified for fungicidal activity against *C. gloeosporioides* and *F. oxysporum* which have been described to inhibit the occurrence of wilt caused by *Fusarium* in tomato, capsicum and lettuce.

Molybdenum NFs

Molybdenum is required in very small quantities (in ranges between 0.3 and 1.5 ppm) for most of plant tissues as low as 0.01 mg/L and 0.20 mg/L for a growing medium. Molybdenum deficiency or toxicity is rare, but its deficiency is commonly found in poinsettias (*Euphorbia pulcherrima*) (Thomas et al. 2017). Molybdenum is important for two enzymes that convert nitrate to nitrite and then to ammonia prior to its use in the synthesis of amino acids within the plant (Mendel and Hänsch 2002). In legumes, it is required by symbiotic nitrogen-fixing bacteria for the fixation of atmospheric nitrogen (Self et al. 2001). It is also used by plants for the conversion of inorganic phosphorus into organic forms. Due to the alluring benefits of NFs, attempts have been made to study the effects of molybdenum NFs as a fertilizer. Taran et al. established colloidal molybdenum NFs and colloidal molybdenum along with microorganisms NFs for chickpea where both were observed to be highly effective in terms of activity, yield and resistance against disease of legumes during unfavourable situations (Taran et al. 2014). Similarly, biosynthesized molybdenum NFs (2–7 nm) at dose of 4 ppm using a fungus *Aspergillus tubingensis* TFR29 have revealed significant development in root area, root diameter, root length, tip number, beneficial enzymes and microbial activities in the rhizosphere, biomass and grain yield (Thomas et al. 2017).

Selenium NFs

Selenium occurs in diverse forms comprising oxyhalides, selenides, halides, oxides, acids, oxyacids, selenoenzymes and selenium nucleic acids (Skalickova et al. 2017). Earlier data has reported it as a toxic element; however, modern investigations have reported its concentration-dependent toxicity (Uttam and Abioye 2017; Meetu and Shikha 2017). Selenium falls in the similar group as sulphur and may be present in different oxidation states. More than one billion people are affected by selenium malnutrition globally; thus, its supplementation in plants as well as animals becomes more crucial for human well-being (WHO 2009). Sewage waste, phosphate fertilizers and farmyard manures are the prominent reservoir of selenium micronutrient (Uttam and Abioye 2017). Selenium nanoparticles exhibit remarkable physicochemical properties and high bioavailability with some vital physiological functions like potential antimicrobial, anticancer or antioxidant properties. These are prominently employed as supplements in plants and food and also extensively utilized in nanomedicines owing to their less toxicity profiles (Hosnedlova et al. 2018). They also perform as detoxifying mediators once they come in contact with heavy metals such as mercury, cadmium or lead; these properties have empowered them to guard living organisms against numerous diseases. Selenium compounds could simply functionalize with ligands such as selenocystin binding with glutathione peroxidase that counteract the free radicals existing in cells, therefore eliminating the detrimental effect of the radicals. However, selenium nanoparticles barely interact with other complexes and are gently released into living systems (Carvalho et al. 2003). Broadly, selenium fertilization can remarkably magnify the production of biochemical compounds such as amino acids, flavonoids, glucosinolates, protein and phenolic compounds (Meetu and Shikha 2017). Schiavon et al. described the improvement in the flavonoid and phenolic content in selenium biofortified tomato fruit (Schiavon et al. 2013). Dinkova-Kostova et al. also reported an escalation in glucosinolates, which hydrolyses to form isothiocyanates that bears outstanding anticancer properties (Dinkova-Kostova 2013). Further, sodium selenite, selenous acid or selenium oxide can be utilized as the precursor compound for the synthesis of selenium nanoparticles and plant substrates from *Vitis vinifera* fruits, *Bougainvillea spectabilis* wild flowers, etc. have been employed (Sharma et al. 2014; Ganesan 2015).

Selenium nanoparticles biosynthesized by *Trichoderma species* unveiled growth-promoting characters in *Vigna radiata* plants (Keswani et al. 2014; Keswani et al.

2016; Barbieru et al. 2019). Table 7.2 summarizes the use of micronutrients as NFs and their impact on different plants. However, their immoderations are damaging the growth of crops, thereby resulting in various nutritional problems.

4.3 Nanomaterial-Enhanced Fertilizers (NEF)

Nanoparticles composed of chitosan and methacrylic acid employed for encapsulation of N, P and K were evaluated on garden pea. It was noticed that the rate of root elongation in plants reduced in a dose-dependent manner along with upregulation of some major proteins at lower concentrations (Khalifa and Hasaneen 2018). Few other NPs, such as TiO, silicon oxide and carbon-based NPs, have been potentially reported to promote the growth of the plant (Chhipa 2017). Similarly, *Lycopersicon esculentum* plants and *Glycine max* also exhibited enhancement in growth and accumulation of nitrogen or seed germination, respectively, once titanium oxide and zinc oxide nanoparticles were applied (Raliya et al. 2017; Changmei et al. 2002).

NPs such as chitosan, zeolites and polymers facilitate considerable enhancements in the absorption of organic nutrients through nanoencapsulation approaches, forming a sustainable rich source of nutrients for the plants (Qureshi et al. 2018).

4.4 Nano-biofertilizers (NBFs)

NBFs embrace a deliberate co-occurrence of a biocompatible nanomaterial and a biological source-driven fertilizer that aims to expedite slow and gradual release of nutrients over a prolonged period for improving NUE and better crop yield and productivity (Duhan et al. 2017; Thirugnanasambandan 2019). NBFs primarily comprise biologically suitable microorganisms like rhizobium, blue-green algae, mycorrhizae and bacteria (such as *Azotobacter*, *Azospirillum*, *Azorhizobium*, *Ascophyllum pseudomonas*, *Beijerinckia* and *Bacillus* species) which along with NFs act synergistically not only by curbing the nitrogen-fixing capacity but also by improving the solubility of insoluble complex organic matter to simpler form. This diverse microflora helps to maintain moisture-absorbing ability of host soil which aids in enhancing the nutrient availability to plants, by maintaining a homogeneous soil texture by replenishing soil and microbial content and augmenting soil aeration and natural fertilization (Itelima et al. 2018). The combined application of NBFs with nanoparticles along with beneficial microbes may ensure delayed/scheduled site-specific nutrient delivery to plants, thus improving the overall activity of NFs.

Although application of NBFs seems innovative and renewable, the assessment of traits such as susceptibility at the nanoscale, field stability, unstable environment conditions (such as fluctuations in temperature, pH sensitivity and radiation exposure), availability of required bacterial strains (along with their vulnerability towards desiccation) and the markedly high amount becomes indispensable for a big zone

Table 7.2 Effect of various micronutrient-based NFs on crops and plants

Micronutrient	Exposure route	Concentration of micronutrient	Plant/crop	Results	References
Fe_2O_3	Spray	0.25, 0.5, 0.75 and 1 g/L	*Glycine max*	Increase in dry weight of leaf, pod and yield	Sheykhbaglou et al. (2010)
	Growth medium	1 g/L	*Lactuca sativa*, *Cucumis sativus*	Increased iron adsorption on the seed surface	Wu et al. (2012)
	Soil	1–6 g/L	*Zea mays*	Improvement in chl pigments and growth	Pariona et al. (2017)
	Growth medium	0.5, 4 g/L	*Arachis hypogaea*	Protein levels improved	Suresh et al. (2016)
	Soil	0.002, 0.02 and 0.05 g/L	*Citrullus lanatus*	Augmented germination of seed, seedling and antioxidant enzyme activity	Li et al. (2013)
Fe	Foliar	0.25, 0.5 g/L	*Pisum sativum*	Improved seed protein, chl content and yield, decreased the firmness of plasma membrane	Alidoust and Isoda (2014)
	Soil	0.25 g/kg and 1 g/kg	*Pisum sativum*	chl and carotenoid content increased, the mass of fresh plant	Mukherjee et al. (2016)
	Foliar	0.05–2 g/L	*Zea mays*	Better growth, quality along with yield	Subbaiah et al. (2016)
	Seed	0.25, 0.50 and 0.75 g/L	*Capsicum annuum*	Heightened root and shoot, seed germination and growth of seedling	Afrayeem and Chaurasia (2017)
	Soil	0.002, 0.004, 0.008 and 0.016 g/L	*Lycopersicum esculentum*	Improved photosynthesis rate and growth, enzymes and proline content	Faizan et al. (2018)
	Foliar	2 g/L	*Helianthus annuus*	Improved leaf surface area, shoot dry weight, chl and Zn content, rate of CO_2 acclimatization	Torabian et al. (2016)
Fe NPs	Foliar	0.5 g/L	*Vigna unguiculata*	Significantly improved the pod number, seed weight, Fe content and chl content	Delfani et al. 2014

(continued)

Table 7.2 (continued)

Micronutrient	Exposure route	Concentration of micronutrient	Plant/crop	Results	References
ZnO	Hydroponic	0.025, 0.05, 0.075, 0.1 and 0.2 g L	*Gossypium hirsutum*	Improved protein content, plant growth, biomass, antioxidant activity, photosynthesis rate	Priyanka and Venkatachalam (2016)
	Soil	1 g/L	*Vicia sativa*	Length of shoot increased	García-Gómez et al. (2015)
	Hydroponic	0.1, 1 g/L	*Cucumis sativus*	Increased germination rate and variation at different concentrations	Zhang et al. (2015)
	Foliar	0.001 g/L	*Pennisetum glaucum*	Improved growth of root and shoot, chl pigments and leaf protein	Tarafdar et al. (2014)
	Foliar	0.001 g/L	*Coffea arabica*	Increased growth, higher biomass production and photosynthetic rate	Rossi et al. (2019)
	Mixed substrate	0.002 g/L	*Triticum aestivum*	Increased biomass production and yield	Du et al. (2019)
	Hydroponics	0.2 μm and 1 μm	*Nicotiana tabacum*	Increased metabolites, growth, enzyme activity	Shang et al. (2019)
	Distilled water	0.005 g/L	*Oryza sativa*	Increased the formation of reactive oxygen species in roots	Wang et al. (2015)
	Hydroponic	0, 0.01 and 0.02 mg/L	*Zea mays*	Improved growth	Adhikari et al. (2016)
	Hydroponic	0.025, 0.01, 0.05, 0.1 and 1 g/L	*Oryza sativa*	Enhanced activity of malondialdehyde, ascorbate peroxidase, superoxide dismutase and proline content	Da Costa and Sharma (2016)
	Soil	≤100 mg/kg	*Cucumis sativus*	Enhanced Zn uptake	Moghaddasi et al. (2017)
	Foliar	NA	*Lisianthus*	Enhanced anthocyanin and chl content with improved number of leaves, branches and flowers	Seydmohammadi et al. (2020)

Micronutrient	Exposure route	Concentration of micronutrient	Plant/crop	Results	References
CuO	After germination	2–100	*Zea mays*	No improvement	Wang et al. (2012)
	Soil	0.08 mg/kg	*Coriandrum sativum*	Accretion of Cu improved	Zuverza-Mena et al. (2015)
	Mixed with soils	<50 nM	*Cicer arietinum* L.	Better germination and root growth	Adhikari et al. (2012)
	Mixed with soils	20 μg/mL	*Allium cepa*	Improved the mitotic index in dynamically dividing cells	Nagaonkar et al. 2015
	Mixed with soils	0.2 g/kg	*Spinacia oleracea*	Enhanced photosynthetic rate and yield	Wang et al. (2019)
	Fruit spray	100 μg/mL	*Prunus domestica*	Limited the symptoms of grey mould (*B. cinerea*)	Malandrakis et al. (2019)
CeO_2	Hydroponic	0.4 g/L	*Cucumis sativus*	Improved content of globulin and scratch	Zhao et al. (2014)
TiO_2	Sand	0.25, 0.5, 1, 2 g/L	*Triticum aestivum*	Unpretentious	Ramesh et al. (2014)
	Nutrition pots	0.05, 0.1, 0.2 mg/L	*Solanum lycopersicum*	Photosynthetic rate, transpiration of water and its conductance improved	Qi et al. (2013)
	Foliar application	0.02, 0.03 g/L	*Oryza sativa*	Better growth and limited cadmium mobilization	Shang et al. (2019)
MnO	Seed	0.00025–0.05 g/L	*Lactuca sativa*	Improved the length of root	Liu et al. (2016)
Mn	Seed	0.05 mg/L	*Vigna radiata*	Increased shoot length by 10%, in root length by 2%, in fresh biomass by 8%, in number of rootlets by 28%	Pradhan et al. (2013)
S	NA	0.5–4 g/L	*Vigna radiata*	Increased dry weight	Patra et al. (2013)
Zn NPs	Foliar	4 g/L	*Ocimum tenuiflorum*	Increased chl pigments in leaves along with phenolic and flavonoid content and antioxidant activity	Abbasifar et al. (2020)
Cu NPs	Foliar	2 g/L	*Ocimum tenuiflorum*	Increased chl pigments in leaves along with phenolic and flavonoid content	Abbasifar et al. (2020)

which limits this technology to a certain extent (Mishra et al. 2017). Such issues also complicate the desired nutrient accessibility to the host plant, which causes a consistent possibility of environmental quality deterioration. Therefore, nanoscale biofertilizers resolve these issues by providing structural protection to biofertilizer nutrients and plant growth-promoting microbes, through nanoencapsulation/coating of nanoscale polymers (Golbashy et al. 2017). The heterogeneous impacts of NBF on soil texture and plant system enzymes manifest significant benefits in enabling improved growth and nutritional quality. The large surface coatings of NPs over the biofertilizer improve the distribution of constituent nutrients.

Further, increased surface area, nanoscale dimensions and higher chemical reactivity of NP-coated fertilizers enable improved interaction and stable chemical texture, thereby allowing efficient uptake via improved bioavailability. Moreover, the steady release from the nanocarriers also ensures long-term availability of administered fertilizers along the diverse stages of plant growth (El-Ghamry et al. 2018). The biological content (microbes) of NBFs gets synergistically benefitted via refining the soil's nutritional content, atmospheric nitrogen fixation, activities of plant roots or rhizobacterium and formation of siderophores for metal chelation, thereby improving the accessibility to plant root, or phosphorus solubilization through phosphorus solubilizing bacterial and fungal strains (Ahemad and Kibret 2014; Mala et al. 2017). The healthy response of NBF administration in crop plants has been reported in a wide array of studies, in terms of improved qualitative as well as quantitative plant growth parameters (Dhir 2017). Table 7.3 summarizes the typical role of NBFs in enhancing plant growth and nutritional content during the last decade.

5 Advantages of NFs over Conventional Fertilizers

NFs (also known as smart fertilizers) exhibit a lot of benefits over conventional fertilizers (as displayed in Table 7.4) for sustainable and eco-friendly crop production regardless of some concerns presented by few researchers regarding the adverse effects owing to their improper usage or application (Tarafder et al. 2020; Iqbal 2019; Zulfiqar et al. 2019; Qureshi et al. 2018; Basavegowda and Baek 2021).

6 Limitations and Risk Management of NFs

Recent progress in the field of NFs for achieving enhanced crop quality and better yield has emerged as one of the spectacular success stories in the agro-food industrial sector. Although the practice of NFs is indisputably opening fresh avenues for smart and sustainable agriculture, their possible menace to plants, soil microorganisms and humans should also be sensibly measured before their commercial application. The extensive use of NFs may have some significant limitations in terms of

Table 7.3 List of NBFs employed in diverse plant applications

NBFs	Exposure method	Concentration (%)	Plant/crop	Result	References
Zinc oxide (ZnO) + (*Pseudomonas fluorescens*)	Foliar	0.02	*Vigna radiata*	Revealed growth in shoot length, biomass of root	Dhoke et al. (2013)
Iron oxide (FeO) + (*Pseudomonas fluorescens*)	Precipitation	0.05	*Triticum aestivum*	The NBF improved the number of spikes and its length, seed number, weight and overall harvesting	Mardalipour et al. (2014)
Iron (Fe) + (*Pseudomonas and Azotobacter*)		0.02			
Zinc (Zn) + (*Pseudomonas and Azotobacter*)		0.04			
Manganese (Mn) + (*Pseudomonas and Azotobacter*)		0.08	*Zea mays* L.	Increased grain yield	Farnia and Omidi (2015)
Chelated (*Phosphorbarvar and Azetobarvar*)		0.03	*Zea mays* L.		
Zinc (Zn) + (*Pseudomonas* bacteria)		1.0	*Zea mays*		
Calcium (Ca) + (*Ascophyllum nodosum*)	NA	4.0	Forage sorghum	Highest Chl$_a$, Chl$_b$, carotenoid and carbohydrates were observed	Biosci et al. (2015)
NPK + (*Rhizobacteria*)	Sol-gel	5.29	*Vitis vinifera*	Overcome the consequences of the abiotic stress with improved quality and yield	Sabir et al. (2014)
Titanium (Ti) + (*Azorhizobium caulinodans*)		0.02	*Triticosecale*	Reduced the damaging effect of ROS along with higher grain yield and weight, chl content	Ghooshchi (2017)
NPK + (*Azotobacter*)	Ultrasonication	–	*Vigna radiata*	Enzyme activities as well as seed vigour index improved	Ruby Celsia and Mala (2014)

Table 7.4 Comparative benefit analyses of NFs versus conventional fertilizers

Advantages	Conventional fertilizer	NFs
NUE	High loss rate during drifting, leakage, overflow	Little loss of nutrients
Controlled release	Additional release of nutrients leads to extra toxicity and causes imbalance in soil	Controlled release
Modified and synthesis as per requirement	Not applicable	Can be manufactured/designed rendering to the nutrient requirements of specific crop
Application of biosensor	Not applicable	Biosensors can be attached to a new smart NFs which can control the delivery of the nutrients according to soil nutrient status
Effective cost	High	Small amounts are required which decrease the cost of transportation and field administration
Loss of nutrients	High	Low
Solubility/diffusion	Low	High
Bioavailability	Low	High
Dispersion of mineral micronutrients	Lesser solubility due to large size	Improved dispersion of insoluble nutrients
Effective duration of release	Used by the plant during administration; the leftover is transformed into an insoluble form	Effective and extended duration
The efficiency of nutrient uptake	Mostly not available for roots and if available the efficacy of nutrient absorption is low	Improved absorption ratio
Soil fertility	Not much involved	NFs improve the soil fertility and design a possible environment for microorganisms
Stress reliever	Low efficiency	Fights against various biotic and abiotic stresses
Soil contamination and environmental hazard	High	Reduced
Antimicrobial activity	Low	New NFs along with microbial flora can be designed for specific use
Fertilizer demand with time	High	Low
Cost-effective	High	Low
Precision	Low	High
Hazardous to the environment	High	Low

the biocompatibility of NFs, which must also be calibrated and assessed critically. In the early phases of crop development, the progress of the crop is directly proportional to the critical concentration of nutrient in the tissue (known as deficiency phase) followed by a rise in the nutrients and no more growth occurs (termed as adequacy phase) and finally when the increased concentration of nutrients in the tissue becomes detrimental for the crops (called as toxic phase) (Mahapatra et al. 2022).

With the dawn of nanotechnological applications in the agriculture arena, it has become fervently imperative to devise vibrant strategies for synthesis, storage, dose regimens, exposure route and proper risk management of NFs, as there is an absolute dearth of regulatory guidelines or standard praxis for the precise calculation of nano-contaminants in farming situation or criteria for their toxicity evaluation. It is a matter of fact that applications of NFs are still in nascent stages, and there are no acceptable scientific regulations that can guarantee or label NFs with no risk (Mahapatra et al. 2022). Therefore, the application of NFs like any other budding technology may have its pros and cons; however, the primary challenge is to reduce the limitations (such as large-scale production, higher cost of production and lack of standardization) after critical assessment of benefit versus environment risk (Aufan et al. 2009; Solanki et al. 2015; Iqbal 2019).

Further on the human health front, it is pertinent to note that NF nanoparticles may enter the human body through oral, respiratory or intradermal routes and even the accretion of these nanomaterials in the environment as well as the food chain could cause significant hazards to human health. Furthermore, it can be implied that these environmental and unanticipated health safety issues may pose obstacles in the application of nanotechnology in crop production. Hence, the design and use of NPs as fertilizers should be systematic in agriculture farming for their long-term effect of bio-accumulation and acquaintance in the plants, which might pose serious impact in the food chain as well (Bundschuh et al. 2018; Tiede et al. 2016).

Additionally, the employment of NPs as fertilizers should address all the safety and ethical concerns (such as exposure on human body or environmental risk) before their commercialization. Consequently, it becomes mandatory to analyse the practicability, risk assessment, risk identification and aptness of new smart NFs for the toxicity evaluation (Bratovcic et al. 2021). Various studies have proposed the pragmatic study of toxicity analysis of CuO and ZnO NFs on soil microorganisms or human health that should be taken into consideration before the application in agriculture settings (Rajput et al. 2020). Further, it was explicated that these NFs may also disrupt biological nitrogen fixation, may impair plant cells or may pose grave hazards to human health. Therefore, a comprehensive analysis of the phytotoxic effects of NFs in plants, their exposure routes, proper usage practices, effect on soil microorganisms and impacts on human well-being should be made mandatory before their possible application of nanomaterials (Seleiman et al. 2021).

7 Conclusions and Perspectives

It is needless to argue that the praxis of nanotechnology has whittled a niche in the agro-food landscape as one of the most expedient contrivances (despite few emerging agricultural and environmental challenges) predominantly associated with the necessities for augmented productivity, sustainability and security of agriculturally produced foods. Such avant-garde applications based on applied nanotechnology exhibit tremendous potential to concoct delivery systems for agrochemicals and plant breeding, thereby reducing the impact on environment and input costs while improving the quality as well as the scale of production yields. In contrast to these beneficial effects, myriad concerns have also emerged related to toxicological hazards and risks associated with application of NFs or nanopesticides (despite controlling the release of active compound, improved plant nutrition and stress tolerance) which primarily include release of nanomaterials into the environment. Several studies and research findings listed in this chapter also highlight the dearth of present level of understanding about the ecotoxicological effects of nanopesticides/NFs. Therefore, in the light of these aforementioned facts, it is warranted to examine the contributing risk factors of nanopesticides/NFs in comprehensive detail by elucidating the mechanism of fundamental steps involved in formulation design of NFs and pathways involved in plant physiology or plant nutrition for the precise and safe application of nanomaterials in agriculture.

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Chapter 8
Nanomaterials for Plants: From Ecophysiology to Signaling Mechanisms and Nutrient Uptake

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1 Introduction

Nanomaterials and advancement in nanotechnology are in limelight for the last few decades due to their remarkable properties to eradicate the bottlenecks in agriculture, biomedical instrumentation, nanosensors, etc., and the list is still growing. Scientists are more interested in these due to their distinctive properties compared to the bulk material. These particles have ranged from a few nanometers to approximately 200 nm. Nanotechnology has been used to improve the growth and development of various plants and control plant disease.

The Food and Agriculture Organization (FAO 2017) has estimated that the population of the world will reach 10 billion by 2050, and approximately 815 million population are undernourished which will increase to 2 billion by 2050 (Usman et al. 2020). These parameters are a key concern to global scientists on how to enhance plant health, physiology, and yield. Researchers found nanotechnology has

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a promising capacity to improve the production and growth of plants. The utilization of different nanomaterials (NMs) has various alterations in plant physiology at different concentrations in different species. Recent studies show NMs improve plant growth, development, germination, vigor, dry weight, nutrient absorption efficiency, and tolerance toward abiotic stresses (Kalteh et al. 2014; Tiwari et al. 2017). Although, there are some limitations of NMs such as effect on soil microbiota, phytotoxicity, etc. which can be decreased by generating these nanoparticles to be more environment friendly by investigating their effect on the surrounding microbiota.

The majority of the publication in the nanomaterial field only talks about the potential toxicity to plants and animals, and only a few of them have investigated nanoparticles to advocate their beneficial effect on plants (Iavicoli et al. 2017). This chapter will discuss the influence of nanoparticles on soil biomass and list some of the nanoparticles and nanomaterials adopted to enhance plant growth and advancement until now and what are the future changes to improve the existing technology. The role of NPs for plant growth and advancement is based on remarkable attributes of NPs and their suitable functional nature which induces plant growth performance via inducing phyto-stimulation, enzymatic activities, plant nutritional status, adaptation against stress, seed germination, etc. (Fig. 8.1), which is briefly reviewed in the following section.

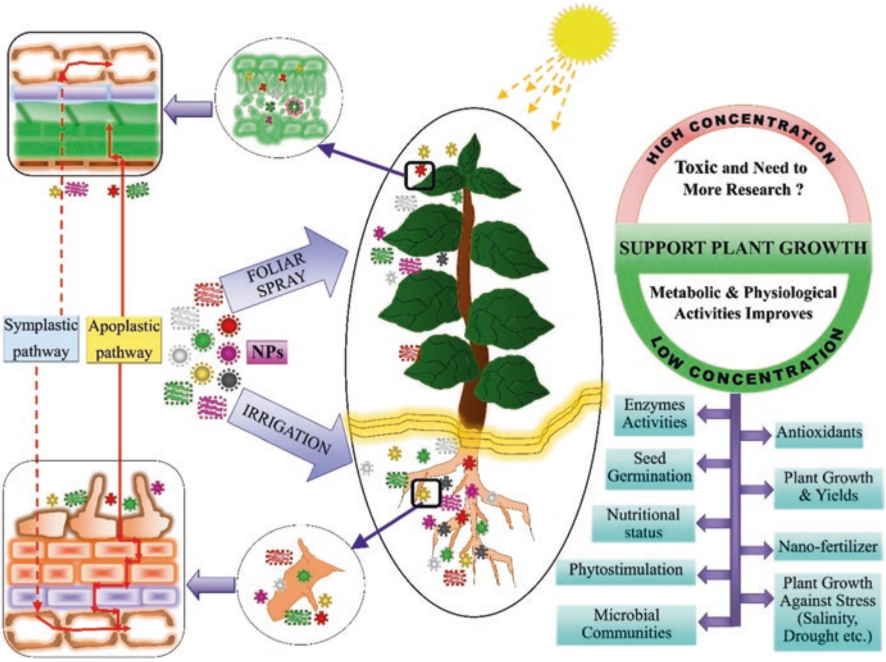

Fig. 8.1 Schematic representation of nanoparticle interaction sites and plant growth promotion activities

2 Impact of Nanoparticles on Soil Biomass

Soil gets elucidated to multiple nano-fertilizers or nanoproducts to encourage the growth and advancement of crops in agriculture. Like Mn, Fe, and ZnO nano-fertilizers (Liu and Lal 2015), the ultimate receptor of such application is soil. After application, these nanoparticles accumulate in the soil and later affect the soil ecosystem. We already know that soil is a living resource that harbors billions of microbial organisms. And this microbial biomass works as an indicator of any microbial variations in soil (Atlas 1984). Soil microbial biomass and their diversity are the main concerns for use of any application (Upadhyay et al. 2019. Because plants and soil are closely associated, thus the influence of soil can easily be noticed in plants and their nutritional quality which later can be located in consumers like animals (Rajput et al. 2018). NPs' accumulation in soil may occur due to other reasons like water remediation technology and indirect release via sewage, air, and sludge (Tourinho et al. 2012). Changes in microbial activity can be determined by quantifying soil respiration and enzymatic activities (Simonin and Richaume 2015). The study demonstrates that soil microbial biomass and enzymatic activities get hindered when the flooded paddy soil is processed with TiO_2 and CuO NPs (Xu et al. 2015).

Similar results were acquired by You et al. (2018), where they examined the saline-alkaline and black soil, which was processed with ZnO, CeO_2, TiO_2, and Fe_3O_4 NPs. The results illustrated those enzymatic activities (invertase, urease, catalase, and phosphatase) and bacterial community are getting changed, and these changes also hinder the biological nitrogen fixation cycle. Many more studies also reveal similar conclusions of NPs on soil microbiota, and here we take those tests to widen our context toward the NPs. The study demonstrates that plate count and inhibition of enzymatic activities of *Azotobacter*, P-solubilizing, and K-solubilizing were found when elucidated to ZnO and CeO_2 NPs (Chai et al. 2015). Cu ions from the Cu NPS are deemed to pose lethality toward both the pathogenic and beneficial bacteria (Lofts et al. 2013). However, there are numerous positive consequences of NPs, which we will discuss in later sections of this chapter.

3 Effects of NPs on Plant Growth and Development

3.1 ZnO Nanoparticles

Evidence from several studies demonstrates that ZnO NPs have a positive effect on plant growth and development. Results from peanut (Prasad et al. 2012), soybean (Sedghi et al. 2013), wheat (Ramesh et al. 2014), and onion (Raskar and Laware 2014) found that ZnO NPs at lower concentration enhance the seed germination, whereas higher doses impaired the germination. Germination and other effects of NPs diverge from crop to crop depending on the strength of application (Siddiqui and Al-Whaibi 2014). For example, de la Rosa et al. (2013) conducted an experiment where they processed tomato seeds, alfalfa, and cucumber with many different concentrations of zinc oxide nanoparticles and observed that only cucumber seed germination was enhanced.

Similarly, Raliya and Tarafdar (2013) showed that there is a substantial improvement in *Cyamopsis tetragonoloba* plant biomass, root growth, shoot growth, root area, chlorophyll, protein synthesis, microbial population in the rhizosphere, alkaline phosphatase, acid phosphatase, and phytase activity in cluster bean rhizosphere (Shoala 2018). Interestingly, ZnO NPs are efficiently exploited in *in vitro* culturing methods also. The study demonstrates that Murashige and Skoog (MS) medium supplemented with nano-ZnO results in promoting somatic embryogenesis, redevelopment of plantlets, shooting, and also inducing the proline synthesis, superoxide dismutase, catalase, and peroxidase activity, thus enhancing the tolerance toward the biotic stress (Helaly et al. 2014).

3.2 TiO_2 Nanoparticles

Recently, researchers found that TiO_2 NPs also improve plant growth and development. It was found that canola seedlings bring about ample growth of radicle and plumule along with better germination after treatment with TiO_2 NPs (Mahmoodzadeh et al. 2013). In underwater deficit stress conditions, TiO_2 NPs-treated wheat plant illustrates an augmented growth and yield (Jaberzadeh et al. 2013). It also controls the activity of enzymes that are involved in nitrogen metabolisms like nitrate reductase, glutamate dehydrogenase, glutamine synthase, and glutamic pyruvic transaminase.

These enzymes assist the plant to absorb nitrate and also advance the transformation of inorganic to organic nitrogen in the form of protein and chlorophyll. This results in increasing the dry and fresh weight of the plant. TiO_2 NPs promote the growth and rapid development of plants also by optimizing the aged seed's vigor, chlorophyll formation, stimulating RuBisCo activity, and enhancing photosynthesis. It also enhances the absorbance of light, protects chloroplast from aging, and prolongs the photosynthetic time (Yang et al. 2006). Above all cited affirmatives of TiO_2 NPs may be due to the enhanced activity of antioxidant enzymes like catalase, peroxidase, and superoxide dismutase by protecting chloroplast from excessive light (Hong et al. 2005).

3.3 SiO_2 Nanoparticles

Nano-SiO_2 also promotes the growth and development of a plant in a different approach from the other nanoparticles. It improves the seed germination in tomatoes at low concentrations (Siddiqui and Al-Whaibi 2014). These nano-SiO_2 enhance the tolerance of crops toward abiotic stresses like salinity or NaCl stress. This tolerance is owing to the accumulation of proline, free amino acids, content of nutrients, and antioxidant enzyme activity under the influence of SiO_2. It also improves leaf's fresh and dry weight, chlorophyll content, and proline accumulation (Kalteh et al. 2014).

3.4 Other Nanoparticles

Similarly, there are more NPs like gold (Au), silver (Ag), cerium (CeO), and carbon nanotubes that promote plant growth and development. But here we will talk about a few of them. For example, AuNPs improve the seed germination in lettuce, cucumber (Barrena et al. 2009), *Brassica juncea* (Arora et al. 2012), *Boswellia ovalifoliolata* (Savithramma et al. 2012), and *Gloriosa superba* (Gopinath et al. 2014). AuNPs also increase the crop yield by improving the number of leaves, leaf area, plant height, chlorophyll, and sugar content (Arora et al. 2012; Gopinath et al. 2014). The report demonstrates that AuNPs also change the level of microRNAs' expression and antioxidant system in *Arabidopsis thaliana* (Kumar et al. 2013).

Biosynthesized AgNPs show significant impacts on hydroponically grown *Bacopa monnieri* by improving seed germination and also inducing protein and carbohydrate synthesis. On the other hand, it decreases the total phenol content and enzyme activity like catalase and peroxidase (Krishnaraj et al. 2012). It is already a known fact that the influence of nanoparticles can be negative or positive, and it is based on factors like concentration, crop type, etc. For example, two contrasting behaviors in plants treated with AgNPs were observed, i.e., root length which was increased in barley whereas inhibited in lettuce crop (Gruyer et al. 2013). Sharma et al. (2012) reported that AgNPs augmented plant root length, shoot length, leaf area, chlorophyll, and protein and carbohydrate contents along with inducing antioxidant enzyme activity in *Brassica juncea*, common bean, and corns.

4 Nutritional Status of Major Food Crops

4.1 Nutritional Status of Cucumber After Treated with CeO_2 and ZnO NPs

Both ZnO and CeO_2 NPs are the most employed oxide nanoparticles. Cucumber is one of the very low-calorie vegetables that contain water, essential nutrient elements, sugar, starch, phenolic compounds, etc. Zhao et al. (2014) compare the impacts of NPs on fruit quality at concentrations of 400 and 800 mg kg^{-1} separately with control (without NPs). Results from the study indicate that the sweetness of cucumber fruit remains unaltered when the plant is treated with CeO_2 NPs. Reducing sugar (glucose and fructose) concentration remains the same; however, nonreducing sugar (sucrose) concentration was modified by CeO_2. At 400 mg kg^{-1} treatment, the content of sucrose decreases noticeably as compared to the control. On the other hand, the content of sucrose noticeably increases at 800 mg kg^{-1} treatment compared to the control. Contrarily, reducing and nonreducing sugar remain unaltered in ZnO NPs treatment at both concentrations. Starch is another important constituent of cucumber fruit; all four treatments show the positive effect of NPs on starch content compared to control.

But at 400 mg kg^{-1} ZnO NPs, the difference was significantly increased. Previously, the report showed that the accumulation of starch and sucrose in cucurbits is owing to copper stress. This could indicate that the increased starch and sucrose in cucumber are also owing to the stress caused by the NPs. Although cucumber is low in protein content, it contains albumin and prolamin as predominant proteins (84–92%) and globulin and glutelin but at very low concentrations. Results showed that globulin content increases significantly by CeO_2 NPs at 400 mg kg^{-1}, whereas at the same concentration of CeO_2, NPs decrease the glutelin content in cucumber compared to control. CeO_2 at 800 mg kg^{-1} did not alter any protein content. More research is necessary to explain the cause behind this concentration-based phenomenon. ZnO NPs increase the globulin and glutelin content at 400 and 800 mg kg^{-1}, respectively. There is no significant effect of ZnO and CeO_2 NPs on the flavonoid content of cucumber. Among the macronutrients, a significant change was observed in the case of Mg. Both ZnO and CeO_2 NPs at 400 mg kg^{-1} increase the 18% and 17% of Mg, respectively. At all concentrations of both CeO_2 and ZnO NPs, molybdenum (Mo) content significantly decreases with a range of 57–76% for CeO_2 and 40–53% for ZnO NPs (Zhao et al. 2014).

4.2 Nutrition Status of Tomato After Treated with TiO_2 NPs

Tiwari et al. (2017) performed an experiment on 2-week-old seedlings of tomato (*Solanum lycopersicum*) in a hydroponic process with different concentrations of TiO_2 NPs (0.5, 1, 2, and 4 g L^{-1}nat.tchernikova2013@yandex.runat.tchernikova2013@yandex.ru). The results from the experiment demonstrate that the growth is nearly enhanced by 50% and also enhances the photosynthetic parameters like chlorophyll content at low concentration (0.5–2 gL^{-1} of TiO_2) compared to control. The activity of catalase and peroxidase enzymes was also boosted in elucidated plants compared to govern, but all these impacts are altered as we uncover plants with different concentrations (Tiwari et al. 2017). TiO_2 NPs are synthesized in three forms, namely, rutile, brookite, and anatase, with specific characteristics (MacWan et al. 2011). TiO_2 NPs have been used in multi-sectors; thus, it is produced in relatively higher quantities about 7800–38,000 tons/year in the USA only (Hendren et al. 2011). A lower concentration of TiO_2 promotes growth, whereas higher concentration of NPs inhibits the root growth due to the acquisition of nanoparticles in the root cells. Macronutrients like P, S, and Mg contents were also improved in elucidated plants with respect to control.

Thus, they are responsible for optimizing the photosynthetic ability of plants as Mg plays a role in chlorophyll synthesis and P is a limiting nutrient that constraints the growth when not accessible in the necessitated quantity. In contrast, the content of Fe was substantially reduced in elucidated plants' root and shoot. The study from the above experiment concluded that Ti NPs interact with plants both in a positive and negative manner. At low concentrations, it promotes growth and overall plant health, whereas higher concentrations produce high oxidative stress in plants and also diminish the growth. TiO_2 NPs at higher concentrations begin accumulating in fruits and pose a threat to food and agriculture.

4.3 Nutritional Status of Maize After Treated with Silica Nanoparticles

Suriyaprabha et al. in 2012 performed an experiment on maize with four different concentrations (5–20 kg ha^{-1}) of silica NPs in comparison with bulk silica (15 and 20 kg ha^{-1}) in sandy loam soil. After the completion of the experiment, they found that Si NPs up to 15 kg ha^{-1} promote the growth in maize, whereas no significant variations in growth were observed at 20 kg ha^{-1}. Higher content of chlorophyll a was observed in nano-silica-treated plants in comparison with bulk silica. Also, the maximum content of chlorophyll was found at the 15 and 20 kg ha^{-1} NPs than any other concentrations of NPs or bulk. Root wt% of maize was also found higher in nano-silica treatments with regard to bulk and control (untreated). It was found that root wt% at 15 kg ha^{-1} NPs was 24.290.4%, whereas at bulk and control, it was 5.6% and 7.73%, respectively. Protein content shows the proportionality relation with the concentration except at 20 kg ha^{-1} nano-silica. Data shows protein content at 5, 10, 15, and 20 kg ha^{-1} NPs (27.31, 27.53, 29.08, 27.09 mg g^{-1}); 15 and 20 kg ha^{-1} at bulk (26.77 and 27.08 mg g^{-1}); and 25.28 mg g^{-1} protein at control.

No particular trend was observed in total phenol content. Phenol content in 20-day-old maize plant found at 5, 10, 15, and 20 kg ha^{-1} NPs (0.192, 0.202, 0.06, 0.422 g Ml^{-1}); at bulk 15 and 20 kg ha^{-1} (0.323 and 0.43 g Ml^{-1}), and at control (0.364 g Ml^{-1}). As a result of this application, SiO_2 starts accumulating in plant tissues. Significant accumulation was found only in the case of 15 kg ha^{-1} nano-silica (19.18%) in comparison with others including control. The contents of total organic compounds like aldehydes, ketones, phenols, etc. are found to be diminished in the leaves of the maize plants grown in the nano-silica-treated soil in comparison to the bulk and control. Hence, it was proved that nano-silica is a better alternative to promote the growth and nutrient content of maize plants in comparison to others. But again, we have to remember that the influence of nanomaterials varies from crop to crop, and these nanomaterials can have both positive and negative effects (Suriyaprabha et al. 2012).

5 Natural Biopolymers and Their Nano-Formulations and Use in Modern Agriculture

Living organisms produce groups of covalently bonded monomeric units in nature called as natural biopolymers, which are biodegradable and thus environmentally friendly and better known as necessity. Later advancements in chemical sciences allow us to produce similar polymers by using biologically originated materials such as proteins, fats, sugars, and amino acids which are known as synthetic biopolymers (Nacu Hernandez et al. 2014). The natural biopolymers possess peculiar characteristics by their folded molecular assemblies and crafted by nature as special and active molecules. Gelatin is a very important biopolymer and belongs to the animal protein group according to the amino acid's backbone. Gelatin is obtained by thermal denaturalization from collagen which is found in bones and skins of animals. Various functional groups such as NH_2, SH, and COOH within its structure make it possible to fabricate into nanoparticles for different purposes in health, food, and agricultural objectives (Ikada 2002).

This material is abundantly found in nature and ensures the availability in low cost; however, the stabilized nanoparticle formulation showed limitations owing to its high thermal dissolution and hydrophilicity (Li et al. 2011). Later technology advances by inclusion of new cross-linking agents and anti-solvents improved the nanoparticle formation from gelatin, although limitations for food grade use and applications were prominent (Tan et al. 2014, 2017). Further utilization of natural cross-linking agents in this series made it possible to use this biopolymer in food and agriculture sectors by reducing the toxicity and improving the stability (Heimbuck et al. 2019; Focaroli et al. 2014; Ramos-de-la-Pea et al. 2016; Semenova et al. 2017; Kim et al. 2005; Gattazzo et al. 2018; Lau et al. 2018; Xin Feng et al. 2019).

Starch and glycogen are also one of the most abundant biopolymers in plants and animals, respectively. Linear polymerization of (14)-linked a-D-glucopyranosyl units makes the amylose and (14)-linked D-glucopyranose chains make the amylopectin, and later these molecules produce the natural starch (French 1984; Glenn 2001). Lower mechanical strength of naturally occurring starch was the major limitation for its commercial use, although later the technological advances by inclusion of nanofibrils in the matrix improved its strength and stability and ensured its broader use in food and agriculture sectors to meet various aims of industrial importance (Curvelo et al. 2001; Wollerdorfer et al. 1998). Their biodegradability, cheaper and large-scale availability, and environmentally friendly properties are enormous and made them excellent biopolymers for various applications in paper industry, textiles, glues, pharmaceuticals, and pesticides as additives.

Cellulose is the most ample natural polymer on earth and made up of $\beta(1 \rightarrow 4)$ linked D-glucose units in a linear manner. Highest fraction of cellulose is noticed in cotton fibers up to 90% and has been adopted for larger industrial sector since a long time (Nishiyama et al. 2002). Plant cell walls are generated up of cellulose and offer remarkable mechanical strength to secondary xylem upon deposition. Nanofibrils of cellulose have been evolved by removing the lignin content by high-pressure treatment and mechanical grinding, which results into 5–20 nm thin and numerous micron meter long nanofibrils. These processed cellulose nanofibrils from several sources like coir, banana, sugar beet, hemp, softwood, and hardwood pulps have been an outstanding material for environmental friendly biofilms for multiple purposes (Zhu et al. 2016; Habibi 2014). Several other biopolymers such as polylactic acid or polylactide (derived from cornstarch, tapioca roots, or sugarcane), poly(e-caprolactone), poly(vinyl alcohol), polyvinyl acetate (PVAc), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) are discovered and examined for additional nanotechnological material development (Sneha et al. 2016).

Chitosan is obtained by deacetylation of chitin which is a major component of arthropod's exoskeleton and cell wall of fungi and carries highly favorable properties (biodegradability, biocompatibility, and non-allegenicity) to make it valuable for sustainable and improved agricultural purposes (Malerba and Raffaella 2016). Chitin is the second most abundant material on earth and thus ensures the availability in higher amount to meet the production challenges. -(14)-Linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit) are randomly distributed in the structural bone of this linear polysaccharide which is obtained from chitin by using an alkaline substrate. Chitosan was introduced for agricultural purposes in the 1980s, but the first report in plants as an elicitor was in pea (*Pisum sativum* L.) and tomato (*Solanum lycopersicum* L.) (Walker-Simmons et al. 1983) with improved stress responses and secondary metabolite contents.

After it was implemented to induce secondary metabolite accumulation in many plant species including sunflower (*Helianthus annuus* L.) (Cho et al. 2008), papaya (*Carica papaya* L.) (Ali et al. 2011), litchi (*Litchi chinensis*) (Zhang et al. 1997), grape (*Vitis vinifera* L.) (Meng and Tian 2009), apricot (*Prunus armeniaca* L.) (Ghasemnezhad et al. 2010), loquat (*Eriobotrya japonica*) (Ghasemnezhad et al. 2011), soybean (*Glycine max* L.) (Khan et al. 2002), tomato (*Solanum lycopersicum* L.) (Badawya et al. 2009), Greek oregano (*Origanum vulgare* ssp. *hirtum*) (Yin et al. 2012), sweet basil (*Ocimum basilicum* L.) (Kim et al. 2005), and spinach (*Spinacia oleracea*) (Singh et al. 2016). There are very few reports on grapevine with chitosan application. Combined impact of chitosan with yeast showed reduced decay of fruits during cold storage (Meng and Tian 2009), and in vitro-cultured grape plantlets supplemented with chitogel (1.75% v/v) demonstrated improved growth and protection against fungal pathogen *Botrytis cinerea* (Barka et al. 2004). Elicitor responses of chitosan on grapevines under field condition has been demonstrated recently (Singh et al., 2019, 2020; Silva et al., 2020).

In spite of these studies, basic process behind this interaction is still not apparent and needs further attention and detailed study. Recently, foliar use of chitosan demonstrated enhanced fruit weight, productivity, and resistance against fungus in tomato (Sathiyabama et al. 2014; Sathiyabama and Charles 2015), improved yield and vegetative growth in strawberries (EL-Miniawy et al. 2013), and improved quality and shelf life in red kiwifruit (Kaya et al. 2016).

Preparation of nanoparticles of chitosan is extremely simple and viable process, although the studies on its implication in plants are very limited. Chitosan nanoparticles have been observed to induce total phenolics and upregulation of antioxidant enzymes and defense relevant genes in *C. sinensis* (Swarnendu et al. 2015). Despite having numerous unique properties, ability of chitosan can be enhanced by utilizing it as a nanoparticle which is easy to expand and exert on plants. Nanoparticles of chitosan may induce the secondary metabolism pathways more effectively as compared to standard molecular form. Despite being very popular among agriculture scientists, chitosan nanoparticles application in the form of elicitors on plants to investigate its effect on secondary metabolite content are limited. In spite of modulating many biological responses in plants, mode of action of chitosan/nanoparticle is not yet fully unraveled and urgently necessitates an inclusive metabolomic, transcriptomic, and proteomic tests to know the intricate mechanism behind. Recent reports from our group demonstrated the nanotechnology application in agricultural sciences (Rajput et al., 2021a; Faizan et al., 2021; Kolesnikov et al., 2021; Shende et al., 2021) and has been reviewed for their potential impacts (Rajput et al., 2022; Verma et al., 2022; Rajput et al., 2021b, c, d).

6 Conclusion

This chapter presented some of the new nanomaterials being deployed to increase the nutritional quality and plant growth promotion. So far mostly metal or metal oxide nanoparticles have been adopted for plant growth responses. Lately, some carbon-based nanomaterials have also been adopted for their impact on plant growth. To deploy all the nanomaterial-based bio-stimulants, large-scale studies have to be conducted to assess their effect on the local biome. Also, certain nanomaterials have a good impact on one plant crop, whereas they are toxic to other species; because of this, the researchers need to understand the mechanism of plant growth promotion by nanomaterials to safely deploy them in the field. The future is certain that shortly we will be utilizing nanomaterial-based fertilizers and disease control solutions to minimize the impact on the surrounding biome and increase crop production to meet the growing demand.

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Chapter 9
Nano-biosensors for Plant Biomass: Concept and Applications

Sanjam Chandna, Kunal Gogde, Ravneet Kaur, Varsha Sagar, and Jayeeta Bhaumik

1 Introduction

A biosensor is a device that measures both chemical and biological reactions through the generation of signals, which are directly related to the concentration of the analytes (Jędrzak et al. 2018). Currently, biosensors are employed in various applications including drug discovery and disease monitoring, along with the detection of harmful micro-organisms and pollutants (Li et al. 2021). Figure 9.1 explains the various components of biosensors, including their classification and applications.

A typical biosensor consists of the following components:

- *Bioreceptor*: In a biosensor, bioreceptor is a molecule that specifically recognizes the analyte (Burcu Aydın et al. 2020). For instance, enzymes, deoxyribonucleic acid (DNA), cells, aptamers and antibodies are some important examples of bioreceptors (Abid et al. 2021). Moreover, when the bioreceptor interacts with

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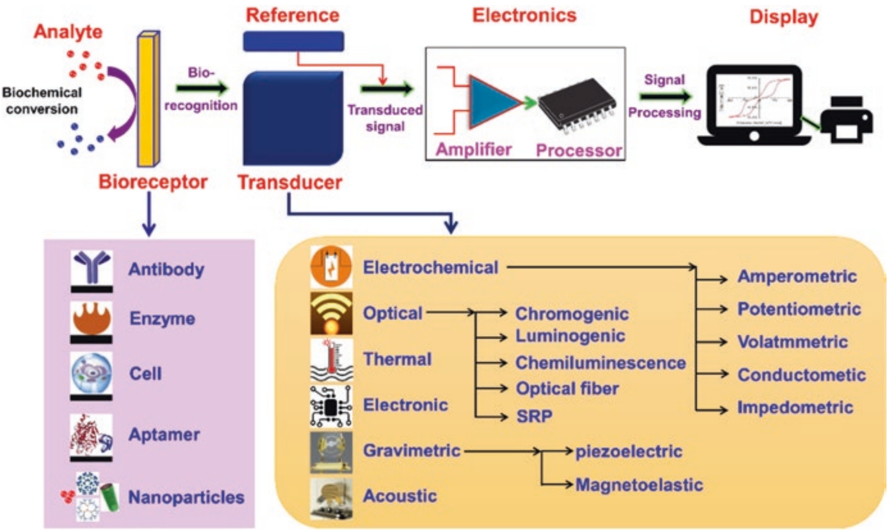

Fig. 9.1 Biosensors: components, classification and applications. (Reproduced from Naresh and Lee (2021))

the analyte, the signal is generated (in the form of heat, light, mass, charge or pH change, etc.). This process is known as biorecognition (Karunakaran et al. 2015).

- *Analyte*: Analyte is the substance of interest which needs to be detected through biosensing approach. For example, in a biosensor designed for the detection of glucose, the 'analyte' is glucose (Xiao et al. 2019).
- *Transducer*: The element that leads to the conversion of one form of energy into another is known as transducer. A transducer converts the biorecognition phenomenon into a measurable signal, and this process is known as signalization (Rakesh et al. 2019). Most transducers lead to the production of either electrical or optical signals (Ahmed et al. 2014).
- *Electronics*: The part of a biosensor that does the processing, signal transduction and preparation for display comprises the electronics. It comprises complex electronic circuitry that leads to signal conditioning (Khan et al. 2020). Moreover, the signals are amplified and converted from analogue to digital form. This is followed by quantification of the processed signals by the display unit of the biosensor.
- *Display*: A user interpretation system which produces curves or numbers or the liquid crystal display of a computer comprises the display system (Sireesha et al. 2018). For display part, a combination of software and hardware is required, which is used for generation of results of the biosensor in a manageable approach. On the display, the output signal can be an image, graphic, numeric or tabular, which highly depends upon the requirements of the end user (Sireesha et al. 2018).

The research in biosensor field started in the 1960s by the pioneers Clark and Lyons, when they created the first biosensor for the measurement of glucose in

1962. The materials used for the immobilization of an enzyme and its assembly mechanism on electrode surface significantly affect the performance of an enzyme electrode (Jędrzak et al. 2018). Various techniques such as covalent coupling, drop-casting, physical adsorption and encapsulation are generally utilized for the immobilization of the enzyme on electrode surface (Putzbach and Ronkainen 2013). The 3S that characterize the good-working biosensors are selectivity, sensitivity and stability. For the creation of a novel biosensing system for transfer between an electrode and an immobilized enzyme, these 3S are important (Jędrzak et al. 2018).

Biosensors having high sensitivity and selectivity, along with a low detection limit (attaining pico−/nanomolar concentrations of biomolecules), are important for evaluating physiological and metabolic parameters in plants (Krishnan et al. 2019). Over the last decade, various kinds of materials have been employed for designing highly efficient biosensors to detect different types of analyte biomolecules (Krishnan et al. 2019). However, for the development of highly efficient sensing technologies, the key aspect lies in the thorough understanding of the biorecognition and transduction mechanisms (Semenova et al. 2019). Therefore, designing of analytical approaches for gaining deeper insights into the bio- and electrochemical processes would lead to significant acceleration of progression in the field of biosensors (Wongkaew et al. 2018).

This book chapter will discuss about the latest developments in nano-biosensors for monitoring plant growth and detection of pathogenic infections, pesticides, abiotic stress, heavy metals, some contaminants and genetically modified plants. It will also give insights on various nanomaterials along with the detection methods used by the researchers.

2 Nano-inspired Biosensors: An Innovative Approach

Advancements in the field of nanotechnology have been helpful to develop biosensors with extraordinary performance (Wu et al. 2019). The unique customizable and tunable properties of the nanomaterials such as electrical conductivity and optical activity render them capable of providing important functional properties to the biosensors (Yao et al. 2014). Moreover, better shock bearing capability of the nanomaterials offers ultra-sensitive responses/detection mechanisms to the nano-biosensors (through the measurement of relevant properties such as thermal, optical, electrical and piezoelectric). Therefore, nano-biosensors have attained a vital role to enhance the quality of life through different environmental, clinical and quality-controlled applications (Kumar and Arora 2020). Nanomaterials are largely defined as materials that comprise particles in the aggregated or individual state, in which at least 50% of the comprising particles have dimensional range between 1 nm and 100 nm (Simeonidis et al. 2020). Last decade has witnessed the nanomaterials' driven extraction, concentration and analysis of environmental contaminants, pollutants and novel functional devices (Zhang et al. 2019).

The utilization of nanomaterials in the development of various biosensors leads to an increase in the sensitivity of these systems. By designing the interaction between the nanomaterial-based transducer and the biological element, we can have biosensors that can be employed for wide usage in detecting disease diagnostics and biomolecules in plants (Tiwari et al. 2016). These devices can quickly analyse various environmental samples for pesticides and microbial contamination. Different nanomaterials (e.g. metal and metal oxide-based, polymers, composites, etc.) are utilized in the form of nanotubes, nanoparticles, quantum dots, nanowires and nanorods leading to faster detection and reproducibility in an effective way (Karimi et al. 2016). Figure 9.2 illustrates the different types of nanomaterials being utilized to develop nano-biosensors.

Below are the various nanomaterials which are being applied by researchers in biosensing applications:

- *Carbon-Based Nanomaterials*

Among various carbon-based nanostructures, graphene oxide is considered as the most appropriate choice for the detection of systems due to its various properties like being biocompatible and cost-effective and having natural source (Mokhtarzadeh et al. 2017). An interesting advantage of the carbon-based nanomaterials is the ability of surface modification, in order to be an efficient host for immobilization of various entities such as enzymes, ligands, etc. (Das et al. 2017). Graphene is known to be made up by mechanical exfoliation of graphite; however, graphene oxide (GO), which includes phenol hydroxyl, carboxylic and epoxide groups, can be produced by graphite oxide (Guo et al. 2011).

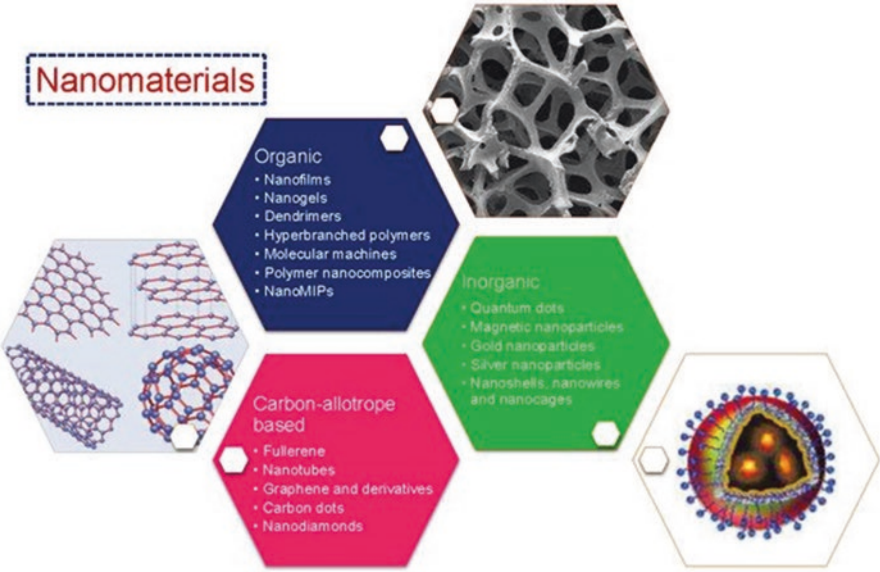

Fig. 9.2 Different nanomaterials are utilized for the development of nano-biosensors. (Reproduced from Pirzada and Altintas (2019))

Carbon nanotubes (CNTs) also provide an interesting area of scientific research owing to their various properties, such as electrical, thermal, chemical and mechanical behaviour (Cha et al. 2013). There is high utility of such carbon-based nanomaterials in the field of biosensors. To the interest of researchers, CNTs play a relevant role in the development of biosensors, which have the ability to detect the target molecules in trace amounts (Zhu et al. 2012).

Carbon dots (CDs) comprise another important class of carbon-based nanomaterials, which are zero-dimensional quasi-spherical nanoparticles and are primarily composed of carbon and oxygen (Chen et al. 2021). CDs usually have size below 10 nm and have attained enormous attention due to their optoelectronic properties similar to quantum dots (QDs), especially when it comes to fluorescence (Chen et al. 2021; Alas et al. 2020). However, CDs have high biocompatibility (unlike QDs) owing to their low toxicity and ease of synthesis (Chen et al. 2021).

- *Silica-Based Nano-biosensors*

Along with having wide surface area, silica nanoparticles are known to have stability in various chemical as well as thermal conditions. Moreover, they are known to possess appreciable compatibility with different biomolecules, such as proteins (Tang et al. 2012). Many biomolecules, such as peptides, antigen-antibodies and DNA can be linked to silica nanoparticles, which render these nanomaterials exceptional elements for incorporation into bio- and immunosensors (Knopp et al. 2009). Additionally, the biocompatibility of silica nanoparticles and optoelectronic properties make them important in development of nano-biosensors for various applications (Chen et al. 2018).

- *Metal and Metal Oxide Nanomaterials*

Metallic nanoparticles (MNPs) such as silver, gold, platinum, copper or aluminium are being widely used to develop the nano-biosensors (Ahmad et al. 2015). These nanomaterials possess interesting properties such as easy surface functionalization, large surface area and surface plasmon resonance (SPR) phenomena (Abdel-Shafy and Mansour 2018). Moreover, they are reported to have non-linear spectral properties and good conductivity that are employed for the development of colorimetric, optical, biomolecular and electronic systems (Jain et al. 2020). Owing to their broad absorption spectrum which makes them good acceptors for FRET (fluorescence resonance energy transfer) processes, MNPs are also considered to be admirable quencher agents in various fluorescent systems (Yao et al. 2014).

The metal oxide nanomaterials which are widely used in biosensing include titanium dioxide, iron oxide and zinc oxide nanomaterials. Among the metal oxide nanomaterials, zinc oxide (ZnO) is currently being majorly used in development of various sensing platforms (Kumar et al. 2015, Shanmugam et al. 2016). ZnO is known to have piezoelectric properties, which allows it to play efficient role in some special sensors called mechanochemical (Parangusan et al. 2018). Moreover, ZnO is known to be an innocuous material along with being environmentally friendly and biocompatible, which allows it to be employed without special necessities in the clinical field (Figueira et al. 2019).

- *Metal-Organic Frameworks*

Metal-organic frameworks (MOFs) of materials consist of a network of oxides or metal ions (known as nodes) which are efficiently connected by organic molecules (Yuan et al. 2018). Owing to their high porosity, large surface area and thermal stability, MOFs have received considerable attention in the last decade. They are also known as porous coordination polymers. Moreover, they can be presented in 3D or 2D structures and have been utilized lately for the detection and quantification of degradation products from environment (Pastore et al. 2018). There are different materials that can be developed from the combination of different organic molecules and nodes, which gives rise to different properties to the developed nano-biosensors.

- *Quantum Dots (QDs)*

Quantum dots (QDs) are zero-dimensional semiconductor crystals. QDs are known to possess fluorescent properties, which highly depend on their size and composition (Yan et al. 2013). Moreover, QDs are found to be better than traditional fluorescent compounds, as they have a narrow emission bandwidth, a wide excitation spectrum and a fairly strong fluorescence emission (Xu et al. 2018). The photoluminescence and surface properties of QDs determine their utilization for the development of optical biosensors (Xu et al. 2018). Generally, upon the interaction with an analyte, mediated by a bioreceptor, a turn-on (increase) or turn-off (decay) of the emission is generated (Costa-Fernández et al. 2006). Currently, research in carbon-, silver-, silicon- and indium-containing QDs has revealed superior biocompatibility of these materials (Xu et al. 2018).

3 Applications of Nano-inspired Biosensors

Nano-biosensors are being widely used in various spheres, plant ecosystem being one of them. Integration of nanotechnology with biosensors significantly increases their applicability in different dimensions. Herein, we discuss the research conducted in the relevant fields for the development of nano-biosensors and their efficient utilization.

3.1 Detection of Pathogenic Infections

Micro-organisms including bacteria, viruses and fungi have been an important part of our lives since ancient times. Various micro-organisms have been exploited to produce a wide range of products due to their ability to reproduce rapidly. Detection of the disease-causing pathogen is of the utmost importance for successful cure of the disease (Syam et al. 2012). Microbial detection commonly requires particular techniques and instrumentation such as nucleic acid detection, hemagglutination detection analysis cell culture assay, antigen and antibody assay and gene sequencing (Mokhtarzadeh et al. 2017). However, the above-mentioned analysis methods are time intense, expensive and laborious, therefore are not appropriate. Therefore, there is requirement of cost-effective and easy technique for pathogen detection that does not require complex instruments and laboratory setup and requires less time so that the disease can be cured on time.

Nano-biosensors comprise a probe made up of a biological material (nucleic acid/protein) that recognizes the target, a transducer that provides the signal, an enhancer that multiplies the signal and an output (Jyoti and Tomar 2017). Nano-biosensors utilize the magnetic, chemical, electrical and optical properties of materials to detect pathogens. Nano-biosensors are suitable for field detection of pathogens, require less time and are cost-effective. Figure 9.3 shows how DNA is collected and processed to detect pathogenic bacteria from samples. Nano-biosensors are the nanosensors used for the biological sample analysis. Nano-biosensors show high sensitivity, specificity and rapidity for sample analysis. Some pathogens show low infections that cannot be detected using traditional methods, but nano-biosensor can detect such pathogens due to their high sensitivity. The primary aim of nano-biosensors is the detection of biochemical and biophysical signals associated with a particular disease. They can also be combined with other technologies. Figure 9.3 illustrates the various types of nano-biosensors utilized for sensing and diagnosis of plant pathogens.

Plant pathogens can adversely affect the global food grain production and under some circumstances can lead to the complete failure of crop (Khiyami et al. 2014, Kashyap et al. 2019). Currently, plant/crop pathogen detection techniques include visual observation, microbial culturing, bioassays, microscopic analysis, serological assays and various molecular techniques (Kashyap et al. 2019). Nanoparticle-based nano-biosensors offer enhanced detection limits in the diagnosis of diverse classes of diseases caused by bacteria, fungus and viruses (Shende et al. 2021). Different types of nanomaterial are used for the detection of plant pathogens. Figure 9.4 explains various types of nanomaterial and techniques used for plant pathogen detection.

Detection of Bacterial Pathogenic Infections

Bacteria are single-celled invisible organisms (1–2 μm) which cannot be seen with naked eye. Bacteria associated with plants could either be helpful or harmful depending upon their types. Bacteria live either on the surfaces or inside the plants. Bacteria are normally invisible but in huge number get aggregated to form biofilm on plant surface (Vidaver and Lambrecht 2004).

Mostly plant-associated bacteria are beneficial; however, some are known to cause plant diseases (Jackson 2009). Some plant-associated bacteria are *Xanthomonas*, *Pseudomonas*, *Agrobacterium*, etc. Gold nanoparticle-based immunoassay was reported for *Ralstonia solanacearum* (causes brown rot in potato) detection (Razo et al. 2019). Similarly, a silica nanoparticle-based nano-biosensor was reported for detection of *X. campestris* (causes bacterial spot).

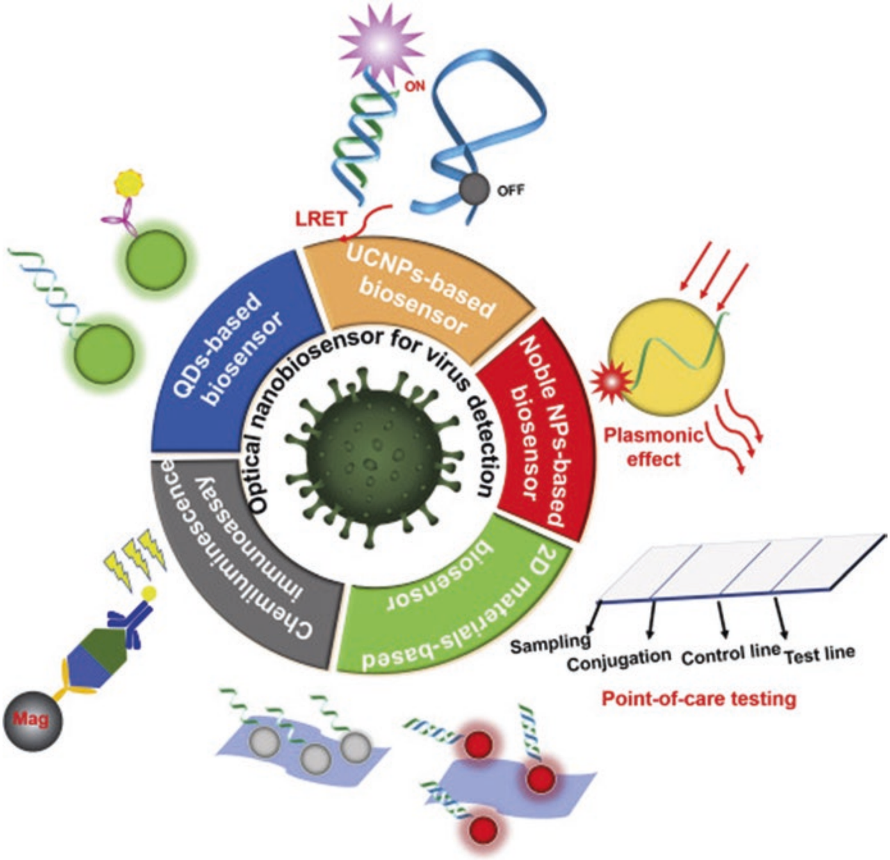

Fig. 9.3 Schematic representation of use of different types of nanomaterials for plant pathogens diagnosis. (Reproduced from Song et al. 2021)

Bacterial plant pathogen diagnosis utilizing nano-biosensors is in very early stage. Figure 9.4 explains the procedure for detection of plant pathogen utilizing nano-biosensor (Li et al. 2020). Despite availability of the nano-biosensors for bacterial detection, they are not utilized much for plant bacterial pathogen detection. Diagnosis of plant bacterial infections still relies on conventional methods. Great scope exists in the field of the nano-biosensors for bacterial detection in plant infections.

Detection of Fungal Pathogenic Infections

A major amount of infections are caused due to fungi in plants, leaf blight and downy mildew being most common among them. A chromium and gold thin film based surface plasmon resonance (SPR) immunosensor has been developed for

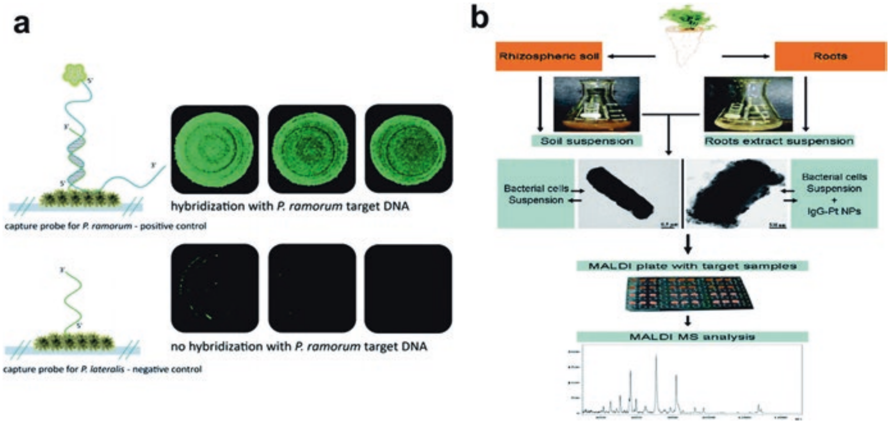

Fig. 9.4 (**a**) Fabrication of metallic nanoparticles for preparation of nano-biosensors for plant pathogen detection; (**b**) Flowchart describing method for bacteria detection using nano-biosensor. (Reproduced from Li et al. 2020)

Pseudocercospora fijiensis detection in banana (Luna-Moreno et al. 2019). A SPR-based immunosensor was fabricated for recognition of HF1 protein of *P. fijiensis*. Potato is an important crop which suffers loss due to fungal infection caused by *R. solani*, *S. subterranea*, *S. endobioticum*, *A. solani*, *C. coccodes*, *Fusarium* spp., etc. In order to diagnose the fungal diseases caused by these pathogens, qPCR-based microarray was reported (Nikitin et al. 2018). Yellow rust is the common fungal infection in wheat which is triggered by *Puccinia striiformis*. Timely detection of the *Puccinia striiformis* fungal infection in the early stage is very important for crop productivity. Zheng et al. have developed optimal spectral indices based diagnosis method for diagnosis of *Puccinia striiformis* (Zheng et al. 2019).

Late blight infection caused by *Phytophthora infestans* is very common in potatoes and tomatoes. Gold nanoparticle-PCR-based biosensor has been developed by Zhan et al. (2018) to detect *P. infestans*. The nano-biosensor was used to detect infection in *P. infestans* infected leaf and stem. Fungal infections in plants cause severe losses; therefore, accessibility of sensitive, fast and simple methods for easy and early detection is extremely significant. Most of the research related to fungal detection in plant-focused mainly on gold nanoparticle-based nano-biosensors. There is vast scope for the use of other comparatively less costly nanomaterials in diagnosis, which will further reduce the diagnosis cost.

Detection of Viral Pathogenic Infections

There has been constant increase in infectious diseases due to emergence of viruses such as *Cucumber mosaic virus (CMC)*, *Pantoea stewartii*, *Plum pox virus (PPV)*, *Prunus necrotic ringspot virus (PNRV)*, *Citrus tristeza virus (CTV)* and *Potato virus x (PVX)* (Kumar and Arora 2020). These viruses generate serious infections in population in a brief time interval. Detection of the viral pathogen is essential for timely and effective cure of infection leading to prevention of diseases (Narayanasamy 2010) (Narayanasamy 2010). There are different diagnostic methods that have been utilized for the detection of the infectious viruses. These diagnostic methods including enzyme-linked immunosorbent assay (ELISA), antigen diagnosis, antigen-antibody agglutination assay, electron microscopy and some molecular strategies are reported for the detection of viruses utilizing immunoassays (Narayanasamy 2010). Nano-biosensors have been utilized to improve the traditional diagnostic methods due to the simplicity of the procedure as well as instant response in a few minutes. Recently, a gold nanoparticle inspired biosensor was designed for detection of *Tomato yellow leaf curl virus* (Razmi et al. 2019). In another study, researchers have reported gold nanoparticles-based immunoassay was reported for *Potato leaf roll virus* detection (Panferov et al. 2018). In a similar type of study, gold nanoparticles were used for development of immuno-chromatographic biosensor for detection of *Grapevine leafroll-associated virus 3* (Byzova et al. 2018). *Interestingly,* SPR gold surface chip was utilized to detect *Barley stripe mosaic virus* in leaves of wheat crop (Florschütz et al. 2013).

In order to achieve better management of infectious diseases, development of nano-biosensors is an important area of research. Through nanotechnological interventions, the diagnosis of pathogenic infections has been achieved with high sensitivity. The progress in this diagnosis field is picking up speed, and extensive research have been carried out in order to develop novel nano-biosensors for the diagnosis of various infectious pathogens. However, critical market analysis has concluded that diagnosis of infectious diseases will continue to be the critical area of nano-biosensor applications.

3.2 Monitoring Plant Growth

Plant hormones or phytohormones play a vital role in the regulation of plant growth and metabolism by influencing the physiological processes at low concentrations (Isoda et al. 2021). Along with this, they have responses to both biotic and abiotic stresses. They are usually chemical messengers and each of them has a unique role (Isoda et al. 2021). The phytohormones including cytokinins (CK), auxins, abscisic acid (ABA), gibberellins (GA), ethylene (ETH), jasmonates (JA), brassinosteroids (BR), salicylic acid (SA), strigolactone (SL) and some peptides present new families of phytohormones. These hormones are known to be signalling molecules for plants, which act as biomarkers (Isoda et al. 2021).

Nano-biosensors have been emerging as significant tools for monitoring plant signalling pathways and metabolism. These sensors are sensitive to a physical or chemical stimulus (acidity, heat, metabolism transformations) which can detect signals and measure chemical fluxes even at the single-molecule level (Prasad 2014). These devices can confer information about the endogenous concentration and endogenous fluxes of plant hormones (Prasad 2014). Moreover, development of various genetically encoded biosensors has been carried out that also have the unique ability for the detection of rapid changes in the distribution and concentration of phytohormones in living plant cells (Isoda et al. 2021)

Scientists working from 1999 to the date across the globe reported that nano-biosensors can be used for the molecular detection of phytohormones associated with monitoring plant growth. In 1999, Kugimiya and Takeuchi et al. developed a piezoelectric sensor that can detect indole-3-acetic acid (IAA) and provided a linear relationship between frequency shift and its amount in the nanomolar concentrations (Kugimiya and Takeuchi 1999). Indole-3-acetic acid is the natural auxin phytohormone which plays an important role in cell growth and cell expansion of stem as well as in morphogenesis, organogenesis and cell proliferation (Isoda et al. 2021). Su et al. (2019) demonstrated label-free and sensitive electrochemical immunosensor for identifying and detecting indole-3-acetic acid by utilizing a glassy carbon electrode with gold nanoparticle-coated porous graphene layer. These highly dispersed AuNPs have also been reported to significantly improve amperometric biosensing performance.

Additionally, a group of researchers have developed a self-referencing IAA microsensor utilizing surface modifications of platinum black and carbon nanotube (CNT). Interestingly, various optimization measures were employed in this sensor for non-invasive measurement of endogenous IAA flux near the *Zea mays* root surface, without the addition of exogenous IAA. Thereby, the oscillating IAA influx and efflux within this boundary layer surface could be detected. It was found that the majority of the transport occurred near the distal elongation zone (McLamore et al. 2010). It has been previously reported that electro-polymerized safranine T (PST) film can strongly attract indole-3-acetic acid. To enhance the electrochemical response of indole-3-acetic acid, they have done the fabrication of stainless steel microelectrode by the polymerized safranine T film (PST) (Fig. 9.5).

Li et al. (2018) have utilized sol-gel-alginate-carbon composite electrode (SACE) and reported a renewable amperometric immunosensor for the detection of phytohormone β-indole acetic acid. Figure 9.6 depicts an immunoassay procedure involving amperometric measurement performed by the immunosensor. The developed immunosensor was used for determination of β-indole acetic acid (IAA) in plant samples (Li et al. 2003)

Jasmonates are fatty acid-derived cyclopentanones that include jasmonic acid (JA) and its various derivatives (Giraldo et al. 2019). They coordinate the several types of biotic and abiotic stresses responding to plant health and development (Giraldo et al. 2019). A group of researchers have reported a JA perception biosensor (termed Jas9-VENUS), for quantifying the dynamic changes in JA distribution in response to stress with substantial spatiotemporal sensitivity. Interestingly, the developed quantitative sensor Jas9-VENUS showed the high-resolution spatiotemporal data regarding hormone distribution which are responses to plant abiotic and biotic stresses (Larrieu et al. 2015).

Many techniques have been evolved for the quantitative detection of phytohormones such as flow injection fluorimetry, gas chromatography-mass spectrometry (GC-MS), capillary electrophoresis-chemiluminescence, high-performance liquid

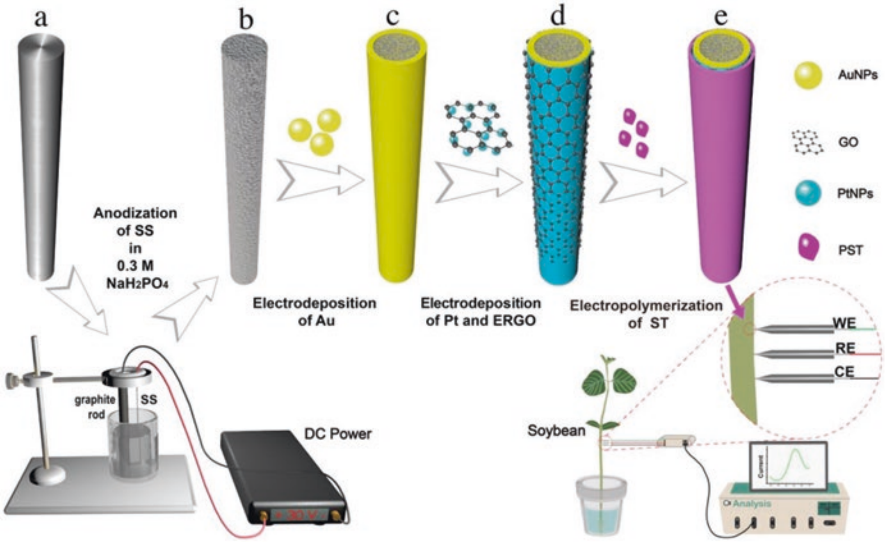

Fig. 9.5 Stainless steel (SS) microelectrode involving the fabrication: bare SS (**a**), a-SS (**b**), Au/a-SS (**c**), Pt-ERGO/Au/a-SS (**d**), PST/Pt-ERGO/Au/a-SS (**e**). SS stainless steel, AuNPs gold nanoparticles, ERGO graphene oxide, ST safranine T, PST poly-safranine T, PtNPs platinum nanoparticles. (Reprinted 2018 Elsevier Ltd. Reproduced from Li et al. (2018))

chromatography (HPLC/MS), enzyme-linked immunosorbent assay (ELISA) and visual colorimetry. A wide range of phytohormonal nano-biosensors with different principles has also been developed (Wang et al. 2017). Its advancement makes it very useful to detect ultralow level of phytohormones by utilizing nanomaterials. Moreover, they are fast in determination as compared to the previously reported techniques (Wang et al. 2017). For the future scenario, different signalling molecules that can be targeted for novel nano-biosensor development would be salicylic acid and isoprenes.

Salicylic acid is involved in plant growth and development, thermogenesis and plant pathogen defence. Reactive oxygen species and salicylic acid are the key signalling molecules that are produced by chloroplasts and accumulated by the plants. Therefore, these phytohormones could act as plant health indicators. By applying the advanced technology, novel phytohormonal nano-biosensor can be developed and explored for phytohormone dynamics (Li et al. 2019).

3.3 Detection of Abiotic Stress

Exposure of plants to the deleterious environmental factors including extreme temperatures, salinity, drought, pollutants, flooding, high salinity, UV radiation, wounding, heavy metals, etc. poses a negative impact on the plants. This causes abiotic

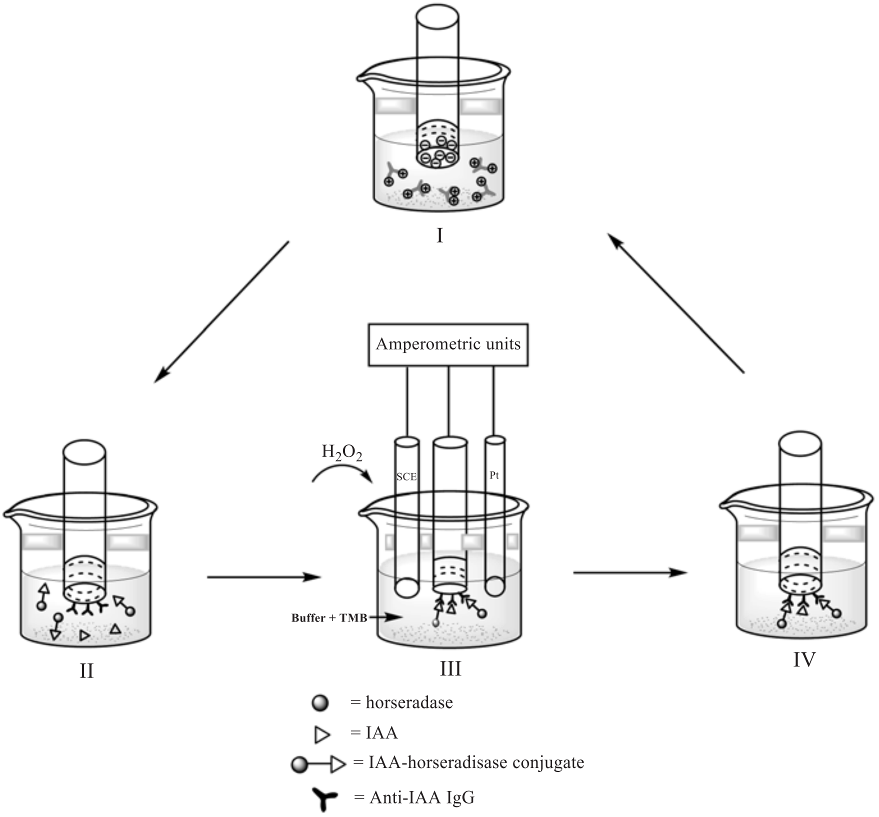

Fig. 9.6 An immunoassay mechanism involving the antibody, i.e. immobilized on the surface of the SACE: (I) Anti-IAA IgG antibody self-assembled SACE. (II) Incubation involving competitive immunoreaction. (III) Amperometric quantification. (IV) Reconstruction of the SACE. (Reproduced from Li et al. (2003))

stress to plants, which leads to the retarded growth and loss of crop production in plants (Gull et al. 2019). Intensive studies on distinct molecular levels such as genomic, transcriptomic, proteomic and metabolomics have been carried out for the identification of abiotic stress prevalence and response mechanism to them (Piasecka et al. 2019).

Subsequently, it has been revealed that such changes are based on biochemical and physiological processes originated by the extreme environmental factors (Zhuang et al. 2014). During the initial stages of the recognition of abiotic stress, an important role is played by phytohormones (Wani et al. 2016). Owing to the high prevalence of signalling compounds (ethylene, abscisic acid, etc.), oxidative stress signalling is initiated in plant tissues (You and Chan 2015). In response, the plant initiates intensive synthesis of compatible solutes such as glycine, proline, betaines or sugars possessing osmotic properties along with the compounds with strong

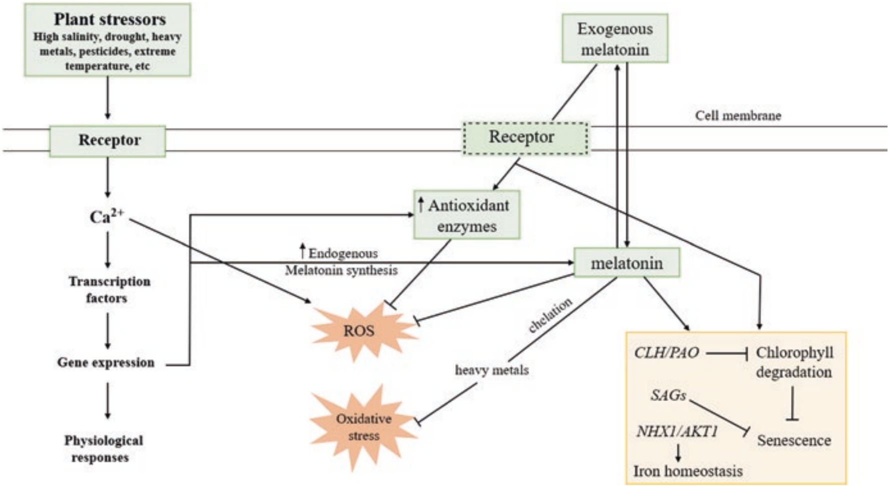

Fig. 9.7 Involvement of abiotic stress in plant physiology. (Reproduced from Reiter et al. (2015))

antioxidative properties and in essence, a decline in stomatal conductance (Sharma et al. 2020). The oxidative stress leads to different processes, which start after signalling pathways, explained in Fig. 9.7 (Devireddy et al. 2021).

Numerous disadvantages such as long assay time, high maintenance and expensive instruments, complicated sample preparation, non-portability, non-versatility and poor sensitivity have caused the emergence of better sensing technologies to overcome the cons of conventional methods. With the profound understanding in the field of nanotechnology (owing to the unique tunable physiochemical properties), the development of nanostructures such as nanowires, nanoparticles, nanotubes and nano-rods has offered various advantages over traditional methods such as faster detection, better reproducibility and versatile ultra-sensitive responses. Until now, numerous nano-inspired techniques are being developed using microneedle patches, nanopore sequencing platforms, plant wearables and nanoparticle- or array-based sensors for the diagnosis of abiotic stress (Dar et al. 2020; Li et al. 2020; Kumar and Arora 2020).

The state of art attained in the diverse fields of microelectromechanical system (MEMS) technology and nanotechnology have led to exponential growth in the field of novel nano-biosensor development. Plant wearables have emerged as a new frontier of plant diagnostics, serving the purpose with the selective slender and ultra-lightweight nano-biosensor for versatile attachment directly on plant tissues for continuous surveillance. For instance, Nassar et al. have done transfer printing of 180-nm-thick gold electrodes onto flexible polyimide (PI)/polydimethylsiloxane (PDMS) substrate for fabrication of a butterfly-shaped multisensory platform (Nassar et al. 2018). This aided in the necessary localized study of the surrounding microclimate, i.e. temperature and humidity. Additionally, the vapour-printed polymer electrodes were developed, for long-term monitoring of environmental factors such as drought and photodamage, which offers the opportunity to be directly printed on living plant tissues (Kim et al. 2019). Oren et al. reported an easy and universal method to record the water evaporation from plant leaves by manufacturing graphene-based nanomaterials with a strategy of patterning and transferring them onto various types of tape to develop flexible microscale sensors. The mechanism of this nano-biosensor relies on the changes in graphene's electrical resistance in varied humid conditions (Oren et al. 2017). Quantum dots (QDs) have shown promising potential as optical nano-biosensors for the detection of abiotic stress. Various factors accounting for an ideal nano-biosensor, which include unique and advantageous photophysical properties along with a zero-dimensional size of QDs (1–10 nm), make them ideal fluorescent probes. Chen et al. developed a paper-based fluorescent (Tb (III)-CD) probe for the detection of 3′-diphosphate-5′-diphosphate, produced in plants in response to extreme environmental conditions (Chen et al. 2018).

Array-based nano-biosensors are capable of multiplexing as well as discrimination of various structurally similar analytes or their mixtures, due to advantageous assembly of cross-reactive sensors or several chromophores. A group of researchers have developed a gas sensor platform based on capacitive micro-machined ultrasonic transducer (CMUT) array for the detection of volatile organic compounds (VOCs) released from plants under distinct abiotic stress. In order to increase the selectivity, the elements of the CMUT array were functionalized by employing materials such as polymers, phthalocyanines and metals. Among others, 1-Octanol appeared to display the strongest across different channels. The results calculated manifested the classification of gases with an accuracy of 97% even at low concentrations. However, the study also included the humidity level to compute the ambient atmosphere for plants.

3.4 *Detection of Genetically Modified Plants*

Despite accomplishment of the Green Revolution in agriculture, hunger and malnutrition persist (Hazell and Wood 2008). Additionally, the gradually increasing population along with other external factors such as inappropriate socioeconomic infrastructure leads to deforestation, soil erosion and pollution (Hazell and Wood 2008). Therefore, all these factors lead to the emergence of another revolution for the survival of humankind. Notably, the gene revolution approach includes the revolutionary biotechnological advances in plant breeding with a sole purpose of improving agricultural yields (Kumlehn et al. 2018). Therefore, the origin of genetically modified (GM) crops that acquire genes that are artificially inserted instead of the plants acquiring them through sexual means was developed (Kumlehn et al. 2018).

Various conventional techniques are available for the detection of transgenic crops, which include western blots, southern blotting, enzyme-linked immunosorbent assay (ELISA), polymerase chain reaction (PCR, multiplex PCR, qPCR, etc.), microarrays, strip tests including biosensors, etc. (Neethirajan et al. 2018). These traditional methods have certain drawbacks, which include being cost-ineffective, labour-intensive, time-consuming, etc. (Neethirajan et al. 2018). The era of revolutionization through the advancement in nanotechnology has refined the performance of the biosensor, such as high sensitivity and selectivity, portability, need for sample preparation prior to DNA-based sensing and multianalyte detection in single run. In addition, most recent nano-biosensor research for transgenic plants are based on the principle of optical and electrochemical transduction mechanism owing to the properties exhibited by nano-range materials (Stobiecka 2013).

Lv et al. have also synthesized a QDs-DNA nano-probe integrated by Mn-doped ZnS room-temperature phosphorescence (RTP) quantum dots (QDs) and DNA (Lv et al. 2017). Further, on the basis of the phenomenon of phosphorescent resonance energy transfer (PRET), an RTP sensor was built using the synthesized probe for the quantitative detection of CaMV 35S GMOs sequence. In another study, a homogeneous process of fluorescence resonance energy transfer (FRET) between CdTe quantum dots (QDs) and multi-walled carbon nanotubes@ graphene oxide nanoribbons (MWCNTs@ GONRs) was utilized for synchronous monitoring dual targets DNA of P35S and TNOS from transgenic crops (Li et al. 2017).

Until now, for the detection of GM plants, nano-biosensor-based different optical methods such as RAMAN spectroscopy, surface plasmon resonance (SPR), fluorescence-based spectroscopy are available. A study performed by Grzeskowiak et al. based on SPR, amplified by the functionalization of AuNPs on SA sensor chip, was developed for the detection of transgenic tobacco plants carrying a *Streptococcus mutans* antigen (Grześkowiak et al. 2019). A second type of biotinylated probe was layered over SA-functionalized AuNPs for the enhancement of sensitivity. The reduction in cost and time of the analysis process was possible because of skipping the DNA amplification step (one of the advantages of nano-inspired biosensors).

Since many decades, electrochemical biosensors have been a vogue among researchers working in the area of biosensors. A group of researchers have strategized a novel proposal for the ultra-sensitive detection of specific gene sequence of MON89788 in transgenic soybean sample by developing an electrochemical sensor (Chen et al. 2019). They have utilized AuNPC/DNA-labelled multiple probes which accounts for the enhancement in sensitivity of the analyte. Thus, the limit of detection was achieved to be 4.5×10^{-17} mol L^{-1}. Additionally, the study displayed the recoveries from 97.3% to 102.0%. Another group of researchers reported the first study on the development of quantitative point-of-care testing (POCT) (Gao et al. 2019). The modelling of the so-called electrochemical immunosensor employed for the detection of CP4-EPSPS present in the GM crops includes a portable bio-inspired analytical device integrated with a disposable screen-printed carbon electrode (SPCE) for POCT.

3.5 Detection of Pesticides

The introduction of nanomaterials in sensing technology has led to invention of new signal transduction technology. The immobilization of nanomaterials onto the surface of sensor generally forms novel interfaces that enable the sensitive optical or electrochemical detection of analytes. However, various issues including the desired reliability and repeatability in trace level detection, availability of the nanomaterials sensitive to common pesticide residues, ease of sensor fabrication techniques and instrumentation, cost and issues related to nanomaterial exposure to the surrounding environment need to be considered (Songa and Okonkwo 2016).

The subsequent rise in pesticide usage has proven to be fatal not only to pests, but their residues are deteriorating and creating havoc in the health of living beings including humans (Dhananjayan et al. 2020). The diverse range of the pesticide include compounds such as insecticides, fungicides, rodenticides, herbicides, molluscicides, nematicides and plant growth regulators (Dhananjayan et al. 2020). Dyspnoea, pulmonary oedema and eye and skin irritation account for the acute exposure effects caused by pesticides, whereas the chronic exposure effects lead to more fatal consequences such as carcinogenesis, mutagenesis, pre- and postnatal damage and reproductive system damage (Karalliedde et al. 2000). Therefore, it has become the need of the hour to track and detect the biocidal in order to ensure the safety of humans. Fluorescence polarization immunoassay, multienzyme inhibition assay, liquid chromatography-mass spectrometry and high-performance liquid chromatography are the conventional methods employed for detecting pesticide residues (Zhao et al. 2019). Unfortunately, these methods are complicated, laborious and time-consuming and require sophisticated instruments and trained personnel for operation.

Additionally, these techniques are incapable of onsite/in situ application and multiple sample analysis. Due to significant advancements in nanotechnology, the transformation has directed the development of nano-inspired biosensors. Owing to improved sensitivity, selectivity and multiplexing capacity, the conventional technology has been replaced by emerging nano-biosensors for monitoring the trace amounts of pesticides.

The demand for biosensor development using enzymes as recognition elements has risen because of the feasible integration of enzymes with nanomaterials. Such systems are being used to detect pesticides by various researchers (Saini et al. 2017). A group of researchers have performed an ultra-sensitive electrochemical detection study for the detection of organophosphates (OPs) in real samples using polyaniline (PANi) and carboxyl functionalized multi-walled carbon nanotubes (FMWCNT) (Nagabooshanam et al. 2020). The results showed LoD of 10.2 ng/L with sensitivity 0.58 mA/ng/L/cm^2 for methyl parathion (MP) and 8.8 ng/L with sensitivity 0.41 mA/ng/L/cm^2 for chlorpyrifos (CPF).

The stability of the sensor was for a period of 30 days. Another group of researchers built an enzyme immobilized glutathione (GSH)-capped CdTe quantum dot (QD)-based fluorescence assay for the detection of organophosphate pesticides (Korram et al. 2020). The sensor is based upon the principle of GSH-capped CdTe QDs showing enhanced sensitivity towards H_2O_2, which is produced from the active enzymatic reaction of choline oxidase (CHOx) and acetylcholinesterase (AChE), resulting in the fluorescence (FL) ‘turn-off’ of the GSH-capped CdTe QDs. In the presence of organophosphate (OP), a ‘turn-on’ FL of the CdTe QDs at 520 nm was observed. The FL changes of the GSH-capped CdTe QD/AChE/CHOx biosensor indicated the amount of OP pesticides. A highly sensitive enzymatic biosensor for the detection of chlortoluron was reported, which was based on herbicide-induced inhibition of tyrosinase activity (Haddaoui and Raouafi 2015). To develop the sensing platform, ZnO nanoparticles were utilized to electrochemically nanostructure the tyrosinase-modified screen-printed carbon electrodes (SPCEs).

4 Conclusion and Future Perspectives

For rapid and inexpensive detection/analysis of several analytes from plant biomass, biosensors have been considered as an important analytical tool. Enormous transformations in the emergence of biosensors have been observed in the last decade, which has led to the sophistication of sensing technology. Moreover, the integration of nanotechnology into biosensors has led to rapid development in this field and has led to a huge rise in interest in nano-biosensor-based research.

However, the emerging market trend is behind the corresponding technological advancements, despite exponential outgrowth in research and academics of nano-biosensor-based publications. Conclusively, future work in nano-biosensors should majorly focus on minimizing the cost involved in the development of nano-biosensors. This may involve a shift towards the utilization of bio-inspired approaches for the development of nano-biosensors. Moreover, the difficulties associated with the assembly of nano-biosensors and the technological shift from academics to industries, should be addressed and minimized. Noteworthy improvements in specificity, throughput rate, integrity and long-term stability comprise important steps for developing the next generation of nano-biosensors.

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Chapter 10
Applications and Implications of Nanoparticles in Food Industries

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1 Introduction

During the past few years, nanotechnology (NT) has increasingly been taken into consideration as an innovative technology that has revolutionized many industrial sectors including food (Mansurov 2020). The nanoparticles (NPs) possess one or more dimensions on the scale of 1–100 nm and unique physicochemical and biological characteristics. The specific characteristics such as surface to volume ratio, color, optical and magnetic property, solubility, diffusivity, toxicity, and many others make NMs unique for applications (Elemike et al. 2019). Nanotechnology has brought a revolution in every sector that developed and many developing countries are investing a huge amount of funds in NT research (Tahmooresnejad and Beaudry 2019). Consequently, NT offers a large variety of opportunities for the development

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of agricultural (Pramanik et al. 2020) and food products (Otles and Yalcin 2010; Bieberstein et al. 2013) that help in enhancing the food quality, storage, and fortifications (Ameta et al. 2020).

Nanostructured material and nanosensing are two major areas in the food sector where NMs have gained popularity (Azar et al. 2020; Yang and Duncan 2021). It includes a range of applications that is from food processing to packaging (Katouzian et al. 2017). These nanostructures are used to act as additives, anti-caking agents, and smart delivery agents/carriers for the delivery of nutrients, to improve the durability and mechanical strength of the packaging material. However, nanosensing is used to apply for attaining improved food quality and safety assessment (Casalinuovo et al. 2006; Wong and Khor 2021).

The rising applications of NMs are giving a major concern to consumers about food safety and that persuade the researchers to work on improving the food quality without altering the nutritional quality (Berekaa 2015). In the last few years, the application of NPs in the food industry has significantly increased as many of them are resistant to high temperature and pressure, have essential elements, and are also nontoxic under a certain dose (Talebian et al. 2021). Nanotechnology can guide the food industry in manufacturing, processing (Bochicchio et al. 2020), quality control (Jildeh and Matouq 2020), and also its packaging (Bieberstein et al. 2013; Naskar et al. 2018) that can truly lead to a major change in the food industry for sustainable food technology (Ameta et al. 2020; Bhusare and Kadam 2021) (Fig. 10.1).

Nanoencapsulation of nutraceutical compounds (Subramani and Ganapathyswamy 2020), enhancing the flavors and aromas (Saifullah et al. 2019), nanobiosensing for identification and recognition of pathogenic bacteria or allergen (Joyner and Kumar 2015), and quality monitoring (Raju et al. 2020; Wang et al. 2021) are potential

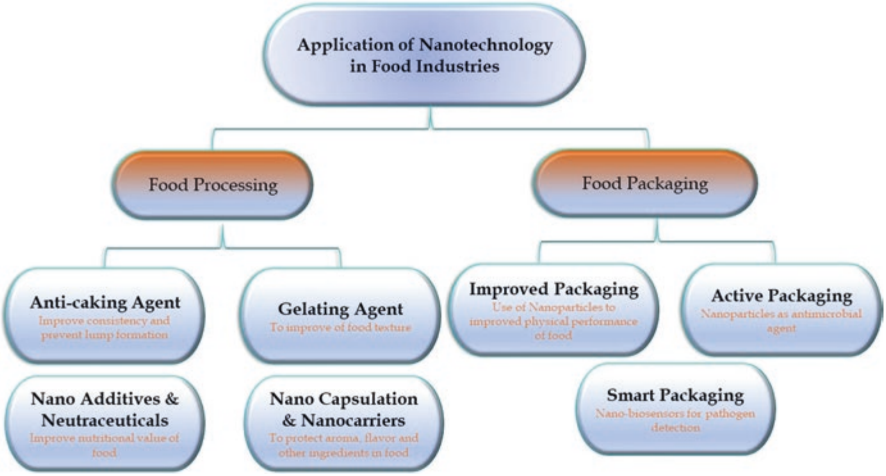

Fig. 10.1 Nanotechnology and its application at various steps in the food industry

applications and advances in the food sector. Apart from these applications, improvement in the food packaging quality is also being researched for a better alternative of packaging or smart packaging that can improve the shelf life of the food and protect it from the pathogen (Mohammadpour and Naghib 2021). Nanocomposite food packaging materials are also very promising in terms of protection from foodborne pathogens (Bumbudsanpharoke and Ko 2019).

In the last decade itself, the application of NMs in every sector has greatly increased (Talebian et al. 2021). The high demands and application of NMs are posing a greater environmental concern (Maiga et al. 2020; Temizel-Sekeryan and Hicks 2020). Nanomaterials have been reported in the abiotic and biotic components of the environment including food chains (Martínez et al. 2021). The presence of NMs in the water that is used for irrigation and presence in the soil can easily affect the agriculturally important soil microflora and alter the growth characteristics of crops (Du et al. 2017; Odzak et al. 2017; Rajput et al. 2020a). The entry of NMs into the food chain via any routes can be a major threat to several aquatic (Rajput et al. 2019a; Blinova et al. 2020) and terrestrial species (Rajput et al. 2017; Bobori et al. 2020) as well as to human health. Owing to their unique physicochemical properties, NMs are very prone to affect and alter the biomolecules (AshaRani et al. 2009; Maurer-Jones et al. 2010; Ding et al. 2017). Several metal-based NPs have been reported to have toxicological implications for human health (Rajput et al. 2020b; Irshad et al. 2021; Ranjan et al., 2022).

This chapter critically discusses the application of NMs in the food sector, starting from manufacturing to packaging, NMs used in food processing, smart food packaging, and nanosensing for food quality and safety. The chapter also discusses the growing environmental health concern due to the inevitable release of NMs by several applications.

2 Nanomaterial in the Food Industries

Ample new opportunities have sprung up in the food industry with NT as the novel properties of NMs are greatly useful in several industries including food (Cho et al. 2008). Nanostructures with a variety of functionalities are used as basic components for introducing unique food processing methods by utilizing the nanostructures that include nanoemulsions, NPs, nanoliposomes, and nanofibers (Weiss et al. 2006; McClements et al. 2007). In the food sector, both inorganic- and organic-based NMs find their usage. Nanoparticles with the possibility of being found in nanofood products, engineered nanomaterials (ENMs) are categorized as inorganic, surface-functionalized materials, and organic ENMs (Lombardo et al. 2020; Gulin-Sarfraz et al. 2021; Makvandi et al. 2021).

2.1 Inorganic Nanomaterials

In ENMs mostly d-block metals like silver (Ag) and iron (Fe), alkali earth metals like magnesium (Mg) and calcium (Ca), and nonmetals like silicates ($SiO^{4-)}$ and selenium (Se) are used for their application in food, food packaging or storage, and food additives (Ganesh and Ramakrishna 2020; Jafarzadeh et al. 2020; Medina-Reyes et al. 2020). Titanium dioxide (TiO_2) is another crucial ENM that can be effectively used in the food sector (Gunputh et al. 2018; Zhang et al. 2019). For metal/metal oxide ENMs, food packaging is a sector that finds a major proportion of its application. Nano-silver, having outclassed all kinds of ENMs, is currently used in different divisions as an antimicrobial, anti-odorant, and a health supplement (proclaimed). It is now also gaining popularity in several consumer products like edible products, food contact surfaces, drinking water, and packaging materials in terms of its effective uses (Hoseinnejad et al. 2018). Amorphous nano-silica finds its use in food contact surfaces and food packaging applications (Biswas et al. 2019; Lu et al. 2021). After numerous proclaimed health benefits of selenium in the human body, the marketing of nano-selenium as an additive to a green tea product has subsequently increased (Ye et al. 2020). Intended to be used in chewing gums and reportedly known for aiding remineralization of tooth enamel, nano-calcium salts also have a greater scope (Gao et al. 2020). Studies on Ca NPs and Mg NPs salts for development as health supplements are also on the rise (Naghsh and Kazemi 2014; Erfanian et al. 2017; Longbaf Dezfouli et al. 2019).

Iron NPs have also gained popularity as a health supplement (Pereira et al. 2018). In the process of development is a soluble nanomaterial, known as nanosalt, whose smaller quantities will be able to cover a larger surface area of food substances and help consumers to keep a check on their salt intake (Vinitha et al. 2021). Two nanotechnology-based food products, namely, cola-tasting nano-milk and with less fat content, nano-mayonnaise, have been developed by Wageningen University, Holland, which is the best demonstration of future nano-foods (Bayram and Gökırmaklı 2020). To drastically prolong the shelf life of edible products and to ease further transportation, NT would also help to manufacture "smart" packaging (Mohammadpour and Naghib 2021). Containing nano-sensor and antimicrobial activators, smart packaging is developed in a way that will be able to identify spoilage of food products and would also expel nano-antimicrobials to enhance the shelf life of food substances (Biswas et al. 2019; Jafarzadeh et al. 2020). This would enable groceries to store food for longer durations before it can be sold. Invisible to the human eye, nano-sensors in the form of tiny chips that are embedded into food products would also function as electronic barcodes (Dobrucka 2020; Mohammadpour and Naghib 2021).

2.2 *Surface-Functionalized Nanomaterials*

Their role is to enhance various kinds of functional utilities to the matrix, like antimicrobial activity or absorbing oxygen and performing a preservative function. The use of functionalized ENMs in food packaging materials is by binding with the polymer matrix, offering robustness and mechanical strength or preventing the movement of gases, volatile constituents (like flavors and odors) or moisture, by acting as a barrier. Compared to inert NPs, these functionalized ENMs may not be available to migrate out of packaging materials, or movement to other organs exterior to the gastrointestinal tract as there is more chances of reaction with other food components and may bind to the matrix of food. Montmorillonite or bentonite is the principal nanoclay mineral. It is mostly natural clay acquired from volcanic ash/rocks (Guo et al. 2018). With a natural nano-scaled, layered structure, nanoclays are organically modified to enable binding with polymer matrices. In food packaging, using functionalized nanoclays will help develop materials with greater gas-barrier properties (Echegoyen et al. 2016; Ahari et al. 2021).

2.3 *Organic Nanomaterials*

Most organic NPs are naturally occurring or have been formulated for their usage in food products or feed for animals. As compared to conventional bulk equivalents, they ensure enhanced uptake and absorption, and the bioavailability of vitamins and antioxidants is also reported to be increased (Khalid et al. 2020). Several materials in this group are available, such as food additives (e.g., benzoic acid, ascorbic acid, citric acid) and nutraceutical supplements such as vitamins A and E, lutein, omega-3 fatty acids, beta-carotene, isoflavones, and coenzyme Q10 (Li et al. 2012; Soveyd et al. 2017; Ahamed et al. 2019). A popular example of organic nanomaterial can be tomato carotenoid lycopene which is a synthetic nanosized form of lycopene, equivalent to the natural lycopene (Ahmed et al. 2021). Other examples of organic NPs are proteins, fat and sugar molecules, and nutraceuticals comprising food additives that are derivatives of plants. Nanotechnology has also opened new avenues for introducing different functional utilities, such as antimicrobial activity in decomposable/biodegradable materials (Gutiérrez 2018; Jafarzadeh et al. 2020).

3 Food Processing and Nanotechnology

The food sector includes four basic areas that are crucial for its function, and it includes production or farming, processing, fortification (if necessary), and packaging. Nanomaterials that have been proclaimed to enhance taste, consistency, and texture, food ingredients are being manufactured largely and used for food processing (Ameta et al. 2020). It has been extensively helpful in prolonging the storage life span of different food materials and successfully reducing wastage of food that occurred because of microbial/pathogenic infestation (Pradhan et al. 2015). Without modifying the basic structure of the food products, nanocarriers have been used as transport systems to deliver food additives into them. Transporting any bioactive substance to active sites inside the body may be directly influenced by the particle size. It has been observed in some cell lines that only submicron NPs could be effectively absorbed not the larger particles (Ezhilarasi et al. 2013).

An ideal delivery system in food processing should possess properties: (i) delivery of the active compound precisely at the site of action (ii) ensures the availability at a target time and a specific rate and (iii) must be efficacious enough to maintain appropriate levels of active compounds for extended periods concerning storage. Encapsulation, emulsions, biopolymer matrices, simple solutions, and association colloids developed using NT provide effective transport systems at target sites with all the aforementioned properties (Liu et al. 2021; Rashidi 2021). In food packaging, nanopolymers are serving as replacements for conventional materials. Using a nano-sensor, one can substantiate the presence of contaminants, microorganisms, and mycotoxins in food (Bratovčić et al. 2015).

Encapsulation and release efficiency of NPs have been reported to be far better than the conventional encapsulation systems. Nanoencapsulation helps mask odors or tastes, controls interactions of active compounds with the matrices of food, and controls their release and offers protection against moisture, heat, and biological or chemical degradation during processing, storage, and usage. It also provides conformity with other compounds in the system (Hosseini and Jafari 2020; Mahato et al. 2021). Furthermore, these delivery systems can penetrate deeper into the tissues because of their submicron size and hence allow efficacious translocation of active substances to various target sites in the body (Rashidi 2021).

Supplementary to this, the significance of NT in the food processing industry can be assessed by contemplating the job it plays in improving the quality of food products in terms of their (i) texture, (ii) appearance, (iii) taste, (iv) nutritional value, and (v) shelf life. It is worth mentioning that NT not only enhances the abovementioned aspects but also has contributed significantly to the improvement of food products by introducing novel attributes and utilities to them (Table 10.1).

A schematic figure also elaborates the individual segment in the food sector and the category of application the NT has gained popularity (Fig. 10.2).

4 Nanotechnology in Food Packaging

Typical packaging material should have gas- and moisture-absorbing capacity, which possesses both strength and biodegradability (da Silva Filipini et al. 2020; Amin et al. 2021). Several advantages of nano-based "intelligent" and "active" food packaging over the traditional packaging methods can be listed which range from improved mechanical strength of packaging material, barrier properties, and

Table 10.1 Nanomaterials, types, and their application in the food sector

Nanomaterials	Types	Applications	References
Metal oxide NPs	Ag, ZnO, Mg, SiO_2	Packaging material, protecting from the contaminants and antibacterial properties by oxidizing them	Jafarzadeh et al. (2020)
Polymeric nanocapsules	Bioactive compounds	Enhance the efficacy and solubility of ingredients/ bioactive compounds and controlled release	Sabliov and Astete (2015)
Nano-cochleates	Coiled NPs	Food fortification: Improves the nutritional value of food, adding antioxidants, provides better food protection and shelf life	Ahiwale et al. (2021)
Nanocomposite	Fe-Cr/Al_2O_3 Ni/Al_2O_3	Increases the shelf life of the food, protects the food, and is also used in the food packaging	Naskar et al. (2018), Mathew et al. (2019)
Nanoemulsion	Tweens or spans; gum arabic or modified starch, soy, caseinate, lutein	Encapsulation of ingredients, or antimicrobial compounds, storage, shelf life, and colorant	Liu et al. (2021)
Nano-micelles	Hydroxyethyl starch, Aquanova (NovaSOL® technology)	Liquid carrier, enhanced solubility	Chen et al. (2020)
Nano-sensors	Nanobiosensors or aptasensors that detect DNA, RNA, antibodies, or any other biomolecules	Detection of toxins, pathogens, allergens, carcinogens, etc.	Shawon et al. (2020)
Nano-sieves	Silicon nitride (Si_3N_4), ceramic, carbon nano-sieves, Au-PP SANSs, etc.	Ultrafiltration and removal of pathogens	Chang et al. (2020)
Nanospheres	Starch nanosphere, selenium nanosphere, carbon nanosphere, etc.	Food encapsulation, synthetic adhesives	Wang et al. (2020)

antimicrobial films to nanosensing for detecting pathogens and informing consumers about food safety status (Kaushal and Wani 2017; Shawon et al. 2020).

Similar to active materials for material coating and packaging of food, the use of nanocomposites can also improve food packaging (Pinto et al. 2013). Significant studies have been conducted in the interest of organic compounds like essential oils, organic acids, and bacteriocins and their use in the matrix of polymers as antimicrobial packaging (Faleiro and Miguel 2020; Gumienna and Górna 2021; Papadochristopoulos et al. 2021). Nevertheless, as these compounds are extremely sensitive to physical conditions like those of temperature and pressure, they are not suitable for many food processing (Ben Braïek and Smaoui 2021). A very high antibacterial activity can be obtained at comparatively low concentrations with more stability in extreme conditions with the use of inorganic NPs. Thus, the use of

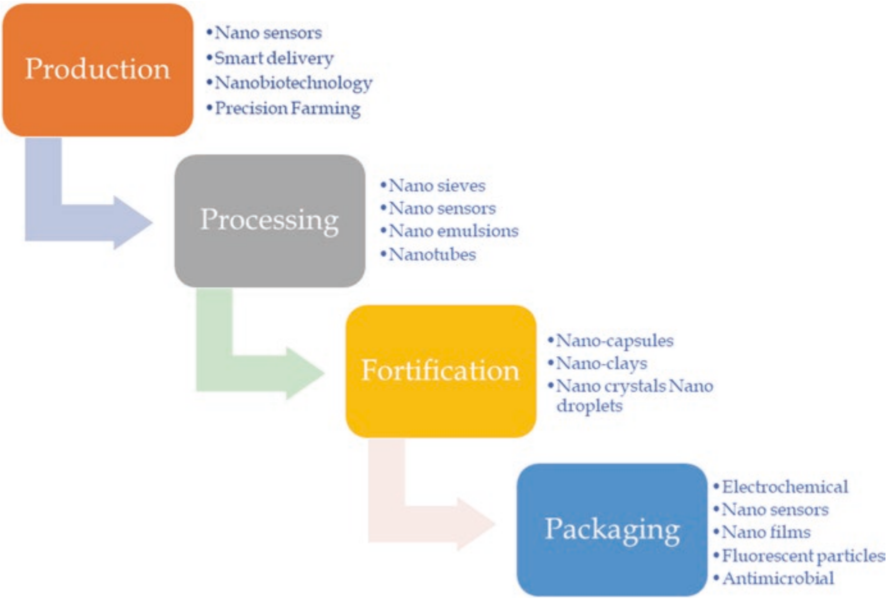

Fig. 10.2 Category of applications in the individual sector of food production where NPs are playing key roles

these NPs in antimicrobial food packaging has shown increasing interest recently (Jafarzadeh et al. 2020). A type of active packaging with biological properties, antimicrobial packaging, comes in contact with the food product or the space inside to retard microbial growth which might be present on the surface of food particles (Yildirim et al. 2018). Antibacterial properties have been reported in several NPs such as Ag, copper, chitosan, and metal oxide NPs like titanium oxide or zinc oxide (Longano et al. 2012; Gunputh et al. 2018; Biswas et al. 2019).

4.1 Active Food Packaging

Active packaging is comprised of the outcomes of materials science and engineering that have brought packaging technology with certain attributes that help to protect and preserve the food quality (Yildirim et al. 2018). The active food packaging mainly has three unique properties, (a) a releasing system that delivers antimicrobial substances, antioxidants, and flavors (Subramani and Ganapathyswamy 2020); (b) scavengers or absorbers to control O_2, CO_2, or odor (Lee et al. 2018); and (c) a control system to limit the moisture, temperature, or microwaves (Singh et al. 2018; Gaikwad et al. 2019). Nanoparticles have played a crucial role in the development of varieties of the active packaging system, and it has significantly enhanced food quality. It has helped by bringing precision farming (Chiranjeeb and Senapati 2020), delaying oxidation of food like meats (Lee et al. 2018), controlling moisture (Gaikwad et al. 2019), and limiting microbial growth (Gumienna and Górna 2021). The packaging system has also been developed for selective modification of gaseous content within the package (Kumar et al. 2021).

Nanoparticles are not just employed in antimicrobial food packaging; but nanocomposite and nanolaminates have also been used in food packaging to create a barrier against high temperature and mechanical shock, hence prolonging food shelf life (Aragüez et al. 2020; Aga et al. 2021). Hence, incorporating NPs into packaging materials provides high-quality food with a longer shelf life. In this context, biopolymer composites or PVC-based CMC-hydrogels have also been developed to provide more thermostable and mechanical packing materials (Kochumalayil et al. 2010; Roy et al. 2012). To generate better polymer composites, many inorganic or organic fillers are used, and metal NPs and carbon nanotubes have also been used as nano-filler (Rezić et al. 2017). The use of NPs in polymers has enabled the development of more cost-effective packaging materials (Sorrentino et al. 2007). Besides, the inclusion of inert nanoscale fillers into the polymer matrix, such as clay and silicate nanoplatelets, silica (SiO_2) NPs, chitin, or chitosan, makes it lighter, stronger, and more fire-resistant and and has increased thermal properties (Duncan 2011; Othman 2014). Thus, because of their structural integrity and barrier qualities, antimicrobial nanocomposite films formed by impregnating fillers with at least one dimension in the nanometric range of NPs into polymers provide for a two-way benefit (Rhim and Ng 2007; Shankar and Rhim 2017).

Antimicrobial Food Packaging

Antimicrobial packaging inhibits the growth of those microorganisms by outspreading the lag phase of the growth (Jafarzadeh et al. 2020). Inorganic antimicrobial agents are the most suitable substances as they have better stability and lesser safety concerns. However, organic antimicrobial substances may pose consumers' health risks and alter the flavors (Hoseinnejad et al. 2018). The choice of antimicrobial packaging agent is again dependent on factors like the type of food products, temperature, moisture content, and chemical nature and composition of food products. Organoleptic properties, toxicity, and resistance to microbes are key points to consider before the selection of antimicrobial agents (Ahari et al. 2021; Anvar et al. 2021).

Other aspects about packaging materials can be considered as control release of antimicrobial agents, physical and mechanical properties of packaging materials, and its permeation (SeyedReihani and Ahari 2020; Subramani and Ganapathyswamy 2020). Controlled releases of ingredients have been popularly used in the delivery of drugs by the pharmaceutical industry, however its evolving concept in food packaging. For efficient antimicrobial packaging, the microbial growth rate and the release of antimicrobial agents should be the same; both too slow and too fast release rates of the ingredients would lose the characteristic of antimicrobial packaging (Almasi et al. 2020). Nanosized inorganic antimicrobial agents are used in food packaging due to their enhanced reactivity and potential. Nanoparticles like Al_2O_3, Au NPs, CuO NPs, Fe_3O_4/Fe_2O_3, TiO_2, SiO_2, and ZnO are popularly used (Jafarzadeh et al. 2020). The nanosized particles have advantages over the bulk compounds and other antimicrobial agents in that they have high efficiency, require comparatively lesser time to kill the microbes, and can also overcome the microbial resistance that commonly develops in the conventional/organic antimicrobials (Rezić et al. 2017).

5 Nano-sensor for Pathogen Detection

The food sector always needed stringent quality control and monitoring potential applications that nano-sensor has fulfilled. It provided better sensitivity and detection abilities. In the food sector, nano-sensor or nanobiosensors help detect the pathogenic microbes and allergens during the food processing (Weng et al. 2021) (Aquino and Conte-Junior 2020), carcinogen detection and quantification (Wong and Khor 2021) assessment of constituents/ingredients (Joyner and Kumar 2015), etc. The nano-sensor principally works on changes in the condition of the environment, such as a change in the temperature in the storage (Manoj et al. 2021), change in relative humidity (Mohammadpour and Naghib 2021), contamination with microbes, or degradation of food products (Shawon et al. 2020). The nanostructures like NPs, nanofibers, nanorods, and nano-films have been evaluated for their use in food industries (Hsieh 2018; Prakash et al. 2019; Baysal and Doğan 2020).

Detection of pathogenic microbes has been feasible by immune-sensing, which involves a thin-optical film coated with suitable antigen/antibody/protein molecules against the microbes. The binding of microbes/their epitope/protein with the molecules coated on the films emits the signal that is being detected (Pires et al. 2021). A rapid detection method using dimethylsiloxane microfluidic-based immunosensor combined with specific antibodies restrained on alumina nanoporous membrane was developed for the detection of *Staphylococcus aureus* and *Escherichia coli* O157:H7 (Tan et al. 2011). In recent years, NMR-based detection system has been developed for the rapid detection of pathogens using NPs of superparamagnetic ultrasmall iron oxide integrated with membrane filtration and low field nuclear magnetic resonance (Jin et al. 2020). Time-domain nuclear magnetic resonance (TD-NMR) has also been helpful in the rapid detection of *Salmonella* in the milk samples. The superparamagnetic nanoparticle (SMN) is used in the development of this biosensor that works on the free binding of biotinylated antibodies to the *Salmonella*, and this approach can detect the 10^4 CFU mL^{-1} within 2 h (Zou et al. 2019).

The presence of pesticides and toxins has also been assessed using a nano-sensor to improve food quality (Palchetti and Mascini 2008). The nano-sensor based on carbon nanotubes has gained so much popularity because of its ease of use, low cost, and rapid detection. It has been successfully used for the detection of microbes (Choi et al. 2017; Hasan et al. 2018; Sobhan et al. 2019), pesticides (Wang et al.

2020), carcinogens (Wu et al. 2021), etc. in food products. Nano-immunosensors are also utilized for the detection of nano-diagnostic purposes, where they help in the identification of pathogenic fungal in the crops. Antibodies against the specific toxins are used to detect the presence of toxins and changes in the conductivity are assessed (Wang et al. 2009). Nanomaterial-based myco-sensor helps to detect the presence of mycotoxins (FB1/FB2, ZEN, DON, and T-2/HT-2) in real time and for multiple crops like barley, corn, oats, and wheat. It can well detect the mycotoxins below the EU limits (Lattanzio et al. 2012).

Modified quartz crystal surfaces with a set of functional groups or molecules such as amines, enzymes, lipids, etc. are used for the identification of key components of aroma and flavors. An array of such nano-sensor is also used as electronic noses or tongues for monitoring aroma, flavors, and other food conditions (Tan and Xu 2020; Wong and Khor 2021).

6 Health Safety and Environmental Issues

Nanomaterials, owing to their properties, have acquired a wide range of applications in every industrial sector including food. To fulfill the ever-increasing demand, NM manufacturing has increased many folds in the past few years. Large-scale manufacturing and applications of NM are posing a greater environmental and health risk. Sources, fate, and effects of NPs in the environment have now been broadly understood by researchers, and their findings have made significant progress in recent years. Nanoparticles enter the environment during the manufacturing of nanoaided products and also from raw materials. They are also released during application and after disposal of nanoproducts or waste (Gottschalk et al. 2013; Tolaymat et al. 2017). The release of NMs follows two fundamental ways, directly and indirectly. Directly, NPs are emitted to the environment during manufacturing and handling; however, in an indirect way, they are being released through NP-based products like agrochemicals (Campos et al. 2015; Fatima et al. 2020), fertilizers (Kopittke et al. 2019), pharmaceutical and cosmetic products (Nyström and Fadeel 2012; Subramaniam et al. 2019), and electronic appliances (Tang et al. 2019) and also from the leachates from landfills and effluent (Kaegi et al. 2010; Al-Kattan et al. 2015).

The release pattern and the extent depend on the type of NPs and their application. Modeling studies have been helpful to understand some extent for estimation of their concentration in the environment and their emissions and also predict their fate (Boxall et al. 2007; Mueller and Nowack 2008). Metal-based NPs enter the food chain with significant toxic consequences. They directly or indirectly find their ways to air, soil, sediment, and water or in the food chain. NPs like Ag NPs have been analyzed in the soil, surface water, and sediment (Li et al. 2018; Wimmer et al. 2019a, b).

After entering the environment, these NMs face a series of modifications that impact their outcome in tropical transfer, for example, dissolution, binding to environmental ligands, and aggregation/agglomeration. These alterations play a critical role in assessing the toxicity, higher bioaccumulation, and precipitation (Tangaa et al. 2016).

In recent studies, ecotoxicological profiles of Ag NPs have been evaluated using *Daphnia magna* and *Raphidocelis subcapitata*, which are representatives of two different levels of the aquatic trophic chain, and seeds of *Lepidium sativum*, *Cucumis sativus*, and *Lactuca sativa*. The study infers that *Daphnia magna* is easily affected by the presence of NPs (Falanga et al. 2020).

The presence of NPs is also expected to increase in soil mainly through agricultural applications (Rajput et al. 2018). Nanoparticles, when get accumulated in the soil, affect the flora and fauna, and they are transported via interfaces of soil particles (Rajput et al. 2017, 2019b). They form aggregation and are immobilized or also adsorbed on the particles of the sediments/soil where they are easily taken up by soil microbes. Metal NPs like Ag NPs enter into the water bodies and tend to be engrossed by the muds and sewage wastes and also reach farms through irrigations. This way the NPs have a greater chance to reach the crops and plants and affect them negatively (Blaser et al. 2008).

TiO_2 NPs are reported to be transported across the trophic chain and accumulate in the freshwater as well as sandy loam sediment where they are easily absorbed by the lower plants like duckweeds, water dropworts, and quillworts. They are also taken up by the organisms like earthworms (*Eisenia fetida*), juvenile bullfrogs (*Rana catesbeiana*), river snails, and Chinese muddy loaches (Unrine et al. 2012). Bioaccumulation of NPs through the soil in the various organs such as the kidney, liver, muscle, spleen, and intestine of the juvenile bullfrogs infers that it is also a threat to higher trophic level animals (Bertrand and Leroux 2012). TiO_2 is broadly used as a water disinfectant to control the coliform, they get a route from the sewage/wastewater treatment plants where the NPs cannot be removed effectively, and it results in its flow with the water and surface waters and also to the organisms (Westerhoff et al. 2011).

The presence of NPs in the food chain is also threatening the consumption of fish and seafood and making consumers chances of exposure (Ward and Kach 2009). However, very few studies are available on the presence of NPs in meat and animal tissues. In a study, Ag NPs have been reported to accumulate in the livers of 80-week-old male broiler chickens when fed with Ag NPs-contained feed/drinking water at various concentrations (4, 8, and 12 mg/dm^3) for 42 days (Loghman et al. 2012). A recent review on the migration of NPs from the food packaging to the food materials has discussed the scenario in detail. Most of the studies included in the review have confirmed the migration levels to be lesser than the permitted levels. However, the migration of Ag NPs is identified to be higher in the acidic environment. It has been observed that studies on the migration of Ag NPs are not congruent with each other; however, all studies in this regard agree upon the fact that Ag NPs have high migration levels in acidic environments. The studies also highlighted the migration of various NPs depending upon the factors like the concentration of additives used, area of food products in the contact of packaging material, the solubility of packaging material, the density of remaining segments, duration of contacts of food material, and heat. Unfortunately, the information is very insufficient about the NPs' toxicity of food materials, and it would be too early to draw any conclusion (Paidari et al. 2021).

Besides its potential application, the environmental and health threat cannot be neglected in the absence of information or research data. Researchers however have taken up the issues and emphasized the consumer's health (Bradley et al. 2011). Although certain NPs are referred to as GRAS (generally regarded as safe) substances (Naseer et al. 2020), additional studies are of utmost necessity to gather more knowledge about its toxicological implications. For instance, the silica (SiO_2) NPs are commonly used as anti-caking agents found to be cytotoxic in human lung cells (Athinarayanan et al. 2014), Chromium NPs have been reported to affect human lymphocytes by elevating reactive oxygen species (ROS), reducing matrix metalloproteinases (MMP), and altering the membrane system of lysosomes. Cr NPs have also been reported to cause lipid peroxidation (Seydi et al. 2020). A study on ZnO NPs reports that ZnO NPs do not cause significant toxicity to intact human skin; however, after the dissociation of NPs, the zinc ions are released and can cause toxicity to the viable epidermis if the stratum corneum has been penetrated (Holmes et al. 2020). Similarly, at higher doses, Cu/CuO NPs are also reported to affect the human intestinal cell lines Cao-2 by having moderate solubility, ROS-dependent DNA damage, and apoptosis (Li et al. 2020).

Again, the toxicity of NPs in humans is also dependent on dissolution, surface morphology, concentration, surface energy, aggregation, adsorption, etc. (Cushen et al. 2014). It is also expected from the regulatory authorities and policymakers to come up with frameworks that can enable standards and guidelines/regulations to check the possible emissions and identify concurrent sources of emission that may affect the biotic and abiotic components.

7 Conclusion

In the past few years, industrial or technological innovations have been revolving around the application of NPs. In the food sector, they are extensively used for enhancing the quality of foods in terms of flavors, aroma, shelf life, balanced ingredients/constituents, quality monitoring control, and also packaging. The manifold growth in the application of NPs certainly poses a greater risk to the environment, to food chains, and also to human health; however, the effective application of NPs in the food sector is still a handful and limited.

The application of NT in the food sector enables innovative challenges for the industries and policymakers. The industries have to ensure the consumer's health and confidence for having greater acceptance of NM-based food/food products. International and local regulatory agencies should also play key roles in the safety evaluation of the food and packaging concerning the environment and human health. Mandatory testing of NM-based foods with suitable guidelines supported with stringent scientific evidence can certainly help to limit the chances of exposure of consumers. In the absence of evident research data and regulatory guidelines, consumers may have a state of dilemma for the safety of food. In that case, labeling the NM-based foods with suitable and easy symbols must be helpful for the consumers. Further scientific exploration with novel approaches toward the study of NPs on various human cell lines should also be promoted for further assessments. Last but not the least, development of new analytical methods for the detection of NPs would also be a key contributor not only in strengthening the food sector but also for environmental and health monitoring.

8 Future Perspective

With the potential to transform almost every aspect of modern life, NT is regarded as the fastest emerging technology of our times. In anticipation of the future perspective of NT in the food industry, it is quite obvious that more sound research in this domain would definitely result in creating tools and mechanisms for expansion and improvement in the industry in terms of enhanced shelf life, smart and antimicrobial packaging, efficient nutraceutical supplements, fortified food products, pathogen detectors, etc. with the greater population being benefitted from such advancements. It may also help in tackling persistent issues related to food and nutrition and has the potential to offer long-term economic gains. Cost-effective, healthy, and environmentally sustainable food production is the need of the hour, and NT is the answer for all such global problems.

Nevertheless, the need to address the safety concerns remains the topmost priority of the moment. With extensive acute and chronic toxicity studies, careful safety assessment would enable faster commercial availability of such products. With the introduction of new nano-based products and technologies in the market also lies a requirement of attaining social and environmental collaboration to ensure that the respective interests are not undermined. So far, only a handful of nations have standard regulatory guidelines for the use of NT in the food industry, which is why insufficient scientific research and data are available for concluding on efficacies and safety of nano-food and packaging. If managed well, there is no end to the opportunities offered by NT in the food industry. Properly guided scientific exploration is the key in gaining indefinite insights into the future of this industry.

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Chapter 11
Environmental Emissions of Nanoparticles

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1 Introduction

The coming period is going to be challenging in terms of climatic and environmental conditions affecting biotic and abiotic components. Nanotechnology (NT) is a relatively new discipline compared to existing sectors, which limits the amount of time available for research and risk assessments. The enormous production volume of NPs for a variety of applications including building, electronics, manufacturing, cosmetics, and medicine is rapidly increasing (Jeevanandam et al. 2018). Along with this achievement, their presence in the environment and associated risk is increasing as a global problem. Metal-based NPs enter the environment by mishandling during the manufacturing of nano-aided products from the raw materials (Bundschuh et al. 2018). They are also released during application (e.g.,

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nano-agrochemicals) and after disposal of nanoproducts or waste that may contain NP-based products (Gottschalk et al. 2009; Piccinno et al. 2012; Tolaymat et al. 2017).

The emission of NPs is occurring in two distinct ways: directly and indirectly. In a direct way, they are emitted to the environment, while in an indirect way, emissions happened through the leachates from landfills and effluent (6–8). However, their release pattern and masses depend on the NPs type and its application (Jeevanandam et al. 2018). Modeling approaches have been used up to some extent for estimation of their concentration in the environment. Few analytical techniques used for their detection are under development to characterize them efficiently with a low level of concentration (Nowack 2017). Computational modeling is recommended to detect the environmental concentrations as very few analytical methods are available to assess the concentration of NPs in the environment (10–12). Metallic NPs are entering into the food chain with significant toxic consequences. Various studies have been conducted in this regard; in one of the recent studies, ecotoxicological profiles of silver NPs (Ag NPs) were evaluated using *Daphnia magna* and *Raphidocelis subcapitata*, which are representatives of two different levels of the aquatic trophic chain, and seeds of *Lepidium sativum*, *Cucumis sativus*, and *Lactuca sativa* (Falanga et al. 2020).

After entering the environment (Fig. 11.1), these NPs face a series of modifications that impact their outcome in tropical transfer, for example, dissolution, binding to environmental ligands, and aggregation/agglomeration. These alterations play a critical role in assessing the toxicity, higher bioaccumulation, and precipitation (Tangaa et al. 2016). Metallic NPs find their ways in air, soil, sediment, water, or the food chain. In many studies, Ag NPs have been analyzed in the soil, surface water, and sediment (Stolzenburg et al. 2018; Wimmer et al. 2019).

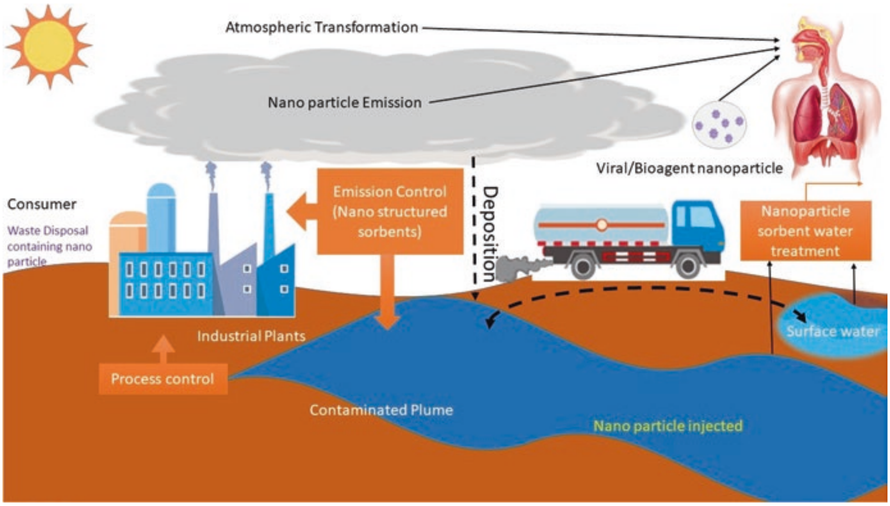

Fig. 11.1 Emission of NMs in the environment

The presence of these NPs is expected to increase in soil as it is a major sink of all kind of pollutants. Nanoparticles, when gathered in the soil, affect the flora and fauna, and are transported via interfaces of soil particles and then get aggregated, adsorbed, or immobilized in the sediments or soil particles to be further taken up by bacteria resulting in their introduction in the food chain (Azeez 2021).

For example, Ag NPs reach to the water bodies after they are attracted by the mud and sewage, get paths to the farm, and ultimately bioaccumulate in plants when the water is used for irrigations. It causes a major risks of ecotoxicity of NPs on the plants (Blaser et al. 2008; Karimi et al. 2018). Titanium dioxide (TiO_2) NPs that are transported across the trophic chain have been reported to accumulate in the freshwater and sandy loam sediment and then again relocate themselves to the biota. Few aquatic flora and fauna such as quillworts, water dropworts, duckweeds, biofilms, river snails, and Chinese muddy loaches are reported to be affected by TiO_2 NPs (Kim et al. 2016). Another study that featured soil, earthworms (*Eisenia fetida*), and juvenile bullfrogs (*Rana catesbeiana*), to explore the impact of NPs on a three-step terrestrial food chain, reported the bioaccumulation of NPs in the kidney, muscle, liver, spleen, stomach, and intestine of juvenile bullfrogs. This study proved the translocation and biomagnification of soil NPs to higher organisms (Unrine et al. 2012). Similarly, NPs, when entering water bodies, travel as far as water is the best transporting medium and their deposition certainly makes water unpotable (Pulit-Prociak et al. 2015). TiO_2 application is majorly used in cosmetics, pharmaceuticals, etc. and people are deliberately exposed to its harmful effects; it is also used to disinfect water from *coliform* bacteria (Rizzo 2009). During the sewage treatment, it goes into wastewater treatment plants where small particles can't be removed as a result they flow to the surface waters and spoil the organisms (Westerhoff et al. 2011). Contamination of the aquatic environment happens when NPs present in runoff and sanitary and industrial sewages get their way to the water (Müller et al. 2020). These NPs migrate and accumulate in water and affect their normal biota and cause harmful alterations to the visible live organisms, human, and ecosystems (Mammo et al. 2020). Further, they also pose threat to the life of marine and benthic organisms. This may affect the safety of seafoods and consumers may also be affected (Ward and Kach 2009).

In this chapter, domestic, natural, industrial sources of NPs have been discussed in detail. Nanoparticles in water, soil, and air or in the food web and life cycle of NPs in the environment have been documented for improving the understanding, recommendations, and future directions in NT.

2 Domestic and Natural Sources of Nanoparticles

The use of domestic NPs in daily life has increased with wide applications, especially in areas of medicine, nutrition, vehicular/industrial/domestic exhausts, cosmetics, building materials, agriculture, physical and chemical computational models, etc. Similarly, some major natural sources of NPs in the atmosphere includes volcanic eruptions, suspensions, desert surfaces, and dust generated from cosmic sources. Some of the sources have been briefly highlighted.

2.1 Domestic Sources

Domestic NPs may be produced by unintentional endeavors like cooking, internal combustion, material fabrication, and transportation. These NPs are quite rigid and stable that their degradation cannot be achieved easily. As a result, they lead to many environmental toxicities. For example, domestic refrigerators contain working fluid made up of mineral oil with TiO_2 NPs (Bi et al. 2008). Some common sources of domestic emission of NPs are discussed.

Cigarette Smoking

Although cigarette smoking is injurious to human health, many people habitually smoke because it brings pleasure and enjoyment. Cigarette smoke has more than 100,000 chemicals in the form of nano- and micro compounds ranging from the size of NPs of 10–700 nm (29–31). Nanoparticles are being used in cigarette for good performance in removing pollutants such as CO, CO_2, NO_3, etc. from smoke, and their characterization has been done by SEM, XRD, and BET techniques (Kamsuwan et al. 2021).

A high concentration of NPs formed by cigarette combustion causes air pollution and is a potential risk to humans (Van Dijk et al. 2011). Based on the size and number of NPs, validation of e-cigarette generation system inhalation toxicity was carried out. Metallic NPs such as Ni and Cr (Williams et al. 2013), produced from e-cigarette, are reported to be of size 32–57 nm. A report suggests that MgO NPs act as an absorbent in the reduction of air pollutants emitted from cigarette consumption in air pollution (Talaiekhozani and Amani 2019).

Building Construction and Demolition

Construction and demolition of larger buildings are responsible for releasing nano- and micro size particulate material into the atmosphere (Kaegi et al. 2017). The construction waste having lead, glass, and asbestos NPs are the common NPs released in the environment and responsible for inducing hyper-bronchial and coughing activity by affecting the human respiratory system (West et al. 2016).

A depth study of NPs that are released in the environment during demolition and construction of buildings is the need of time to manage the adverse impact on human health (Mohajerani et al. 2019). Demolition of construction materials forms inhalable NPs such as the detected NPs containing a number of elements that could cause adverse health impacts on local communities. Aluminum, arsenic, gold, cadmium, calcium, cobalt, chromium, copper, mercury, sodium, iron, potassium, sulfur, tin, and silica along with carbon nanotubes were commonly observed NPs from the construction waste material (Oliveira et al. 2019). In addition to other ultrafine particulates, silica (SiO_2), TiO_2, ferric oxide (Fe_2O_3), copper or copper oxide (Cu/CuO), and silver (Ag) NPs are being used in construction to increase the strength and performance of ceramic, steel, paint, and concrete (37, 39–40). Zinc oxide (ZnO) NPs are also being partially used in cement composites (Garg and Garg 2020).

Nanoparticles from Vehicular Exhaust

Urban as well as rural areas are now affected by vehicular air pollution. However, apart from that, gas engine exhaust is also reported to release NPs. Diesel and gasoline engines release 20–130-nm-sized NPs in the environment such as boric acid, tungsten nanospheres, copper NPs, and graphene (Moradiya 2019). The diesel engine generates 90% of carbon NPs present in the current atmosphere and is the major source of air pollution (Hussein 2015). Fe NPs are important from the prospect of the urban area development. However, they possess pathogenic effect and are associated with neurodegenerative diseases like Parkinson's and Alzheimer's (Gonet and Maher 2019).

Vehicular emissions releases toxic elements such as CO_X, NO_X, SO_X, metal NPs, etc. (Müller et al. 2020). High cardiopulmonary mortality rate, granulomatous-oxidative stress and inflammation reactions, lung-associated neoplasia and fibroplasia (Knight 1998; Kolosnjaj-Tabi et al. 2015), early age cancers due to pre- and postnatal exposure to engine exhaust (Knox 2005; Ghosh et al. 2013), and pro-inflammatory and prothrombotic hemolytic responses (Riediker et al. 2004) are the major human symptoms associated with elevated exposure to engine exhaust in extremely populated cities.

2.2 Natural Sources

Emissions of NPs from natural sources are common geographic phenomena. These include combustion of products, storms, forest fires, ashes from volcanic eruption, ocean spray, and radioactive decay of gases. They can also be generated through the weathering processes of metals, anionic rocks, drainage from acid mine sites, etc. These natural methods have been discussed below in detail.

Nanoparticles from Dust Storms and Volcanoes

Pollutants generated due to anthropogenic activity can travel from thousands of kilometers through atmospheric transport and are responsible for major pollutant migration. About 50% of atmospheric aerosol dust storm has particulate material within the range of 100–200 nm (Stolzenburg et al. 2018). Studies have reported that Saharan desert region could be influenced by the dust storms that can form Fe NP-based clouds that may alter the pH and physiochemical and atmospheric properties of the region (Shi et al. 2012; Rodriguez-Navarro et al. 2018).

Volcanic eruption releases nearly 30 million tons of NPs in the form of ash into the natural atmosphere, thereby affecting the air quality and the resident within 10 km range of volcano site.

Releasing of bismuth oxide (Bi_2O_3) NPs into the stratosphere has been observed in 1980 and later confirmed in 1985 (Enghoff and Svensmark 2008). Nanoparticles from the volcanic ash when separated and analyzed were found be enriched with toxic elements as compared to bulk volcanic ash. Very high concentration of Cd, Hg, Tl, Pb, Bi, Se, and Te has been reported in the NPs obtained from the volcanic ash (Ermolin et al. 2018; Trejos et al. 2021).

Kaposi's sarcoma disease is due to releasing toxic heavy metals through volcanic eruption and the major cause of cancer and dysfunction of blood and lymph vessels (Buzea et al. 2007).

Geochemical Cycling and Forest Fires

Nearly 3% of earth's surface face fire annually. Depending on the type of vegetation pattern, fuel moisture, prevailing weather, and climatic conditions, the generated NPs are released into the atmosphere where they persist. This leads to increase in the levels of nitrates, carbons, hydrogen, etc. (Ball et al. 2010; Archibald et al. 2018). Asian brown clouds are responsible for the heavy deposition of black nanocarbon and soot over the Himalayan glaciers which is a further major cause of absorbing more sun's heat and accelerating the melting process of the glacier (62–65). Metal NPs have been reported to travel long distances due to the high melting rate of the glacier and also to contamination of the local water bodies and rivers (Napper et al. 2020). The melting glaciers have NPs of varieties of elements such as Al, Cu, Fe, Mn, Si, etc.; however, Fe is higher in concentration in the melted water (Kumar et al. 2018).

Aerosol with size varying from 100 nm to a few micrometers particulate materials is formed due to ocean water evaporation (Kim et al. 2021). Due to $CaCO_3$ NPs aerosol formation from Michigan Lake, the vicinity areas face weather and temperature changes. These aerosols may act as a carrier for pathogens and pollutants and are responsible for accelerated casualties in humans as well as in plants (Buseck and Pósfai 1999).

Due to forest fire, ash, and smoke release in the environment, the standards of ambient air quality are also being affected (Bakshi and Abhilash 2020; Isley and Taylor 2020). A study reports 75% deaths occur due to smoke inhalation released by forest fires (Buzea et al. 2007). Black carbon NPs have been reported very often from the forest fire; they are very fine carbon NPs and can easily penetrate into the finer blood vessel once inhaled (Bisiaux et al. 2012).

3 Industrial Source of Nanoparticles

Heavy metals, cosmetic particles, dyes, and gaseous particles that are introduced by industrial activities lead to generation of NPs. Exhaust, chemical effluents, release of oils/grease, waste water discharge, etc. are some of the examples of nonpoint sources. Emissions from industrial sources contribute as one of the major sources of NPs (Müller et al. 2020).

3.1 Cosmetic Industries

Nanoparticles such as TiO2 and ZnO are highly used NPs in the cosmetic industry. They are very much known for their sun-filtering properties. TiO_2 helps in protecting on a broad-spectrum range against UVA and UVB. However, ZnO is used as either UVB or UVA filters. TiO_2 has properties to protect from sunburn and ZnO is known to show its fileting ability which helps in protecting from UV-induced aging. TiO_2 is very much effective in terms of SPF at very specific concentrations, 220 nm of crystal size of TiO_2. Pigmentation provides UV protection along with attenuation of visible light which gives a white appearance on the skin (De Navarre 1941).

Gold (Au) NPs is another important material being used in cosmetics as it has additional benefits of providing antioxidant properties. A study on *Panax ginseng* leaves' mediated gold NPs on B16BL6 cells reveals that it can provide moisture retention and whitening effect. It also shows antioxidant activity, therefore making it a very suitable candidate to be used in cosmetics (Jiménez-Pérez et al. 2018). The recent advancement in the cosmetic industry is the use of nano-carrier for delivering the active ingredient, vitamins, antioxidants, and other cosmeceuticals in burst release as well as sustained release.

The use of NPs in cosmetics is becoming crucial and therefore the inclination of scientific research in this area is obvious. The development of drug and nutraceuticals delivery systems using NPs has shaped the interest of cosmetic experts to adopt such methods for cosmetics too. A large number of cosmetic products are already using nano-formulations or novel nano-carriers to deliver the active ingredients or cosmeceuticals. The nano-carriers are very similar to drug or nutraceuticals delivery systems. The future challenges for such novel approaches are achieving better biocompatibility, stability for prolonged action with the loading capabilities, and tissue/site-specificity.

There are many studies that have explored the possible side effects, health hazards, and toxicity of NP use in cosmetics (Fytianos et al. 2020; Kim et al. 2021). The greatest future challenge ahead of all of us is to generate reliable and reproducible reports for the consumers for the benefits of using NPs, its toxicity, and safety/regulatory measures. The precise information of the product carrying NPs must be specified on the label of the products.

The major concern regarding the use of NPs in cosmetics is its adverse effect on the skin (Kim et al. 2021). The safety concern is not just bonded to humans but also to environmental safety. When we discuss human safety, it includes the safety of consumers and occupational hazards. The environment safety concern is especially for lower animals such as krill, fish, etc. followed by the entry of NP through the food chain which poses a huge threat to biodiversity (Kim et al. 2016). Smaller size NP can easily penetrate the skin or cell membranes and enter into the system, thereby causing damage to cellular machinery and processes as well as DNA damages (Siivola et al. 2020). Some studies reported the unusual biological consequences of NPs having a larger surface area with stronger correlations; however, few studies also report reverse cases (Monteiro-Riviere et al. 2009). Therefore, rigorous studies are required which can emphasize NP-specific and case-specific toxicity.

3.2 Textile Industries

Textile industries' wastewater effluent contains a wide range of chemicals including NPs and various dyes (Shahidi 2019). The advancement of technology also brought the application of NPs in textile industries for making smart fabric touch pads, invisible coatings, bullet-free jumpsuits, and advanced fibers. Nowadays, Ag NPs-treated fabrics are in the current market for effective antiseptic treatment (Montes-Hernandez et al. 2021). Incorporation of Au, Cu, and Ni NPs for making conductive ink for pressure pad sensors is also in trend (Salvadori et al. 2014, 2015; Malik 2022). Magnetic NPs and Ag NPs have gained popularity in industrial applications. These have been observed to be highly reactive and play toxic role for microorganisms (Shahidi 2019; Montes-Hernandez et al. 2021). Likewise in vitro studies using animal models have highlighted that the use of plastic-generated NPs has been detected in air, water, and soil samples, thereby affecting overall biota (Kik et al. 2020).

3.3 Chemical Manufacturing Industries

Nanotechnology application has immense application in chemical industries; however, to produce and commercialize NT with unique performance and customer benefits with affordable costs require competencies like nano-synthesis, nanofabrication and nano-processing, nano-incorporation, and nano-characterization (Zhao et al. 2003). The chemical industry governs virtually all the industrial sectors, viz., electronics, pharmaceutical, performance, and functional materials, e.g., production of digital displays (Kim and Kwon 2007), printers (Hänninen et al. 2010), chemical-mechanical polishing materials (Kao et al. 2014), chips, diodes (Kowshik et al. 2002), cells and batteries (Sclar et al. 2009; Latorre-Sanchez et al. 2012), solar panels (Wang et al. 2003), and photonics (Prasad 2006). Field emission displays that are based on carbon nanotubes are recent inventions of NT in electronics.

Nanocatalysis is one of the emerging applications of NT in the chemical industry which aims to produce catalysts that can be 100% efficient and can have higher selectivity, less energy consumption, and comparatively longer life. Such catalyst can be obtained only when its size and shape, spatial distribution composition of the surface, and its electronic, thermal, and chemical behavior are stable. Nanocatalysis is further considered as homogeneous and heterogeneous catalysis. The heterogeneous catalysis examples are conventional metal NPs semiconductors and oxides, whereas the homogeneous catalysis involved transition metal NPs that are finely dispersed in colloidal solutions of an organic or aqueous solution, or a solvent mixture (Cuenya and Behafarid 2015). Nanotechnology adds a new dimension in the chemical industry which enables it to produce a variety of products such as drug delivery systems (Kohane 2007), gene therapy (Perez-Martinez et al. 2012), tissue engineering, biosensors (Ding et al. 2013; Pilolli et al. 2013), biopolymers (Nitta and Numata 2013), diagnostic systems (Yezhelyev et al. 2006), protein-assisted self-assembly (Nikitin et al. 2010), and biocatalysts (Jarullah et al. 2020).

Nanotechnology has strengthened every innovation and in the chemical industry sector, where chemistry is the backbone of any industry, and it has no look back from the production point of view. Therefore, both demand and opportunity are having equal importance for this sector. The more demand for the product is going to provide, the major opportunities for the industry to innovate. In chemical industries, the opportunities are immense due to integrated and overlapped sectors.

The unique portrayal of NT absolutely would require having a perfect blend of chemistry, materials science, life science, and engineering/technology. This would enable us to produce customer goods of unique properties and performance as well as cost cum customer benefits. Few very important sectors where NT is playing a key role with chemistry are electronics, biomedical and bio-based products, performance and functional materials, and human and environmental safety products.

Yet another important aspect for further strengthening the product-oriented innovation is the use of modeling and simulation. Molecular modeling is one of the advanced computational methods for understanding and predicting the structure, computational fluid dynamics models where the process parameters and rector design can be devised with optimal performance, nano- and mesoscale modeling is very useful in understanding the interparticle forces and nanostructures. All kind of modeling and simulation studies requires validation using experimental data; however, it helps to reduce the development time and increase the cost-efficiency.

The potential of NPs is being acknowledged, that is, NPs are capable of providing a significantly enhanced product with several customer benefits. However, the manufacturing and production of goods are required to be scaled up and process integrations. This is a new challenge for established industries. In addition to the development of unit operations, scale-up and scale-down, process integration in manufacturing systems also presents new challenges. The manufacturing of NM would not follow the common process of bulk chemical manufacturing. For the manufacturing of NPs, the preferable manufacturing system must be portable, modular, and integrated, unlike large footprint industries. Along with development and progress in manufacturing the NPs at a commercial scale, the tools to assess the risk of human and environmental exposure also have to be devised. The environmental release or emission check is a key concern for this purpose.

3.4 Automotive Industry

The automotive industry produces millions of cars, scooters, or motorbikes each year and several components in the automotive industry use NM; therefore, there is a huge opportunity for nano-technological applications in this sector. Nanomaterials enhance and improve the properties and performance of materials used in automobile technology (Asmatulu et al. 2013). The automobile industry is aiming to produce next-generation automobiles that are light in weight, resilient to accidents and crashes, and smarter in approach using AI and advanced sensing technologies and have increased fuel efficiency. High strength to weight frames, eco-friendly energy sources, and emission with fewer pollutants are high-end requirements for next-generation automobiles (Murty et al. 2013). Nanotechnology has potential and it can play a key to meet these aims for automotive sectors along with enhanced safety and aesthetics.

The nano-dispersed fluids and lubricants help in heat dissipation reduced friction and erosion of the engine, and also its accessories and gears. Gold- and copper-based NPs are very much suitable for efficiently developing a liquefied protective film that can replace fossil fuel and help the car engine to have a longer life and be more sustainable (Ali et al. 2014). Modern vehicles are having antiglare mirrors and headlights which are very helpful in night driving. To avoid that, an ultrathin layer of aluminum oxide of thickness lesser than 100 nm is applied using the chemical vapor deposition method. It makes mirrors and glasses hydrophobic and dirt-free and develops antiglare properties (Fig. 11.2). This nanocomposite layer has electrochromic properties (Mohseni et al. 2012).

Nanomaterials play a key role in the improvement of vehicles by enhancing the heat transfer, Nusselt number, and engine performance. Table 11.1 shows information regarding the use of various NPs used for improving engine's performance, and Fig. 11.3 shows the diverse use of NP in the automotive industry.

Fig. 11.2 Conventional mirror (left) causing glare of reflecting lights and mirror ultrathin coating with nanocomposite (right) making it glare-free. (Source: Mathew et al. (2019))

Table 11.1 Various NM and fluid combinations to improve the engine's performance, heat transfer, and Nusselt number

S. no.	NMs and fluid combination	Benefits	Reference
1	Al_2O_3–ethylene glycol	1.5% Al_2O_3 NPs helps to improve the thermal conductivity by nearly 4.5% with the addition of	Kole and Dey (2010)
2	Nano-diamond–engine oil	This combination improves engine power performance by 1.15% and reduction in the consumption of fuel by almost 1.27% concerning simple engine oil	Congress (2013)
3	SiO_2–water TiO_2–water	22.5% improvement in Nusselt number with SiO_2 and 11% improvement with TiO_2 nanofluids, respectively	Hussein et al. (2014)
4	Al_2O_3–water	14.7% enhancement in coolant heat transfer coefficient, 14.8% enhancement in heat transfer rate, and 9.5% enhancement in Nusselt number were reported	Ali et al. (2014)
5	CuO–water	0.65 volume % CuO–water NPs helps to improve the heat transfer coefficient by nearly 9%	Peyghambarzadeh et al. (2013)
6	CuO–water	0.4 volume % CuO with water improves the heat transfer coefficient by 8% with respect to pure water	Naraki et al. (2013)
7	SiO_2–water	9.3% improvement in heat transfer was noticed using 0.4 volume % of SiO_2 NP at the temperature 60 °C	Akbarzade et al. (2014)

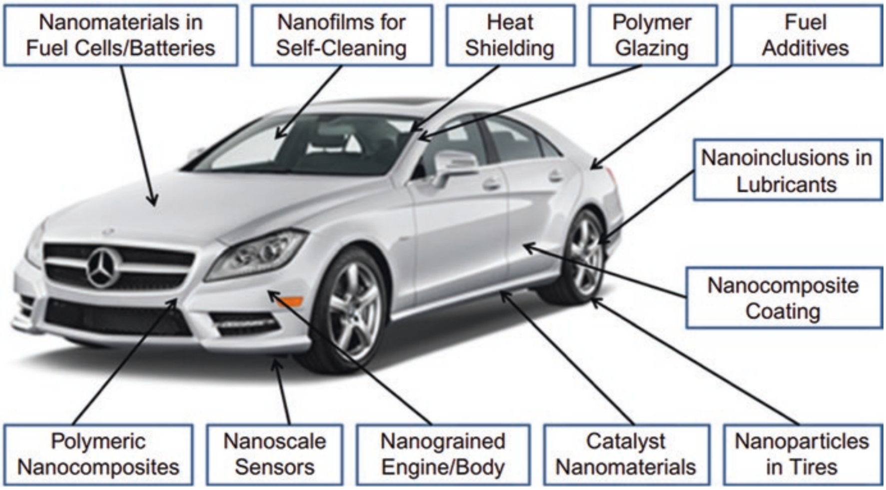

Fig. 11.3 Various uses of NM in the automotive industry. (Image adapted from Murty et al. (2013))

Nanotechnology helps the automotive industry because it has huge applications in producing frames and body parts of vehicles, brake and suspension systems, durables tires, and advanced catalytic converters (Asmatulu et al. 2013). Apart from all these, it is also helpful in making anticorrosion (Raynaud) and antifogging (Yao et al. 2019), sensors for an airbag, pressure monitoring, motion sensing, and atmospheric and security control in the vehicles.

In the twenty-first century, NT has made inroads into nearly every sector of industrial manufacturing. The automobile sector has also been exploring NT to achieve a shinier, safer, and more energy-efficient vehicle. The key areas where NT has played a significant role in improving vehicles are wear-resistant tires; lighter NM built of car bodies, which are lighter though stronger; miniaturized electronic systems and equipment; and fuel-efficient engines. The replacement of conventional windows glasses with nano-engineered tough polymers and rustproof thermoplastic chassis are recent advances in the automotive industry. The near future of the automotive industry is developing a "self-cleaning car" by using hydrophobic nano-paint technology. This product is in the testing phase and may hit the market sooner. One such technology that is feasible to use on vehicles would be very much notable to the environment. It can save millions of liters of water used for car washing. Nano-paints could be another revolution where the use of thermochromic material and special nanostructured material can produce a color-changing effect on vehicles.

Very recently, thermoplastic-reinforced nano-cellulose fibers are providing a very good alternative to synthetic fibers, viz., glass and carbon fibers. Nano-cellulose possesses various superior properties such as low cost, tensile strength similar to aluminum, design flexibility, and low weight, which makes it suitable for different automotive applications. The future of the automotive industry with NT is very brighter, and in the near future, we can witness the changes in vehicles such as smart vehicles equipped with nano-sensors, nano-engineered particulate filters, bodyworks capable of harvesting energy, self-healing paint, and electric vehicles with improved fuel cells.

Next-generation vehicles are using NM for various purposes to enhance the efficiency, performance, and environment of the vehicles. The incomplete combustion of fuel emits carbon-based aerosol NPs. Platinum-based catalysts of the dimensions in the range 0.8–10 nm have been reported to have been released from vehicles. The latest catalyst is having comparatively manifold smaller NPs of platinum and palladium metals. Al_2O_3 as a catalyst is exclusively used in diesel fuel to improve its efficiency. Therefore, the major concern here is the emission of these NPs into the environment. Once released, they can undergo degradation and release these toxic metals. Platinum in nano-dispersed forms is easily transferred to animal tissues. Nanomaterial which is having lesser solubility is very much prone to get accumulated in the biological system. CNTs are one of the least biodegradable NPs which are lipophilic, hence very prone to bioaccumulation. Much attention is needed for studying the toxicological and ecotoxicological aspects before using them in the automotive industry, and this will help to make a healthy and eco-friendly atmosphere.

3.5 Agriculture Industries

Though NM application in agriculture has provided a promising future, it is currently in its budding stage. Synthesis of engineered NM for agricultural usage has a significant potential to enhance modern agriculture (Baruah and Dutta 2009; Subramanian and Tarafdar 2011; Prasad et al. 2014, 2017; Usman et al. 2020; Yadav et al. 2020). It has helped in dealing with existing agricultural shortcomings by using advanced materials and technologies. Problems related to pesticides, herbicides, fertilizers, etc. have been improved by optimal utilization of NT.

NP distribution in plants includes a characteristic pathway with multiple advantages (Schwab et al. 2016). Nanomaterials, due to their properties like size, surface-volume ratio, optical properties, etc., have great capacity in protecting plants (Biju et al. 2008; Islam 2019). A good example of an application of NM would be a method of pesticide and fertilizer distribution by nano-encapsulation which releases the contents in a greatly controlled mode. This method has been seen to be site-specific. It is a highly efficient method and very beneficial in protecting the nontarget organisms and other collateral reparations (Petosa et al. 2017). Nanotechnology offers an effective defense mechanism to plants upon encountering with pathogens. This is achieved by delivering systemic chemicals such as jasmonic acid, salicylic acid, benzothiadiazole, etc. to the specific sites (De et al. 2014; Kashyap et al. 2015). Mitigation of natural and biopesticide and measured and controlled release of NM-assisted bio-fertilizers, fertilizers, micronutrients, and nano-sensors are some other successful approaches of NT in agriculture (Khot et al. 2012; Rai et al. 2012; Birthal 2013; Rameshaiah et al. 2015).

Indiscriminate use of pesticides and fertilizers has already caused numerous environmental and health hazards. Because of their broad spectrum and varied scope, the use of NM, in agricultural applications, is anticipated to increase manifold in the coming decade. Atmospheric transport and deposition, agricultural applications, and industrial wastewater are how NPs enter the environment. The sluggish movement of NPs in the soil allows plants to uptake them easily (Arif et al. 2018). Previously, NPs have been reported in lettuce, zucchini, cucumber, radish, etc. (Lin and Xing 2007). The adverse effects of using NPs are already sprouting. Particularly with respect to agricultural usage, NPs have been reported for adversely affecting the biodiversity of soil ecosystem (Kumar et al. 2011; Rajput et al. 2018), nitrogen fixation processes (Fan et al. 2014), and the decline in the number of pollinators (Brown et al. 2016) and also interfere with the food chain (Kubo-Irie et al. 2016; Luo et al. 2016; Ma et al. 2018).

Owing to their distinct physicochemical properties, different types of NPs produce different effects (Nowack and Bucheli 2007). NPs have both positive and negative impacts on plants. In recent years, Zn NPs and Ag NPs have been successful in grabbing the attention of the scientific masses due to their flexibility and utility in various applications such as cosmetics, agriculture, electronics, etc. In comparison with the boom in NT, the safety requirement for practices has not been met. There have been reports of indiscriminate use and disposal of NM which are at the cost of the environment (Marcelino et al. 2018).

Before the standard methods and models for environmental mutagen testing were devised, the process has always posed a challenge. Higher plants such as *Zea mays*, *Vicia faba*, *Allium cepa*, *Nicotiana tabacum*, *Hordeum vulgare*, etc. are commonly used for evaluating environmental mutagens. Among these, *A. cepa* and *V. faba* are approved and accepted as models by regulatory bodies for testing genotoxicity (Ma 1982; Ma et al. 1995). The root tip chromosomal aberration studies with *A. cepa* and *V. faba* have been approved by the International Programme on Chemical Safety wing of the WHO and UN Environmental Programme as well as International Labour Organization (ILO).

The agriculture sector has adopted NT readily and within a very short period, the industry has gained continuous benefits from it (Mukhopadhyay 2014). Nanotechnology application in agriculture includes modulation of the effectiveness of fertilizers and pesticides, thus reducing the use, yields, early identification of the pathogen, rapid detection of toxic chemical in agri-products, fertilizer delivery system, advanced packaging system, etc. (Ditta 2012; Rai and Ingle 2012; Chhipa 2019; Usman et al. 2020). Nanotechnology has significantly improved plants using the target-based drug and gene delivery, and nano-array-based genetic modification among plants, etc. (Maysinger 2007; Pramanik et al. 2020). Precision farming and Precision Agriculture Monitoring System (PAMS) makes use of varieties of sensors supported by NT, enabling real-time monitoring of crop, soil, and environment, and also including soil temperature and humidity (Rohith 2015). The nano-encapsulation has enormous usage in developing slow and sustained-release fertilizers, pesticides, and nutrients for agriculture. It helps in reducing the use with effective delivery ensuring optimum crop growth (Chiranjeeb and Senapati 2020).

NPs used for the formulation of nano-pesticides or nano-fertilizer have a great tendency to exhibit adverse effects on ecosystem and animal life. Metal-based NPs are posing more threat because, after degradation, they release the metal atoms/ions, thus affecting both biotic and abiotic factors of the ecosystem. Soil is of paramount importance for agriculture. Repeated treatment of soil with nano-fertilizers or nano-pesticides may cause the accumulation of NPs in soil. This later can adversely impact the germination of the seeds, plant growth, biomass, etc. Although we have discussed earlier that NPs can modulate plant growth by affecting seed germination and root growth and increasing biomass, these two aspects become antagonistic to each other. Such issues do pose a concern where rigorous research and study is a prerequisite. Another facet is the dosage of application, which needs to be defined by considering its fate, distribution, persistence in various media, toxicity, and effects on nontarget organisms. An occupational hazard is one of the most significant aspects associated with agro-nanotechnology where production workers, as well as farmworkers, are at high risk. Detailed universal guidelines associated with its manufacturing, application, and handling should be devised for every NP.

Agriculture is one of the sectors where NPs have a straight interaction with the environment, plants, crop plants, animals, etc.; therefore, the environmental and health risks associated with it increase multifariously. Some of the important aspects in this concern are mentioned below:

- For risk assessment associated with NPs.
- Internationally accepted techniques for detection and characterization of NPs must be developed with higher accuracy.
- Permissible limits of various NPs also require to be defined in various media.
- Further research and funding must be oriented toward understanding the underlying mechanism of interaction of NPs with the food chain and its epigenetic effects.
- A unique property of NPs, i.e., high volume-to-mass ratio, makes it very feasible and probable to interact with biomolecules. So, the toxicodynamic and toxicokinetic studies must be understood with respect to agroecosystems.
- Other research areas in agro-nanotechnology need to address issues such as the fate of NPs, distribution, transport, bioavailability, etc.
- Collaborative research and capacity building are also suggested at various levels, viz., laboratory, organizational, geopolitical, etc., for further strengthening the area of research especially its impact on the environment and humans.

3.6 Food Industry

Conventional agriculture practices are costing the world in various ways. It is related to increased use of costlier and toxic agrochemicals, manpower, land use, etc. These factors have generated adverse effect on the environment. Sustainable agriculture ensures good yield, cost-effectiveness, and sufficient availability, which ultimately helps to enhance the agro-economy. These altogether affect the cost of the food products. Nanotechnology is widely applied in the use of nano-formulated fertilizers and pesticides. It has played immense role in food processing and packaging. It can guide the manufacturing of high-quality and safe food with the productive approach of brilliant engineering and scientific challenges. There are several emerging applications of NT in the food industry, for example, use of biosensors for detection and identification of microbes such as bacteria or any allergen (Deisingh and Thompson 2004; Pilolli et al. 2013), monitoring of quality (Otles and Yalcin 2010; Neethirajan and Jayas 2011), and nano-encapsulation of bioactive nutraceuticals (Huang et al. 2010; Jafari and McClements 2017). The quality of food packaging has been enhanced by using NT (Duncan 2011; Silvestre et al. 2011). A simple composite NM coating of food is capable of providing safety from microbes (Bumbudsanpharoke et al. 2015). A novel packaging prepared with clay and/or poly-β-pinene can increase the thermal stability and the tensile strength of polypropylene random copolymer (PPR). It was also capable of decreasing the transmission rate of oxygen and water vapors along with the reduction of *Escherichia coli* by 24% with respect to the control PPR/clay film (Ayhan et al. 2015).

The nano-encapsulation technique has great use in the food industry. This technique uses biopolymer materials such as alginates, synthetics, gums, starches, proteins, dextrins, etc. (Taylor et al. 2005). The liposome-based encapsulation has also gained great importance because of its unique benefits. Such encapsulation helps encapsulate sensitive food supplements and also enhances shelf life. Apart from this, it also helps in enhancing the product bioavailability, solubility, and target-based delivery of encapsulated material to a greater extent (Kim and Baianu 1991; Reineccius 1995). It has great use in the controlled delivery of vitamins, peptides, enzymes, and flavors in various food applications (Taylor et al. 2005). A recent report has been revealed regarding the use of machine learning to improve the application of NT food regulation. This study highlights the Perturbation Theory Machine Learning (PTML) which is associated with standards of the Organisation for Economic Co-operation and Development, European Union regulations, and European Food Safety Authority (Santana et al. 2020).

The use of NPs in the food industry is rapidly increasing and has also raised a growing concern about the safety of products and environment (Rastogi 2012). We require strengthening the system with a comprehensive assessment tool for the risk associated with nano-based food products. The risk assessment must not be just focused on its potential health effect on the human, but it must be extended and assessed for environmental safety as well.

Many agencies and regulatory bodies have provided their guidelines for the potential risk associated with NPs. The European Union has provided a directive that has made safety assessments mandatory for nano-based food products (Cubadda et al. 2013). The French Agency for Food, Environmental and Occupational Health and Safety (ANSES) has also come up with a 2-year project which had a focus on NPs/NMs in food. The objective of this project was the identification of NPs in food, potential health risk, and associated exposure assessment (ANSES-French Agency for Food France et al. 2019). There are other agencies such as FDA, US-EPA, IOSOECD, NIOSH, and HCPDEC that have provided the guidelines as needed; however, there is a need to establish a universal/global guideline (US, FDA; Tiwari et al. 2015).

Nanotechnology has surely gained the momentum in the last few years and has become part of the food industry where it has been used for enhancing the food's shelf life, packaging system, detection, and protection from microbes. Along with the potential risk assessment, these NPs must be studied in the near future for possible environmental health impacts. A strengthened tool is required to establish which can ensure the safety of food, mankind, and the environment. It is still a challenging task for all entrepreneurs, technologists, and scientists to come up with a healthy and sustainable food industry. There is a constant growing concern among the general public similar to genetically modified foods. Though the fate, risk, and toxicity of the NPs might not be understood completely, the concern of the public must be answered. The only possible ways to address such issues are education and awareness upon which acceptance of the product would depend.

3.7 Energy Harvesting Industry

Energy is very crucial for running other industries, cities, transportation, and agricultural activities. It has become a commodity of immense importance for mankind. Many countries in the world still face energy crisis. We are on the verge of consuming fossil fuels. Green energy is always considered a sustainable form of agriculture and it has the potential to strengthen conventional agriculture practices (Chel and Kaushik 2011). Electricity is used majorly for water heating for cleaning farm equipment and cooling of milk (Sain et al. 2020). They alone justify nearly 40% of the total electricity used on a dairy farm. Green energy harvested through solar cells is potentially useful in running and maintenance of greenhouse (Fabrizio 2012), crop drying (El-Sebaii and Shalaby 2012), air heating for livestock (Sultan et al. 2018), and smart irrigation system (García et al. 2018). The advancement in energy harvesting techniques aided with NT has brought many achievements in the past. Developing countries and underdeveloped countries where farmers have smaller lands and significantly poor budgets rely upon electricity provided by the government or agriculture authorities for various farm activities. Green energy, especially solar energy, would certainly help manage their budget, thereby increasing the income of farmers. The government of India has taken up a mission to double the income of farmers by the year 2022 and has worked significantly on increasing the harvesting of green energy in the past few years (Joshi and Yenneti 2020).

With the rising demand need for sustainable and economic agriculture practices, we are yet to identify the most efficient use of fuel and harnessing green energy from various sources. Energy policies of the world are being focused on low carbon emission with sufficient supplies of energy for society. The other challenge for the energy sector is lowering the emission of greenhouse gases (Barnes and Floor 1996; Shahsavari and Akbari 2018). Nanomaterial owing to its unique feature at the nanoscale has immense potential in the energy sector. Certain materials have physical properties, e.g., electrical and thermal conductivity, strength self-assembling feature, and the higher surface to unit weight volume ratio, different at the nanoscale when compared to the bulk. Because of these properties, NM makes the suitable candidate to be used in the energy harvesting sector. The efficiency of fossil fuels can be achieved through research and innovation toward finding or designing a novel catalyst. The nanomaterial is also helping the fossil fuel sector by obtaining sulfur-free cleaner fuels (Behl et al. 2012; Svinterikos et al. 2019; Jarullah et al. 2020). Apart from this application, the NM is highly used in the power system because of its special features such as corrosion resistance and super stronger properties making it suitable for use in components of turbomachinery and making it more environment friendly in terms of pollution (Hsu 2003; Brandvik and Pullan 2011; Jia et al. 2020). Insulators in transmission lines (Plojoux et al. 2007; Touzin et al. 2010), slick coatings (Mauter et al. 2011), and improved conductivity (Mudgel et al. 2010; Minea 2019) are the sectors where NM is playing a wonderful role.

Solar energy has utilized the properties of NM to harness clean energy. It has the ability to have efficient photocells, energy conversion, and storage. Properties of NM such as flexibility of the bandgap enhanced optical path, and unique charge carrier combinations can be modulated with uniqueness in size and shapes. These are the properties responsible for enhancing the light trapping and photon collections. The use of NM has just not enhanced the conventional solar cells but also able to help in producing cost-effective and higher conversion efficiencies along with affordable production costs.

There are classifications for nanostructured solar cells, viz., DSSCs, dye-sensitized solar cells; QDSSCs, quantum dot-sensitized solar cells; HSC, hybrid solar cells; PSC, perovskite solar cells; and OS; organic solar cells, as depicted in Fig. 11.4 (Shukla et al. 2016).

The challenge ahead of scientists and technologists in the energy harvesting sector is manipulating the factors affecting parameters to achieve the best performance solar cells. This challenge can be tackled with a profound understanding of the properties and behavior of NP of varying sizes for its use in developing the crucial components of cells such as electrodes, sensitizers, and electrolytes. It is also important to consider the demerits and drawbacks of devise components and designs of solar cells.

However, the NMs have greatly improved the energy harnessing sectors by providing either nano-catalysts or nanostructured solar cells. In the future, advancement in research and technology in the energy harvesting sector would bring out efficient economic systems and that would strengthen the various industrial sectors and agriculture practices, strengthening the economy and aiding the United Nation's goal of sustainable development.

There are few major concerns for the NM used in the energy sector, especially solar cells. The cost is always associated with the solar cells. Though there are low-cost solar cells available, their efficiency is compromised. Governments also have to play a key role in providing the subsidy to particular sections of society and encourage the use of clean energy. The other aspect is environmental pollutions. The organic and inorganic materials used in the solar cells are hazardous and not at all environmentally friendly. These materials include cadmium telluride, copper indium selenide, cadmium gallium (di)selenide, copper indium gallium (di)selenide, hexafluoroethane, lead, and polyvinyl fluoride. The used or waste solar panels are needed to be disposed of safely to authorized dismantling units for recovery and recycling of metals. Another disadvantage associated with the solar cell is heavy land and water use.

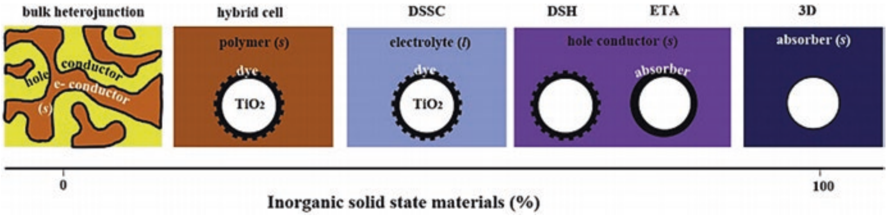

Fig. 11.4 Diagrammatic representation of solar cells (from all organic to all inorganic). (3D, three-dimensional; DSH, dye-sensitized heterojunction; DSSC, dye-sensitized solar cell; ETA, extremely thin absorber) (Shukla et al. 2016)

3.8 Nanomedicine

The global nanomedicine market is continuously increasing from $111,912 million in 2016 to $261,063 million by 2023 (Allied Market Research n.d.). Applications of nanomedicine in various fields like in diagnosis and treatment of disease and health monitoring are also continuously increasing (Mahmoudi 2021). Although the development and market of nanomedicine are still in the embryonic stage as per Nano biotic (a nanomedicine company), more than 230 nanomedicine products are in the commercial market (Allied Market Research n.d.).

A major area where NT has been greatly exploited for product development and application is in biological sciences (Roco 2003; McNeil 2005). Nanomaterials are known to interact with biological systems by various means, such as (a) by the presence of metal ions in solution and its associated chemical effect, (b) producing mechanical effects due to defined shapes and specific interfaces, (c) binding of NPs to target surface by covalent or non-covalent interaction or oxidative effect, (d) catalyzing effect, and (e) inducing the change in chemical environment (Nel et al. 2009; Dietz and Herth 2011).

With an increase in advancement of R&D, the application of NPs in the healthcare sector is rapidly increasing. Nanotechnology is being used in the field of diagnosis, drug delivery, implants, biosensors, and development of imaging devices (Alexiou et al. 2006; Lara et al. 2011; Mukerjee et al. 2012). With the advancement in NT, NPs are now capable of performing more specific applications such as targeted drug delivery, photoablation therapy (laser surgeries), and hyperthermia therapy (Hubbell and Chilkoti 2012; Habibi et al. 2016; Mondal et al. 2017). Researchers are further working toward preparing carbon nano-dot-based conductive bio-hybrids which forms individual nano-circuits. In the future, such efforts may lead to constructing functional nanodevices with immense biomedical potential (Hu et al. 2018).

4 Nanoparticles in the Food Web

Assorted pollutants, which contain these potentially hazardous compounds, may introduce NPs into the food chain. The food chain is a crucial channel for studying NP intake by high-trophic-level species. Many factors can influence NP transfer in the food chain, but the most important ones are the physicochemical qualities of NPs, the duration of exposure, and the various routes of transfer (Fig. 11.5).

Biosorption and bioaccumulation in the food chain are important processes for tracking the trophic transmission of inorganic NPs. Inorganic NPs are ingested by species in the food chain via soil, water, and eating. Furthermore, alterations in the number of reactive oxygen species, neutron activation, cell, mRNA, and DNA damage may all be hazardous effects of these NPs (Maharramov et al. 2019). In a three-level aquatic food chain, researchers looked at the bioaccumulation, tissue-specific dispersion, depuration, trophic transfer, and biomagnification potential of

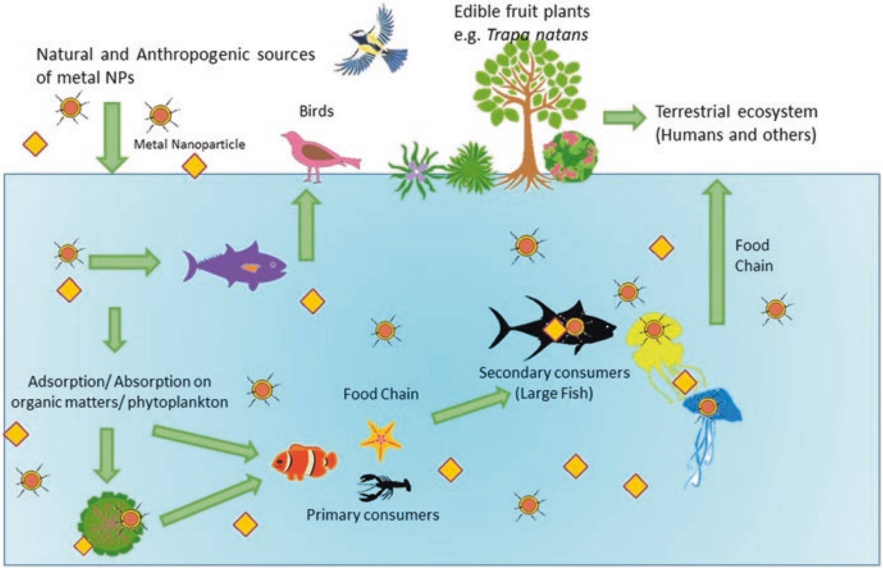

Fig. 11.5 An overview and general principle of release and entry of metal nanoparticles in food chain. (Image is adapted from Kumari et al. (2017))

13C-labeled fuller enols. Water rerio collected fuller enol NPs in *Scenedesmus obliquus*. Intestine > liver > muscle > gills > brain was ordered from highest to lowest fuller enol concentration in *D. rerio* tissues. Although fuller enols eventually make their way into fish tissues through the food chain, the lack of biomagnification reduces the risk to high-trophic-level aquatic animals (Shi et al. 2020). Bioaccumulation of blood-mediated Ag NPs in freshwater fish (*Carpio cyprinus*) was discovered. The liver had the highest level of Ag NP bioaccumulation, followed by the colon, gills, and muscles. Furthermore, the findings revealed that Ag NP bioaccumulation resulted in histopathological changes, including altered gill tissue structure and necrosis (Kakakhel et al. 2021).

5 Nanoparticles as Pollutants

5.1 Nanoparticles in Water

Water quality preservation is becoming a global concern, and it is critical for long-term crop productivity. Nanomaterial contamination of surface and groundwater can result from a variety of industrial activities. These materials can be hazardous to humans and animals, and they may also reduce crop yields (Sousa and Ribau Teixeira 2020). The methods for removing them from the environment have attracted much interest. On the other hand, a recent study showed that Fe_3O_4 NPs can be effective at removing contaminants from an aqueous solution. Manganese oxide can also be utilized to remove As (III) from the environment as an oxidizing agent. A recent study documented the importance of Fe (II) and Fe (III) NPs on the adsorption of As and their role in the microbial cycling of As and Fe. Several nano-metal oxides or oxyhydroxides mostly of Fe and Al can be employed for the removal. In the presence of competing anions like phosphate, adsorption of As and Cr by mixed magnetite and maghemite NPs from aqueous solution is a viable technique to remediate groundwater. Iron oxide NPs work well as a nano-adsorbent for removing Cd from drinking water. Maghemite NPs, for example, have been studied for their ability to remove metal ions and so enhance water quality (Ramírez Ortega et al. 2021). Humic acid and amino-functionalized polyacrylic acid were used to functionalize and stabilize iron oxide NPs. Nonmobile NPs in soils effectively minimize labile P movement and hence improve water quality.

5.2 Nanoparticles in the Soil

The reactivity, mobility, and bioavailability of NPs determine their fate in soils and water. Their fate and behavior are influenced by how their physical and chemical traits interact with the environment. Aggregation/disaggregation, dispersion and diffusion, adsorption and desorption, flocculation and dispersion, biotic and abiotic degradation, and transformation via photolytic reactions are all important mechanisms that might influence the destiny of NNPs in water (Jeevanandam et al. 2018). Other processes include charge enhancement and steric stabilization by naturally present organic material (NOM), charge neutralization by oppositely charged ions, and binding by fibrils (Tiede et al. 2008). Natural water has complex effects on NP stability, aggregation, and sedimentation. Organic matter in colloidal form is more common in soils than organic matter in big particle size. The formation of porous microstructures from the aggregation of this tiny colloidal organic component is critical for microbial activity and nutrient absorption. Pathogen survival and nutrient bioavailability are both affected by these colloidal particle aggregations. The fate and transport of NPs in soil are influenced not only by their physical-chemical properties but also by soil factors. NOM can modify the surface charge characteristics of mineral NPs, and hence play a role in NNP aggregation/disaggregation and sorption to bigger soil and sediment particles. The solubility of minerals is an important component in influencing the fate of NPs in soils. Solubility dependent on size is predicted by a modified form of the Kelvin equation, which states that as particles get smaller through the nano-range of sizes, their solubility increases exponentially (Rashid et al. 2016). Lepidocrocite and $FePO_4.nH_2O$ can produce mineral NPs in soil at lower Fe/P ratios in solution than their bulk solubility predicts (Bakshi and Abhilash 2020).

5.3 Nanoparticles in the Air

Nanoparticles operate as predecessors of coarser particles during the atmospheric aging process, according to a 2007 report by the Intergovernmental Panel on Climate Change (IPCC), altering global climate and urban visibility. They also change the chemistry of the atmosphere and the global climate due to their unique chemical composition and reactivity (Archibald et al. 2018). Furthermore, these particles cause global warming (by absorbing solar energy) and cooling (by scattering solar radiation), both of which have an impact on the global radiation budget. Another notable occurrence is the formation of atmospheric brown clouds (ABCs). According to a study, soot generated from biomass burning makes up 70% of the ABCs over South Asia, contributing to glacier melting, climate change, and reduced sunshine, all of which have an impact on agricultural production (Sonwani et al. 2021). Without a question, anthropogenic emissions are the primary source of atmospheric NPs in metropolitan areas. Various studies have concluded that vehicle exhaust emissions are a major source of air pollution with NPs in urban areas (Slezakova et al. 2013; Müller et al. 2020). Epidemiological studies have regularly demonstrated a link between increased morbidity and mortality rates in both adults and children when particle air pollution levels are high. Studies have also found a correlation between respiratory illness and the number of ultrafine particles in the air (Williams et al. 2013) Ultrafine particles are more hazardous and inflammogenic than fine particles for low solubility, low toxicity compounds like TiO_2, carbon black, and polystyrene beads, according to in vivo and in vitro toxicology studies. In many of these studies, the term “ultrafine particle” can be directly exchanged for NPs, as these particles are manufactured industrially (Rizzo 2009). Nanoparticles produce more reactive oxygen species (ROS) than particles of bulk element/compounds, resulting in enhanced transcription of pro-inflammatory mediators via intracellular signaling pathways such as calcium and oxidative stress (Williams et al. 2013; Bundschuh et al. 2018). Only a few NP compositions and architectures have been studied so far, including carbon, polystyrene beads, and TiO_2 as surrogate particles to simulate particulate air pollution. All of these substances have a low toxicity and solubility (Stone et al. 2007; Nho 2020).

6 Life Cycle of Nanoparticles in the Environment

In the field of agriculture, NPs are applied as nano-fertilizers that increase the growth and yield of the plant, as nano-pesticides to manage disease and pests, and even in nano-sensors to monitor soil quality and health of the plant. All these approaches have the aim to increase the sustainability and efficiency of agricultural activities with less input demand and less waste generation (Bottero et al. 2017).

Nanoparticles released from various sources enter into the soil, water, and air. These get bio-accumulated in microorganisms and plants and further get transferred to higher trophic levels (Donia and Carbone 2018). These NPs can also make their entry into the wastewater treatment plant sludge by entering as residual NPs in agricultural settings. This sludge might also carry viruses, bacteria, pathogens like Salmonella, antibiotics, etc. (Khot et al. 2012; Peccia and Westerhoff 2015).

NMs can enter the environment by finding their ways (Fig. 11.6) intentionally or unintentionally; however, various consumer products like paints, electronics, medical devices, cosmetics, plastics, car catalysts, ceramics, etc. are responsible for their entry. Other than this, several industrial spills, runoffs, and waste can permit the entry of NMs into the environment. These days research is mainly focused on NMs having the potential to cause spills or waste containing metal oxides, carbon nanotubes, etc. that are toxic and can have a toxic effect on the environment when released (Lowry et al. 2010). Kalavrouziotis et al. (2009) studied the impacts of elements such as Pt, Pd, Rh, etc. belonging to the platinum group emitted into the atmosphere by automobile catalyst converters. The study suggested that irrespective of the pollution-reducing capability of catalyst converters released from car exhaust fumes, it is leading the entry of platinum group elements into the environment in the form of particulate matter which gets accumulated in the soil, air, and plants. Because of the nature of these emissions, the particulate matter travels over long distances and has increased significantly in the past 10–15 years especially by the side of highways (Kalavrouziotis et al. 2009). Nanomaterials are released into the environment intentionally while remediating contaminated soil and groundwater (by using iron NPs) (Klaine et al. 2008).

Another intentional release is done by consumer goods, for example, sunscreens, paints, fabrics, healthcare products, etc. The entry of these products is proportional

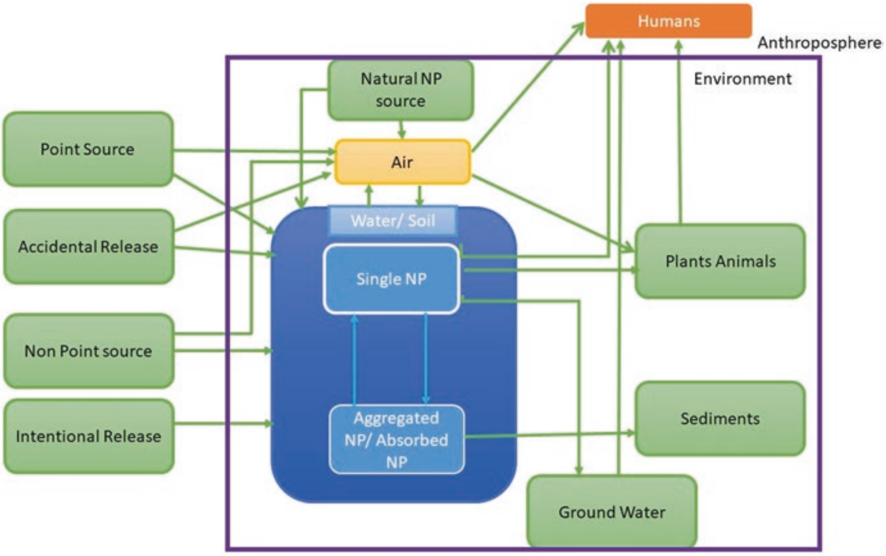

Fig. 11.6 Pathways of NPs into the environment

to their use (Klaine et al. 2008). Researchers have switched to microcosm and mesocosm systems as miniaturized ecosystems to simplify conditions of experiments which will help to know NP's uptake and bioaccumulation (Nam et al. 2014).

7 Occurrence and Exposure of Nanoparticles

The natural NPs in the biosphere enter the environment from active volcanoes (Ermolin et al. 2018). The particles travel long distances during which wind acts as a primary vector and takes other elements including nickel, cadmium, zinc, etc. with themselves (Malakar et al. 2021). The natural origin leads to the mixing of compositions and purity of nanomaterials. Other factors like temperature, physical collisions with high speed, radiations, waves, pressure, etc. can also lead to the formation of nanomaterials in space (Jeevanandam et al. 2018). Various biological or biotic processes like microbial respiration by microorganisms are also a reason for the entry of nanomaterial (having fixed stoichiometry and high monodispersity) in the environment. Nanomaterials like humic matter (inorganic in nature) are microbial degradation products, and nanomaterials like calcium, selenium, iron, etc. (inorganic in nature) are formed by biomineralization.

Humans are exposed to these nanomaterials by various pathways: inhalation (respiration), ingestion, skin penetration, and intramuscular or intravenous injections. The primary route for human exposure is inhalation and hence air with nanomaterials is a serious health hazard. In urban areas, AQI can be a probable indicator for suspended nanomaterials that may cause various types of cancers (Malakar et al. 2021).

8 Conclusion and Future Prospects

Scientists, technologists, and academicians belonging to the scientific arena of the world are looking forward to have improved technology, guidelines, and policy framework for the emissions, disposal, recycling, and remediation of NM toxicity. Nanotechnology is developing faster and setting up the aim higher where high-end technological innovation could be witnessed. Tools and devices equipped with artificial intelligence would help us in precision farming, advanced pollutant detection systems and bio-remedial approaches, robotics, electronics, next-generation medicine, diagnosis, and therapeutic approaches. Industries such as agriculture, medicine, chemicals, etc. are few where NP application has gained popularity and diverse use. Every sector where NMs have been in use would be certainly releasing the NMs at one point of the time in the environment and especially in the soil and water. It has been proven that release of NMs in the soil and water would not only affect and crops, but it can also affect the terrestrial and aquatic system. The potential toxic effects, hazards, and risks associated with the environment must be dealt with utmost care and dedication. The release of NPs in the environment by any means and their persistency, transport, distribution, fate, and ecological implications have to be addressed accurately with suitable guidelines of dosage and handling. Several parameters influence the transport and risk of NMs; thus, toxicity study and health-related assessment are required. To protect the environment and food chain, special care for their disposal and development in nano-waste practices is urgently needed keeping in view the existing regulations. Deactivation and recycling practices should be employed based on the properties and category of NMs using interdisciplinary approaches. Guidelines for protecting the health of occupational workers also need to be addressed, supported, and insured. Universal methods/SOP of detection, characterization, and pharmacological or toxicological studies must be devised for NPs. There should be a proper regulatory framework that provides guidelines for the potential risk associated with emissions of NPs. It is anticipated that NT is going to become a key economic driving force in the future that can help us to combat challenges associated with agriculture, the environment, industries, medications, and electronics (where miniaturization of components has revolutionized the portability of the devices). Studies about nanoecotoxicology are limited and need more awareness when it comes to designing, fabrication, risk, and safety of the next generation of metallic NPs in consumer products. Collaboration among universities, labs, investigators, and industries and even collaborations on a geopolitical level would surely strengthen the approach and would help to boost future endeavors.

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Chapter 12
Ecotoxicology and Toxicology of Metal-Based Nanoparticles

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1 Introduction

Nanotechnology (NT) has witnessed exponential growth in many sectors in the past, and it has potential to revolutionize industrial manufacturing (Islam 2019; Jeevanandam et al. 2018; Virmani et al. 2021), agriculture (Kumar et al. 2019), environment (Isaeva et al. 2021; Rajput et al. 2018b), and healthcare (Włodarczyk and Kwarciak-Kozłowska 2021). The unique physicochemical features of nanoparticles (NPs) enable its substantially wide applications in other sectors such as electronics, building materials, and automotive (Moradiya 2019; Pulit-Prociak et al. 2015). Market of nanotechnology has reached up to US$42.2 billion and is expected to reach US$70.7 billion by 2026 with a surging CAGR of 9.2% despite COVID-19 pandemic in 2020–2021 (Globe News Wire 2021). One of the major applications NPs have gained in the past few years is agriculture (Rajput et al. 2018a; Rameshaiah

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et al. 2015). Metal-based NPs are used in agriculture to enhance the growth of the plant, maintain the health of agricultural plants and nutrient management, and protect them from pest infestation through the use of nanofertilizers and nanopesticides (Chen 2018; Tourinho et al. 2012). Nanoparticles are also reported to protect the plants from abiotic stresses like drought, temperature, humidity, and higher salt concentrations (Liu and Lal 2015; Rajput et al. 2021; Ranjan et al. 2021). They are also used as sensors for monitoring the soil quality of agricultural field (Prasad et al. 2017). They are used for detection of the presence of mycotoxins in several foods (Sertova 2015). The agriculture sector has taken up the application of NPs progressively; several commercial formulations are nowadays available for various applications in agriculture (Kumar et al. 2019; Sabourin 2015).

Metal-based NPs have been greatly explored in the agriculture sector; hence the major goal and prospect should be on the development of formulations and technologies (Grillo et al. 2021; Sneharani and Kumar 2021). Nanotechnology also brought innovative changes in the food industry (Huang et al. 2018). Food processing (Shafiq et al. 2020; Singh et al. 2017), fortifications (Knijnenburg et al. 2019), development of a packaging system for imparting a lasting freshness and longer shelf life (Duncan 2011; Jafarzadeh et al. 2020), and detection of foodborne pathogens (Singh et al. 2017) are the key innovation brought about by NT. It has been intensely utilized for development of products and biological science applications (McNeil 2005; Roco 2003). For developing successful delivery system of NPs, the following properties play crucial role: (a) ability to precisely deliver the active compound at the target site (b) and ensure specific rate of activity at a target time and (c) efficiency to maintain the active compound at suitable levels for longer duration (Singh et al. 2017). Nanomaterials interact with different biological systems by various means: (a) presence of metal ions in solution and their chemical effect; (b) producing mechanical effects by virtue of their defined shapes, specific interfaces, etc.; (c) their catalyzing effect; (d) binding of NPs onto targeted surface by covalent/non-covalent interaction/oxidative effect; and (e) inducing changes in the chemical environment (Dietz and Herth 2011; Nel et al. 2009). Such lucrative properties of NPs have ensured its application in healthcare sector, where they are exploited for medical and pharmaceutical/nutraceutical application (Hook 2007; Ji et al. 2008; Rizvi and Saleh 2018).

With the increasing application of NPs in many sectors, a serious environmental concern is increasing. Presence of NPs in the environmental components like air (Liu et al. 2021; Maher et al. 2020), water (Blinova et al. 2010; Gondikas et al. 2014), and soil (Antisari et al. 2013; Stuart and Compton 2015) has been reported in the past. Such omnipresence of NPs is very likely to enter the food chain and may have toxicological implications to humans and substantial adverse effects on human health (Cedervall et al. 2012; Rico et al. 2011; Zhu et al. 2010). It may affect at molecular level by interfering with key biochemical process as well as at tissue and organ levels (Monteiro-Riviere et al. 2009; Nel et al. 2006).

They have been observed to cause ROS-induced oxidative stress, DNA damage, misfolding of proteins, apoptosis, etc. and exposure symptoms like breathing problems, irritations, and inflammation (Olaru et al. 2019; Yang et al. 2021). Studies of nonporous SiO_2, mesoporous SiO_2, and anatase TiO_2 NPs have reported that these particles have immunomodulatory and immunosuppressive properties, and both properties are undesirable (Maurer-Jones et al. 2010, 2012). The application of NPs has taken a paradigm shift toward the environmental protection. Recent works on air pollution (Gabal et al. 2020; Yang et al. 2019), wastewater treatment (Sadegh et al. 2017), and soil remediation (Rajput et al. 2018b, 2020; Romeh and Saber 2020) are some advanced examples of NT application in environment protection and food security (Dasgupta et al. 2015; Zhao et al. 2020; Ranjan et al. 2022).

In this chapter we have highlighted the growing concerns about the presence of NPs in the environment soil and water and their fate and distributions and ecotoxicology in aquatic and terrestrial animals. This chapter has also discussed the toxicity of metal NPs with special emphasis to human.

2 Fate and Distribution of Nanoparticles

2.1 Nanoparticles in Soil

Soil health is greatly attributed to a framework that is closely associated with the environment and land use to support the plants and life on earth and regulate the water and air quality (Sneharani and Kumar 2021). In recent years, nanoparticles have been popularly used in agriculture as nanofertilizers (Dimkpa and Bindraban 2017), nanopesticides (Kah et al. 2018), nanofungicides (Arciniegas-Grijalba et al. 2019), and nanobionics (Fasake et al. 2020). Soil is one of the mediums where application of NPs has direct implications on the environment. The continuous and repeated application of NPs may lead to accumulation of NPs or their constituent elements in the soil (Rajput et al. 2017). Physicochemical characteristics of the soil are greatly affected by presence of NPs, their constituent elements, and other xenobiotics (Rajput et al. 2020).

Soil pH is a key factor that has direct link with the fertility of the soil and overall health. It also affects the availability of the nutrients in the soil (Fernández and Hoeft 2009). The pH of the soil is greatly affected by the presence or accumulation of NPs of Ag, Au, Cu, Zn, Ti, etc., and their presence also affects the beneficial soil microorganisms and nematodes (García-Gómez et al. 2018). Zinc NPs have been reported to affect the soil beneficial microbes greatly with respect to the dissolved Zn (Waalewijn-Kool et al. 2013). The CuO NPs have been reported to affect the pH of the paddy field soil negatively thereby affecting overall soil health (Shi et al. 2018). The effect of presence of NPs on the soil is dependent on the soil type, the concentration of NPs, and also the enzymatic activity of the soil (Shin et al. 2012). Higher concentration of NPs alters the dehydrogenase activity negatively and influences the balance of the soil nutrient and fertility (Jośko et al. 2014; Shin et al. 2012). The physicochemical properties of NPs determine their fate in soil (Veerakumar et al. 2021). Organic matter in the form of colloids is more common in soil environment. Formation of porous microstructures from aggregation of this tiny colloidal organic component is critical for microbial activity and nutrient absorption.

The aggregation of these colloidal particle affects pathogen survival and nutrient bioavailability (Kumar et al. 2017). Disaggregation of FeO-NP aggregates of 500–1000 nm produced at pH 7.59 can be induced by coatings of NOM on surfaces and within pores. Chemical weathering of silicates, oxides, and other minerals produces amorphous silica, hydrous alumino-silicates (allophone, imogolite), and oxides (hematite, magnetite). A report of January 2015 showed that by weathering of sulfide-rich natural NPs, 871 rocks, goethite, amorphous FeO-NPs, and ferrihydrite, reacted with water due to changes in properties such as temperature, pH, high oxygen concentration, etc. (Kumar et al. 2017). Accumulation of NPs in the soil can also have serious impacts on the crops by affecting germination (Mazumdar and Ahmed 2011), reduced roots and shoot lengths (Castiglione et al. 2011), reduced biomass (Wang et al. 2016), and diminished photosynthetic capacity (Tripathi et al. 2016). They can also induce ROS-dependent oxidative stress followed by genotoxicity in the plants by affecting their genetic content (Ranjan et al. 2021). Due to Source enormously growing use of NPs, their emission in the environment may be hard to characterize precisely however, soil and water, they are major sinks of pollutants, so a graphical illustration can certainly help to delineate the dynamics of NPs across the biotic and abiotic components (Fig. 12.1).

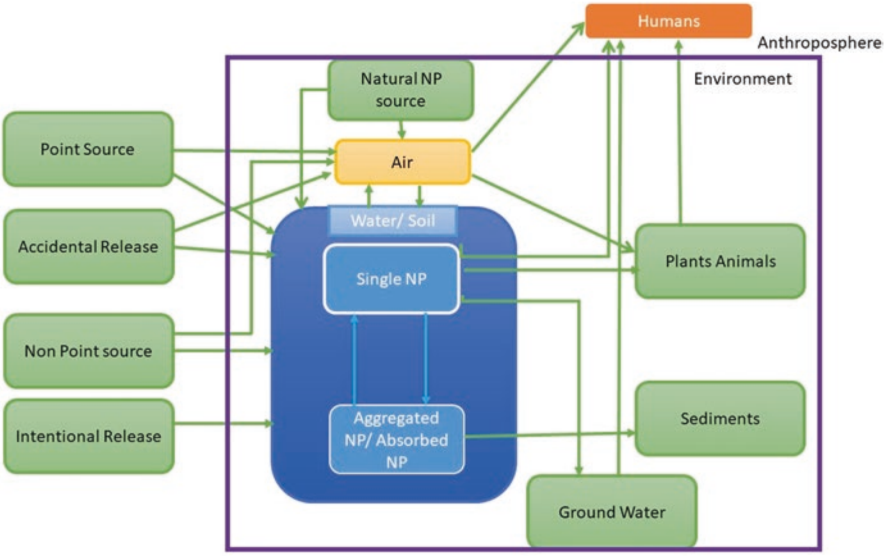

Fig. 12.1 Pathways of nanoparticles into the environment and across the biotic and abiotic components

2.2 Water

Preservation of water quality is becoming a global challenge as contamination of surface and groundwater with heavy metals is caused from a variety of industrial activities. These metals can be hazardous to living organisms and also reduce crop yields (Ding et al. 2017). Research is being focused on removal of contaminants. Phyllosilicates, fly ash, zeolites, biosorbents, and activated carbon are among the inorganic and organic adsorbents that are effective at adsorbing metal pollutants (Nowack 2017; Rashid et al. 2016). Due to unique features, such as adsorption capacity, high surface area, unsaturated surfaces, etc., NNPs have shown to have potential as remedial amendments in recent research (Debiec et al. 2018; Isaeva et al. 2021; Vo et al. 2020). Nanoparticles that are commonly used as adsorbents include oxides such as Fe2O3, Fe3O4, SiO2, and Al2O3(Naseem and Durrani 2021; Sarwar et al. 2021). It has been studied that Fe3O4 NPs can effectively remove contaminants from aqueous solution.

Arsenic (As) contamination of drinking water is a global problem that has been thoroughly reported. Predominantly, As occurs in water in the form of As(III) (H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{2-}$) and As(V) (H_3AsO_4, $H_2AsO_4^-$, and $HAsO_3^{2-}$) (Bhatia et al. 2014; Shankar and Shanker 2014). Oxides of As are not easily converted to insoluble forms. Some methods for removal include adsorption, coagulation, membrane filtration, ion exchange, etc. (Tiede et al. 2008). Activated C, as well as oxides of metals like Mn, Fe, and Zr, are naturally available nanoscale adsorbents that have been widely exploited for As cleanup (Isaeva et al. 2021; Naseem and Durrani 2021; Sarwar et al. 2021). For removing As from drinking water, a combination of MnO_2 and Fe_3O_4 can be effective for oxidation, adsorption, and magnetic removal (Naseem and Durrani 2021; Vo et al. 2020). Ferrihydrite, goethite, lepidocrocite, nano zerovalent iron, and nano-TiO_2 have been well tested as adsorbents for removal of As (Cheng et al. 2021; Gupta and Xie 2018; Vítková et al. 2018).

The application of magnetically assisted chemical speciation of Fe_2O_3 NPs for decontamination process in the water treatment process has received attention (Naseem and Durrani 2021). Along with competing anions like phosphate, adsorption of As and Cr by mixed magnetite and maghemite NPs from aqueous solution has been a viable technical approach to remediate groundwater. This mechanism is due to electrostatic attraction between heavy metals and combination of magnetite–maghemite, which is affected by pH, contact duration, initial concentration of dissolved species, and adsorbent (Samrot et al. 2017; Zhu et al. 2008).

2.3 Fate of Contaminants

In soil/sediment and natural water systems, nutrients concentrate as fine particle fractions (colloid form). These NPs have the potential to carry nutrients from soil to the surface streams (Kraas et al. 2017; Unrine et al. 2012). When it comes to NNP colloid-facilitated transit from soil to river surface, contaminants follow the same patterns as nutrients. These colloidal particles help transport trace metal pollutants by sorbing it strongly and acting like mobile vectors (Chai et al. 2015). Contaminants found in the environment include cationic (Cs+, Cu2+, Ni2+, Pb2+, Cd2+, etc.), anionic (CrO_4^{2-}, AsO_4^{3-}, etc.), and nonpolar- (PAH, DDT, etc.) and polar-organic compounds, whereas colloidal particles are mostly minerals with amphoteric surfaces (Bakshi and Abhilash 2020) such as Fe, Al, and Mn oxides, carbonates, fixed charge surfaces (expansible phyllosilicates), and organic matter-coated mineral phases (Rashid et al. 2016).

Surface complexation, hydrophobic partitioning, and ion exchange are the three main fundamental sorption mechanisms involved in the colloid-facilitated transport of pollutants (Gao et al. 2017). Colloid mobilization mechanisms are also crucial to the possibility of aided transfer. Nanoscale particles can have a big influence on trace metal transport, either slowing it down when they're stuck in the matrix or speeding it up when they're moving (Tiede et al. 2008). By decomposing or immobilizing redox-sensitive pollutants, bio-colloid transport is useful for remediation (Bobori et al. 2020). Natural organic colloids, like humic compounds, were found to be effective at removing hydrophobic pollutants from sediment (Naseem and Durrani 2021). According to a recent study, contaminant sequestration is primarily accomplished by surface complexation, albeit sorbed surface species can be contained in the inner surfaces of NPs (Qafoku 2011). Nanoparticles are the dominant factor that controls the bioavailability and transformation of many contaminants. The effects of NP interactions with soil minerals on pollutant sorption and desorption have been documented. In soil and water, iron-rich NPs effectively compete with NOM for Pb binding as compared to other metal ions (Bundschuh et al. 2018). It has been shown that Pb sorption on ferrihydrite NPs occurs at edges and corners with either mono-dentate or bi-dentate bonding (Bundschuh et al. 2018; Tiede et al. 2008).

3 Ecotoxicology of Nanoparticles

Nanoparticles present in water and soil are absorbed up by primary producers. In aquatic environment, NPs are taken up by phytoplankton followed by the primary consumers/microorganism (zooplanktons) and accumulate at the first trophic level. The secondary consumers especially lower aquatic organisms (e.g., krill) affect their normal physiological activities (Bergami et al. 2020); then those accumulations are biomagnified in other higher trophic level organisms (Asztemborska et al. 2014). Consumption of aquatic organisms as food by higher animals and humans leads to accumulation of NPs in various organs (Kik et al. 2020). Similarly, crops/plants absorb NPs from water and soil through their roots which enter biotic components upon their consumption (Tripathi et al. 2017). Nanoparticles, thus, get bioaccumulated at each tropic level and exhibit toxic effects.

3.1 Effect on Aquatic Animals

The toxicity of NPs on aquatic ecosystem is important to study as most contaminants that are released in the environment get consumed by aquatic species. Toxicity of metallic NPs on *Danio rerio* (*zebrafish*), *Daphnia pulex* (daphnids), and *Pseudokirchneriella subcapitata* (a microalgae) as models of different trophic levels and feeding strategies exposed to common metal NPs (Cu-, Al-, Co-, Ag-, Ni NPs, and TiO_2). The study showed that NMs caused "acute toxicity" and "filter-feeding" in many aquatic species and invertebrates, thereby highlighting highest susceptibility to metallic NP exposure. Daphnids and algae were more affected by metal NP toxicity as compared to zebrafish. This is because daphnids are particulate filter feeders and are more likely to be exposed to larger numbers of NPs. No apparent relation between size and surface area of NPs were observed. Nanoparticles were capable of "causing acute toxicity in multiple aquatic species" regardless of their shape.

Among all metal NPs, Ag- and Cu- were the most toxic, in their soluble forms, in all species because of dissolution of these particles (Griffitt et al. 2008). MacCormack et al. suggested that physical dimension of NPs helps them to interact with cellular receptors and transport proteins. Fishes with more than 60% of the respiratory and ion transport surface area possess larger health threats. It was observed that under "steady-state physiological conditions," interaction of gill ion transport with metal NPs resulted in iono-regulatory failure (MacCormack and Goss 2008). Marine ecosystems possess alterations in factors such as pH, salinity, pressure, temperature, etc. which are not considered when studying NP toxicity in animals. Altered cell membrane structure due to temperature changes can be affected by specifically engineered NPs.

Salinity of marine ecosystems also needs to be considered, because fishes adapt to such changes, for instance, altered gill membrane. Another important factor is exposure of fishes to limited oxygen in water. This increases their vulnerability to NP exposure and toxicity. Hypoxia increases ventilatory effort and cardiovascular changes that are necessary for adjustments. This further increases the risk of toxicity in respiratory system as many aquatic species increase their skin capillary surface area to improve oxygen uptake; and this in turn allows more NPs to enter the system, causing acute toxic effects (MacCormack and Goss 2008). Zhu et al. have observed that chronic exposure to sublethal fullerenes aggregates on carp. The most affected organs were observed to include gills, brain, and liver. This was because of increased oxidative stress due to long-term exposure (Zhu et al. 2008). These findings are important and helpful in creating regulatory frameworks that will monitor the industries and controlling NP release in the water.

3.2 Effect on Terrestrial Animals

Natural NPs are widely present in terrestrial ecosystems. Soil contains many materials of <2 μm that are commonly called as colloidal soil. The colloidal soil component includes FeO-NPs, humic acids, and phyllosilicates. Due to increase in production and utilization of engineered NPs, it is entering the terrestrial environment through direct modes (zerovalent metal for remediation) and indirect modes (spills, emissions) (Peralta-Videa et al. 2011). For example, emissions caused by catalytic converters increase the occurrence of metals such as Pt, Pd, and Rh-NPs (Fatta-Kassinos et al. 2011). The concentration of NPs in soil or terrestrial ecosystems remains to be estimated because of their complexity, separation, and identification techniques. It is assumed that when they are released in environment, their fate depends on their specific chemical and physical characteristics. Properties like ionic strength, texture of soil, and pH have been studied to affect the impact, transport, aggregation, sorption-desorption, stabilization, dissolution, etc. of NMs (Peralta-Videa et al. 2011).

Exposure of water samples containing AgNPs has been studied to be potent nematicide at a dosage of 30–150 μg ml^{-1} for 6 h (Cromwell et al. 2014). The toxic effect of AgNPs is associated with the induction of oxidative stress through the activation of PMK-1 P38 mitogen-activated protein kinase (MAPK) pathway in the cells of targeted nematodes (Lim et al. 2012). They also possess bactericidal and fungicidal effects (Furno et al. 2004; Kim et al. 2007). Similarly, exposure of green-silver NPs (GSN) at a dose of 17 mg ml^{-1} was observed to be very effective in reducing juveniles nematodes *M. javanica* population in soil by 69.44%, while 12.75 mg/100 mL was effective against *T. turbinata* and *U. lactuca* algae (Abdellatif et al. 2016). Mortality of *M. incognita* was seen to increase by 4.3 and 2% at exposure of 800 and 400 mg ml^{-1} of TiO_2 NPs (Ardakani 2013). Decrease in reproduction of *C. elegans* was also observed after incubation with metal- and metal oxide-NPs, viz., silver (Ag), zinc oxide (ZnO), aluminum oxide (Al_2O_3), and titanium oxide (TiO_2) NPs (Wang et al. 2009). Improper disposal of NPs affects soil organisms especially earthworms (Samrot et al. 2017). A study highlights ZnO and TiO_2 NPs significantly damage DNA (Hu et al. 2010). The survival, reproduction, and weight change were affected in *E. andrei* in the presence of Zn- and $ZnCl_2$-NPs (Romero-Freire et al. 2017). Such results suggest excessive reduction of species possessing beneficial features might produce severe effects, such as long-term degradation of soil patterns, altered landscape, decreased soil resilience, reduced soil health, and reduced agricultural productivity (Medina-Pérez et al. 2018).

3.3 Effects on Beneficial Soil Microbiome

The enormous production volume of NPs is indicating their huge application in industry and domestic level for various proposes. Along with this achievement, their presence in the environment and associated risk has increased and become a global problem. Sources, fate, and effects of NPs have now been understood by researchers, and their findings have made significant progress in recent years. Metal-based NPs enter the environment during the manufacturing of nano-aided products and also from raw materials. They also get released during application and after disposal of nanoproducts or waste (Gottschalk et al. 2013; Tolaymat et al. 2017). The emission of NMs occurs through direct emissions or through emissions occurring from leachates of landfills and effluents (Al-Kattan et al. 2015; Kaegi et al. 2010, 2011). The term “nanoinformatics” is also used for studies related to applications of NT and bioinformatics approaches (Anandaram and Rashmi 2020). Metallic NPs have been observed to enter the food chain and cause significant toxic consequences. Studies about nanoecotoxicology are limited and need more awareness when it comes to designing, fabrication, risk, safety, etc. of the next generation of metallic NPs in consumer products. Some abiotic factors such as pH, ionic strength, and presence of organic matter are expected to alter the aggregation, chemistry, and toxicity of NPs (Handy et al. 2008). After entering the environment, these NMs face a process of modifications impacting their tropical transfer. Sulfidation of AgNPs has been observed to be toxic for microorganisms (Kraas et al. 2017).

The presence of these NPs in soil is expected to rise in the future. Nanoparticles, on accumulating in the soil, affect the biota and are transported through soil particle interfaces. It then gets aggregated, adsorbed, and immobilized in soil sediments and particles and is taken up by bacteria resulting in their introduction in the food chain. For example, exposure to TiO_2 NPs has been studied to stimulate immune system, increase ROS, and damage lysosomes, proteins, and DNA (Bobori et al. 2020). Some other common metallic NPs such as ZnO and CuO NPs are widely used as bactericides. However, their toxic effects have been observed to affect non-target organisms also (Exbrayat et al. 2015). The transfer of NPs in aquatic products has also been reported (Vaseashta et al. 2007). The fate of NPs in aquatic environment varies depending upon their properties (physical and chemical), temperature, pH, salinity, etc. (Selck et al. 2016). Testing of aquatic toxicology by NPs still remains a key challenge (Petersen et al. 2015). TiO_2 that are used to disinfectant water from coliform bacteria, when dispose of as urine, get directions to sewage and enter wastewater treatment plants where these small particles cannot get removed. As a result they flow to the surface waters and become hazardous for the organisms (Westerhoff et al. 2011). Contamination of the aquatic environment happens when NPs present in runoff, sanitary, and industrial sewages get way to the water. These NMs migrate, accumulate in water and affect their normal biota, and cause harmful alterations to living organisms, human, and all ecosystems (Lecoanet et al. 2004).

Further, they may make the life of marine and benthic organisms in threat. Consuming contaminated seafood makes consumer exposed (Ward and Kach 2009).

Few studies have been conducted on their presence in meat and animal tissues. However, their presence has been reported due to the usage of nanocomposites packaging. Several parameters influence the transport and risk of NPs. Toxicity study and health-related assessment are required. To protect the environment and food chain, especial care for their disposal and development in nanowaste practices is urgently needed keeping in view the existing regulations. Deactivation and recycling practices should be employed based on the properties and category of NMs using interdisciplinary approaches.

4 Toxicology of Nanoparticles on Human Health

Metal NPs have diverse applications in industries, military, medical, cosmetics, as well as consumer goods. Owing to its several unique characteristics such as size, shape, surface area to volume ratios, chemical composition, nature of aggregation, structure activity, surface coatings, electronic properties, etc., they have been reported to cause substantial adverse effects on human health. It may affect at the molecular level by interfering with the key biochemical process as well as tissue and organ levels. Many metals (e.g., Ag, Au, and Cu) which are relatively poorly toxic in its bulk form however their metals NPs have been reported to have a significant toxic effect and potentially damaging biological interactions (Monteiro-Riviere et al. 2009; Nel et al. 2006). A study in the year 2006 has reported that NPs of metal oxides such TiO_2, ZnO, Fe_3O_4, Al_2O_3, and CrO_3 of size 30–45 nm have a significant toxicity effect on mammalian cells (Jeng 2006). Studies of nonporous SiO_2, mesoporous SiO_2, and anatase TiO_2 NPs have reported that these particles have immunomodulatory and immunosuppressive properties, and both of these properties are undesirable (Maurer-Jones et al. 2010, 2012). Interaction of NPs with biological systems may lead to several cytological endpoints and their corresponding consequences Table 12.1.

Such reports highlight a concern of the future when these NPs could become an integral part of our lives and its usage can be common in day-to-day use products, medicines, agriculture, etc. Therefore, a comprehensive and thoughtful review of NP-associated hazards is required which can be built upon arduous risk assessment studies and safe manufacturing handling and disposal guidelines as well as practices (Oberdörster et al. 2007). In this part of the review article, we have compiled some metal oxide NPs and their toxic effect on human health.

4.1 Cu-/CuO NPs

Copper NPs (Cu-NPs) have got wide industrial applications, and therefore there is growing threat of environmental and health safety. The major target organs of Cu-NPs are the kidney, liver, and spleen (according to the Hodge and Sterner scale).

Table 12.1 Cytological endpoints and consequences of NP interaction

Endpoints	Reasons	Significances	References
Stress on endoplasmic reticulum	Protein folding is affected and unfolded proteins may get accumulated in ER	Initiation of endoplasmic reticulum stress signal and autophagy for balancing homeostasis; apoptosis	Wang et al. (2012), Chen et al. (2014), Tiwari and Rohiwal (2020)
Inflammation	Activation of Toll-like receptors and Nod-like receptors; release ofalarmins and uptake by immune cells	NLRP3 inflammasome activation; release of cytokines	Dobrovolskaia and McNeil (2007), Dobrovolskaia et al. (2009), Wang et al. (2013)
Oxidative stress	Formation of reactive surface, dissolution of toxic ions, mitochondrial dysfunction, and activation of immune cells	ROS-mediated toxicity; cell organelle damage of other organelles; inflammation, genotoxicity and may cause apoptosis	Risom et al. (2005), Xia et al. (2006), Limbach et al. (2007), Meng et al. (2009), Hsu et al. (2015)
Dysfunction of mitochondria	Depolarized mitochondrial membrane and ROS generation	Activation of inflammasome (NLRP3); initiation of autophagy and apoptosis	Poland et al. (2008), Pan et al. (2009), Khan et al. (2012), Coradeghini et al. (2013), Ahmed et al. (2017)
Dysfunction of lysosome	ROS generation and ROS-mediated toxicity; dysregulation of lysosomal pH; lysosomal trafficking is affected	Activation of inflammasome (NLRP3); ROS generation and hydrolytic enzymes; cell organelles dysfunction and apoptosis	Stern et al. (2012), Tahara et al. (2012)
Genotoxicity	NP interruption; ROS accumulation; dissolution of toxic ions; inflammation	DNA damages, point mutations, chromosomal aberrations, DNA strand breakages, point mutations, oxidative DNA adducts formation, and gene expression affected	Singh et al. (2009), Magdolenova et al. (2014, 2015), Golbamaki et al. (2015)
Autophagy dysfunction	Blockage of autophagy reflex caused by particle overloading; excessive autophagy induction	Apoptotic and autophagic cell death	Stern et al. (2012), Panzarini and Dini (2014), Peynshaert et al. (2014)

Several research conducted on effect of Cu-NPs on human's health have revealed that dyshomeostasis in the brain induced by Cu can lead to neurodegeneration and various other associated consequences such as amyotrophic lateral sclerosis (ALS), Parkinson's disease (PD), prion diseases, Alzheimer's disease (AD), etc. (Caviedes and Segura-Aguilar 2001; Gaetke and Chow 2003; Loeffler et al. 1996; Maurer et al. 2000; Win-Shwe and Fujimaki 2011). Reports have claimed that NPs can influence the balance of neurotransmitters being released (Chen et al. 2007;

Win-Shwe and Fujimaki 2011). Since many neurodegenerative disorders are the result of unusual changes in concentration or regulations of neurotransmitters (Sarter et al. 2007), therefore, the various reports of a neurotoxic effect of Cu-NPs could be assessed through this hypothesis. The neurodegeneration caused by Cu in Wilson disease can potentially harm the mitochondrial, trigger ROS levels, and lead to failure of antioxidant defense system (Gaetke and Chow 2003).

A study was conducted to correlate the size of Cu-NPs with the toxicity where 25–100 nm of Cu-NPs were used against various mammalian cell lines such as PLHC-1, RTH-149, H4IIE, and HepG2. The result inferred that the morphological features, the release of ions, and size of Cu-NPs play a significant role in toxicity. This group also reported that Cu-NPs in suspension forms are highly toxic to all cell lines; however Cu2+ (ionic forms) are just producing a significant response, therefore claiming that Cu-NPs are species-specific (Song et al. 2014). Cu-NPs have also been reported to induce cytotoxicity, neurotoxicity, and oxidative stress followed by DNA damage and DNA lesions in several cell lines (Magaye et al. 2012). The DNA damage caused by Cu-NPs could have been due to increased 8-isoprostane levels and the glutathione disulfide (GSSG) in respiratory epithelial cells lines Hep-2 (human airway epithelial cell lines). Increased oxidative stress is also responsible to damage the DNA which can cause carcinogenesis (Fahmy and Cormier 2009; Magaye et al. 2012). A recent study on human bronchial epithelial cells has also confirmed that CuO NPs (<50 μm) were able to cause a higher extent of DNA damage at lower doses with respect to with fine CuO (<10 μm). Study also confirmed that nano-sized Cu-NPs also induced the formation of micronucleus. This study inferred that the potential genotoxic properties of nano-sized CuO particles are the consequences of its vigorous cellular uptake and improved intracellular dissolution (Siivola et al. 2020). Another recent study reports about the absorption and bioavailability of CuO NPs by intestinal cell lines Cao-2. This is possibly due to its moderate solubility. ROS-dependent DNA damage and cell death were also reported (Li et al. 2020).

4.2 TiO_2 NPs

TiO_2 NPs have a wide scale application in cement, coating, and infrastructure sectors, cosmetics, food industry, etc. Studies have shown that inhalation of TiO_2 NPs is capable of causing pulmonary inflammation later leading to fibrotic and proliferative changes, induces inflammation, and increases oxidative stress. Genotoxic effect of TiO_2 NPs on mammalian and human cells has been studied. They accumulate in lungs, alimentary tract, liver, heart, spleen, kidneys, and cardiac muscle (Baranowska-Wójcik et al. 2020; Świdwińska-Gajewska and Czerczak 2014). Dosage of 5 g/kg body weight in mice was determined altered pathways of alkaline phosphatase (ALT), aspartate aminotransferase (AST), and lactate dehydrogenase (LDH), suggesting liver damage (Wang et al. 2007).

4.3 Mg/MgO NPs

Magnesium oxide NPs are very diverse in use and have potentially low toxicity. However, very few studies have been carried out on the toxicity of MgO NP. A study of MgO NPs of 100 nm size on human umbilical vein endothelial cells at a concentration lower than 200 μg/ml exhibited no cytotoxicity by MTT assay. This study however reported that a concentration of more than 500 μg/ml interferes with the growth rate (Ge et al. 2011). Another study on MgO of size 20 nm on normal fibroblasts of lung and other cancerous cell lines reported that MgO NPs are capable of killing cancer cells by ROS-induced apoptosis (Krishnamoorthy et al. 2012). Another MTT assay-based cytotoxic study shows similar findings when MgO NPs of 30 nm size and concentration range of 0–350 μg ml^{-1} on human intestinal cell lines and human cervical cancer cell lines. The study shows no cytotoxic effect on human intestinal cell lines; however it does affect the growth of human cervical cancer cell lines (Patel et al. 2013). However, a recent finding suggests that ion-doped silica-based NPs of Mg are capable of protecting the erythrocyte membrane by combating oxidative stress and providing enhanced hemocompatibility (Tsamesidis et al. 2020).

4.4 Cr NPs

Chromium NPs are highly used in pigments/dyes, chemical catalysts, tanning, electroplating, etc. and are manufactured to be used in industries as catalysts and pigments and in the processes of electroplating and tanning. In the biological system, chromium is one of the metals with high relevance for physiological functions. However, there is evidence of its higher cytotoxic potential. Human lung carcinoma A549 cells and human keratinocyte HaCaT when exposed to Cr_2O_3 NPs exhibited severe cytotoxicity, increased ROS production, and thereby activation of antioxidant defense systems. It also affected the cell viability negatively, Caspase 3 activation, and apoptosis (Horie et al. 2013).

Cr_2O_3 NPs have also been reported to induce DNA damage to human lungs' alveolar cell. Study conveyed that increased levels of ROS could be responsible for the DNA damage. Apoptosis was also noticeable as oxygen species cause a reduction in the mitochondrial membrane potential and surge in the ratio of BAX/Bcl-2. It initiated the even of the mitochondria-mediated apoptosis induced (Senapati et al. 2015). CoCr has a major use in medical as they are used in orthopedic implants. A study of metal-on-metal (MoM) case in which cobalt chromium (CoCr) NPs are used. It affects the decreased the cellular viability and caused DNA damages. Study also reported the chromosomal aberrations and increased metal sensitivity (Gill et al. 2012). Similar study on MoM of CoCr NPs for the duration of 24, 48, and 120 h shows substantial increase in cell number near the debris of MoM implant. Levels of Interleukin-6 (IL-6), interferon-γ (IFN-γ), and tumor necrosis factor-α

(TNF-α) was found meaningfully reduced (Posada et al. 2015). A MoM study of CoCr on dural fibroblast and epithelial cells suggests that it acts in a dose-dependent manner. CoCr particles were able to inhibit the growth of dural epithelial cells but not the fibroblasts. IL-8 level was noticeable in both type of cells, while the estimated dose of exposure was 60.5 mm^3 (epithelial cells) and 121 mm^3 (fibroblasts, epithelial cells) per cell. After 24 h of exposure, ROS was also detected in both types of cells at 50 mm^3 per cell (Behl et al. 2013).

A very recent study on hexavalent chromium NP effect on human lymphocytes shows that it can significantly ($p < 0.05$) induce production of ROS and reduce matrix metalloproteinases (MMP) and destabilization of lysosomal membrane. Lipid peroxidation in human lymphocytes, decrease in intracellular GSH, and raise in extracellular GSSG levels were also noticeable (Seydi et al. 2020).

4.5 Mn-NPs

Manganese if accumulates in the central nervous system (CNS) causes neurotoxic properties, and the occupationally exposed person develops manganism (Mn poisoning) which resembles the Parkinson's disease in later stage (Dobson et al. 2004; Fechter et al. 2002). It's overexposure is linked with symptoms like pneumonia, declined in libido, and sperm health (Hobbesland et al. 1997; Williams et al. 2012; Yamada et al. 1986a). A case study of hypermanganesemia/cholestasis group revealed its effect as severe hepatic toxicity and neurotoxicity (affected globus pallidus and subthalamic nuclei of the brain) (Fell et al. 1996). A study on mesencephalic dopamine-producing neuronal cells revealed that Mn-NPs have potential of entering these cells. It also induced the oxidative stress and cell death by activating caspase-3 along with the proteolytic cleavage of PKCδ (Ngwa et al. 2011).

A report by Alarifi et al. has demonstrated the effect of Mn-NPs on human neuronal cells (SH-SY5Y). The study found increased ROS and declined in mitochondrial membrane potential. The levels of lipid peroxide (LPO), superoxide dismutase (SOD), and catalase (CAT) were also found higher, while glutathione was declined. Study also reported increased caspase-3 activity, and beyond 60 μg/ml of concentration for 48 h, it has significantly damaged the DNA as well, which was assessed through COMET assay (Alarifi et al. 2017).

Another study by Hussain et al. has showed that MnO2-NPs of 40 nm are capable of inducing dopamine (DA) depletion in a cultured neuronal phenotype (PC-12). Author conveyed the association of ROS generation due to oxidative stress with the reduction in dopamine level (Hussain et al. 2006). This study infers previous reported regarding the decrease in sperm quality and libido as dopamine has a strong role to play in libido (Yamada et al. 1986b). Very recent review on toxicity of Mn-NP highlights its role in oxidative stress, inflammatory response, and transporter dysregulation as well (Miah et al. 2020).

4.6 Co-NPs

Cobalt and cobalt-based NPs are greatly used for various products such as sensors, catalysts, or energy storage devices (Liu et al. 2005). These are current concern of many researchers which are involved in metal NP research. There are data which have talked about the toxicity of cobalt ions, and generally it is accepted as toxicity of Co-NPs. However, these data are generated from ionic forms; however the importance of generating more data on nanostructured forms of Co is an impending task which will enrich its relevance further with respect to its toxicity (Roco 2005). Studies have reported the Co-NPs have potential toxic effect in various animal models as well as in vitro assay. One of the reasons behind it is its quick and easy uptake as reported by Papis et al. in year 2009. This group identified that Co-NPs of Co_3O_4 readily enter the cells and get accumulated in vesicles. Very few portion of Co-NPs was also located inside the nucleus (Papis et al. 2009). Another study by Busch et al. in year 2010 reported that tungsten carbide cobalt (WC-Co) NPs induce similar response like cobalt in ionic form does. These NPs interacted with HIF1a in human keratinocytes and inducing hypoxia-like effects. The comparative study of WC-Co with CoCl2 could not be described by studying transcriptomes (Busch et al. 2010).

A study on human T-cells in year 2012 reported that Co-NPs have potential to cause DNA damage in a dose-dependent manner. The damage caused by Co-NPs was comparatively higher than that caused by Co-ions. The activity level of superoxide dismutase, catalase, and glutathione peroxidase was also significantly lowered (Jiang et al. 2012). An interesting study shows the sensitivities of various cell lines toward Co-NPs. The order follows: A549 = MDCK = NCIH441 = Caco-2 > D Cs > $HepG_2$. Study also confirmed cobalt ferrite NPs induced oxidative stress in various cell lines (Horev-Azaria et al. 2011), a study conducted by Nyga et al. (2015) on U937 cell line, human alveolar macrophages, and monocyte-derived macrophages with Co-NPs of concentration range 5–20 mg ml^{-1}. The outcome reported was Co-NPs are able to induce reduction in intracellular ascorbate which cause HIF stabilization and activation of the pathway. The finding was supported with ROS-independent HIF activation. Since Co as metal form has major use in medical prosthetics or implants, its toxicity is major concern. Further research on Co-NPs (Nyga et al. 2015).

4.7 Zn-NPs

Zn-NPs are widely used in agriculture and cosmetics; therefore there is growing concern about their toxicity on human health. The sunscreen contains a significant amount of ZnO NPs; however it has been found that ZnO NPs are not able to penetrate the layer of stratum corneum of healthy human skin (Filipe et al. 2009; Schilling et al. 2010). However, a study on the rat model has shown the loss of collagen after the application of sunscreen containing 20 nm ZnO NPs five doses a week for 28 days (Surekha et al. 2012).

A study has reported that ZnO can be internalized by HEK cells after 6 h of exposure at 14 μg/ml concentration. At this concentration and exposure duration, the evident comet trail of damaged DNA was observed (Sharma et al. 2012a). There was evidence of inhibition of mitochondrial activity after 6–24 h of exposure and concentration of 8–20 μg/ml. This group also reported apoptotic and genotoxic potential cause of ZnO NPs in human liver cells (HepG2). The exposure of HepG2 with 14–20 lg/ml ZnO NPs for 12 h has shown a reduction in cell viability and triggers apoptosis. The apoptosis was reported due to decreased potential across the mitochondrial membrane, thereby increasing the ratio of Bax/Bcl2 study. The study also reported the oxidative stress-mediated DNA damage in the cell lines and DNA damage mediated by oxidative stress. In addition, the ZnO NPs also found to be involved in activating the JNK and p38 and inducing p53Ser15 phosphorylation. The study confirmed that the apoptosis was independent of JNK and p38 pathways induced due to ZnO NPs. This study investigating the effects of ZnO NPs in human liver cells has provided valuable insights into the mechanism of toxicity induced by ZnO NPs (Sharma et al. 2011, 2012b). ZnO NPs have also been observed to reduce cell viability of HaCaT keratinocytes in a dose- and time-dependent manner (Vinardell et al. 2017); 5 mg kg^{-1} of ZnO NPs caused hepatocytes swelling, increased ROS levels, and caused cell death at a concentration of 50 μg mL^{-1} (617 μM) and DNA fragmentation (Ng et al. 2017; Vinardell et al. 2017).

A report has inferred that cell line (human lung cell line, A549) when treated with ZnO NPs of size 15–18 nm of 0.1, 10, and 100 μg/mL concentrations shows sharp increase in Zn2+ in cytoplasm. Cellular viability decrease was observed in time and d dose-dependent manner. The study also revealed the double-strand breaks in DNA and increased intracellular ROS. However, this study claims that the DNA break was not due to ROS (Heim et al. 2015). Hackenberga and colleague in 2017 reported an interesting phenomenon in which the DNA damage caused in human nasal mucosal cell lines by ZnO NPs was found to be reduced by TiO_2 NPs. The study claims that DNA repair capacity was enhanced by TiO_2 NPs and the synergistic effect of Zn^{2+} and TiO_2 NPs could be the reason for toxicity antagonism (Hackenberg et al. 2017).

A very recent study on excised human skin shows that ZnO NPs does not cause toxicity to intact human skin; however, Zn^{2+} generated from ZnO NPs can be significantly toxic to the viable epidermis if the stratum corneum has been penetrated (Holmes et al. 2020). Another recent study on human intestinal cell lines and human liver cell lines (Caco-2 and HL-7702) reports that ZnO are more likely to be absorbed by intestinal cells due to its solubility. This also led to cell death local intestinal inflammation. However, apoptosis was not reported on liver cells. The study also reported an increase in ROS level thereby inducing DNA damage before cell necrosis (Li et al. 2020).

4.8 Other Metallic NPs

A study on mouse model has revealed that exposure of a dose of <50 nm, 500 mg kg^{-1}, for 5 consecutive days leads to apoptotic DNA fragmentation and mutations (Mohamed and Hussien 2016), while it inhibited the growth and development in gold fishes. SiO_2 NPs got trapped in the liver and spleen cells, absorbed through intestinal mucosa, and entered systematic circulation finally showing toxicity effects (Ates et al. 2013; Li et al. 2015). The cell viability was seen to be affected in lung A549 cells and NIH/3T3 cells (Gupta and Xie 2018; Kim et al. 2015). Similarly significant cell damage and altered cell functioning was observed with 200 μg ml^{-1} after 48 h exposure, while 70 nm induced liver injury at 30 mg kg^{-1} dose (Nishimori et al. 2009; Yang et al. 2014). AgNPs used in cosmetics may release "Ag+" ions thereby showing toxic effects, chromosome damage, inflammatory responses, and changes in cellular morphology at a dose of >1.0 mg L^{-1} (Kawata et al. 2009). AuNPs widely used in pharmaceuticals showed moderate toxicity in size-dependent manner (10 nm and 60 nm), significant increase in liver enzymes (ALT and AST), and liver damage (Zhang et al. 2011). PNPs at a higher concentration of above 1 mg mL^{-1} showed significant cytotoxicity (Grabowski et al. 2015), increased rate of cell death, and high levels of ROS (Hu et al. 2011).

5 Future Prospect and Path Forward

Nanotechnology has the potential to revolutionize the agriculture and many industrial sectors. In coming days, it is going to be part of life, and hence the exposure of NPs may become inevitable. The potential toxic hazards and risks associated with the health and environment must be dealt with utmost safety concerns. The release of NPs in the environment by any means, its persistency, transport, distribution, fate, and ecological implications have to be addressed accurately with suitable guidelines of dosage and handling and guidelines for protecting the health of occupational workers also be addressed, supported, and ensured.

To assess the NPs in the various environmental media, food and accumulation in biota, methods of detection, characterization, and pharmacological or toxicological studies must be devised. Advancement in the NT research must assign the objective of ecotoxicological and toxicological aspects of NPs. Such studies should be focused on its properties such as hazardous, physicochemical, and biological activities. The mechanistic of NPs interaction with crucial biomolecules and biomarkers, toxicodynamics, toxicokinetics, and epigenetics are the key area of development where the knowledge generation is extremely required. These issues are fundamental to the success of NT in terms of sustainable environment and ecosystem and human health for safety assessment and risk management and also to a self-sustainable long-term emerging technology in science

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Chapter 13
Interaction of Nanoparticles to Soil Pollutants

Shivani Ghai and Amrit Kaur

1 Introduction

The industrialization has been propagating over a few years, which has brought processes of urbanization involving manufacturing, production, transportation, refining, mining, etc. The pesticides; phenols; heavy metals like lead, arsenic, cadmium, mercury, etc.; and hydrocarbons are produced and used every day, which adds to the list of contaminants that harm the environment (Chaplygin et al. 2021; Medvedeva et al. 2020). The soil and water are gravely affected parts of the environment. The contaminants contribute to the depletion of natural resources by producing hazardous wastes, which in turn threaten human health, causing diseases like cancer, chronic obstructive pulmonary disease, heart diseases, stroke, etc. These are taken up by humans in one way or another from ingestion, absorption, to inhalation. Bioaccumulation of toxic compounds like persistent organic pollutants (Bayen et al. 2005; Kelly et al. 2007; Houde et al. 2008), heavy metals, etc. (Smical et al. 2008; Kumar et al. 2011; Yap et al. 2011) sublimates in the food chains right from the fishes, and biota again pose a risk to human life as well as wildlife.

The requisition for modern technologies and methods to quicken the process of decontamination and the consequent reduction of their costs is growing exponentially. The employment of the technology working on a nanometric scale involving nanomaterials, like zinc, titanium oxide, and iron-based nanoparticles, particularly, has received great attention as an innovative method for remediation. However, several studies have been conducted on nanomaterials, but their behaviour in the soil pores, interaction with the soil biota, adsorption on mineral particles, and their

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interaction with the contaminants have not been discussed yet. The different processes used for synthesizing several kinds of nanomaterials having distinctive traits include photocatalytic deposition (PD), chemical solution decomposition (CSD), deposition-precipitation (DP), chemical vapour decomposition (CVD), ultrasonic irradiation, hydrothermal and thermal processes, etc. (Khajeh et al. 2013).

The basic property that has brought nanoparticle into such light and has made it such an upcoming field for its applications in remediation and various other fields is that despite their small size, nanoparticles offer a very large surface area to volume ratio, when compared to bulk material, which provides better interaction. Nanoparticles exist naturally in nature and can also be manufactured as by-products of combustion reactions or produced through engineering techniques, since nanoparticles can be easily generated and programmed for particular roles that find their functions in various domains. This large surface area allows diffusion across membranes that are allowing molecules, ions, heat, etc. to diffuse through the particles that is in and out, at very high rates. The entire particle reaches homogenous equilibrium in a very short time due to the small diameter keeping it stable during diffusion.

The objective of this chapter is to elaborate the prospects of various nanomaterials and their interaction with the soil pollutants. The viability of amalgamating remediation technologies like bioremediation, biomagnification, biostimulation, etc. as well as monitoring the level of toxicity of nanomaterials to the soil microorganisms is pivotal for effective remediation. A brief review is presented on the soil pollution and the various pollutants that contribute to it via different ways which are followed by the understanding of the nanoparticles (NPs) for contaminated sites, which includes field application and the challenges faced subject to their usage during field application. The effects of NPs on microorganisms, that is, the positive (biostimulant) or the negative (biocide) effects, are also discussed. Finally, the concept of nanoremediation and nanobioremediation (NBR) is proposed, which aims towards collaborating clean-up technologies for efficient and constructive decontamination. The principles are supported with examples and case studies on various nanoparticles like nZVI and graphene oxide nanoparticles and then using the process of photoinduced precipitation for the same. Nevertheless, the anticipation of integrating nanotechnology and bioremediation for the purpose of soil remediation is much more systematic and sustainable.

2 Soil Pollution and Soil Pollutants

Soil contamination is originated by the presence of perilous compounds in the soil. These are heavy metals, a common class of pollutants that are naturally present in the soil but are not very often at toxic levels. The main sources of such heavy metals are landfills of industrial waste, e.g. paint remnants, electrical generated wastes, weedicides, herbicides, chemical fertilizers, municipal or industrial sludge, etc. Heavy metals are non-degradable and persist in the environment. Mercury and selenium are the only exceptions since they can be volatilized by microorganisms. The remedial cure can be performed in situ or ex situ. The ideal procedure to handle the problem is to prevent contamination by heavy metals or by immobilization (Ma et al. 1993). The sorption-desorption reactions with other constituents of soil govern the activity of heavy metals in soil (Singh et al. 2001). Therefore, to manipulate the heavy metal bioavailability and the impediment of their diffusion in soil, amendment agents have been used. The processes involved are adsorption to mineral surfaces, ion exchange methods, surface precipitation, and stable complex formation with organic ligands (Kumpiene et al. 2008).

There are two kinds of amendment agents, i.e. mobilizing and immobilizing agents. The mobilizing agents increase mobility and bioavailability and enhance the phytoextraction process, while immobilizing amendment agents minimize the same, and they also reduce biomagnification risk, i.e. phytostabilization (Robinson et al. 2009).

In the past few years, heavy metal immobilization in the soil and groundwater via nanoscale particles has drawn immense interest. There are two requirements that are requisite while applying amendment agents as nanoparticles, i.e. conveyance of the tangibles to the contaminated zones and that the nanoparticles must remain confined in that very domain of application after removal of external injection pressure (An and Zhao 2012). However, there is a loss in defining properties like high reactivity and specific surface area of nanoparticles due to their tendency to agglomerate into micro- to millimetre scale. Therefore, organic polymers like starch and carboxymethyl cellulose (CMC) are attached to the nanoparticles as stabilizers overcome these problems and prevent agglomeration (He and Zhao 2005, 2007).

Arsenate, a soil and water pollutant was immobilized by the effective enhanced sorption of the starch-stabilized magnetite nanoparticles. The results of this investigation also resulted in the reduction of the toxicity characteristic leaching procedure (TCLP) leachability of As (V) (Liang and Zhao 2014). Phosphate compounds are effective agents for the immobilization of lead (Pb) in in situ heavy metal immobilization, where implementation of phosphate to the soil is in soluble (phosphoric acid) or solid (synthetic apatite) forms (Yang et al. 2001). A new type of apatite nanoparticle along with CMC, i.e. stabilizing agent, was synthesized to elevate the phosphate dispersion rate. The hydroxyl and carboxyl groups are integral in inhibiting further aggregation of nanoparticles (Liu and Zhao 2013). nZVIs are widely used for on-site bioremediation of heavy metals thus altering their redox state in soil.

The capacity of the ZVI nanoparticles to aggregate rapidly results in the loss of reactivity which is the major limitation of ZVI formed by conventional methods. This loss of reactivity was because the agglomerated ZVI particles attain a size in the micron scale, which shows low mobility in soils, therefore making them unsuitable for in situ treatments. This problem can be overcome by the particle stabilizing strategies with coatings or capping the nanoparticles with stabilizers like organic coating stabilizers such as cetylpyridinium chloride (Chen et al. 2004), starch (Reyhanitabar et al. 2012), sodium CMC (He and Zhao 2007), and polyvinylpyrrolidone (PVP) (Fang et al. 2011a).

The chemical reagents used during the conventional preparation such as ferrous sulphate are expensive (Fang et al. 2011b). So, to lower the cost of removal of chromium (VI), CMC-stabilized nZVI was eminently formulated from waste liquor obtained by steel pickling which reduced the 100% TCLP leachability of Cr (VI) (Wang et al. 2014c). Although soluble and solid phosphates have been reported highly effective for in situ stabilization of heavy metals at laboratory scale. On the contrary their addition to the subterrain is constricted by cost as well as the secondary contamination of groundwater by eutrophication due to the addition of increased levels (e.g. 3% of PO_3^{-4} dosage) of phosphoric acid or salts (Park et al. 2011).

3 Nanoparticles and Their Interactions

Before studying the detailed description of nanoparticles' interaction with the soil pollutants, let's first understand nanoparticles and their types. Nanoparticles are small particles that range from 1 to 100 nanometres in size (Timoshenko et al. 2021; Kumari et al. 2022; Rajput et al. 2021b). Nanoparticles exhibit different types of physical and chemical properties, and these properties, in turn, affect their association with the soil pollutants or their bulk counterparts.

Another property is solvent affinity; the nanoparticles have high solvent affinity and can be a part of the suspensions due to this very property. The interaction is significantly strong in that it overcomes density differences, unlike other materials. The following are more details given on the types of nanoparticles, their characteristics, and their functions.

4 Natural Nanoparticles

The natural nanoparticles as the name suggests are already present or occur naturally in the environment. They participate in the essential ecological processes due to their nature and surface properties, which range from cycling elements, through various processes like transporting chemical and biological contaminants, sorbing, regulating water storage, and serving as an organic carbon and plant nutrient source. Nanoparticles and nanostructures are present in all living organisms like insects, birds, plants, animals, and humans including microorganisms, i.e. bacteria, algae, and viruses.

4.1 Nanoparticles in Microorganisms

The naturally occurring nanomaterials are substances and/or by-products produced in bodies of some microorganisms like bacteria, viruses, fungi, algae, cyanobacteria, and yeast (Table 13.1).

Table 13.1 Naturally occurring nanoparticles of natural products (Griffin et al. 2018)

Organism	Examples of the organisms producing nanoparticles
Bacteria	*Lactobacillus* sp. *Shewanella* sp.
	Staphylococcus aureus
Cyanobacteria	*Synechocystis* sp.
	Limnothrix sp.
	Anabaena sp.
Fungi	*Aspergillus terreus*
	Verticillium sp.
	Fusarium oxysporum
Algae	*Coelastrum* sp.
	Botryococcus sp.
	Chlamydomonas sp.
Yeast	*Saccharomyces cerevisiae*
	Saccharomyces boulardii
	Hansenula anomala

4.2 Nanoparticles in Plants

The profound functions of plant parts especially leaves, having nanostructures are used for insect sliding (Gorb et al. 2005), mechanical stability (Bargel et al. 2006), absorption as well as reflection of visible and ultraviolet radiations (Pfündel et al. 2008). Self-cleaning and super-wettability create super hydrophobicity in lotus leaves which is the most common nanostructure property. These properties are useful in various applications, e.g. sewage water treatment plants, wettability switchers, actuators, and transparent coatings of electrodes.

4.3 Nanoparticles in Insects

The membranes of insect wings are composed of crystalline chitin polymer that provides membrane support. These building materials form a complicated vein system that imparts exceptional stability to the structure of the wings. These insect wing surfaces portray a wide range of micro and nanoscale properties of these highly ordered structures which protects them against pollutants and wetting.

4.4 Nanoparticles in Animals and Birds

Animals like spiders and geckos, for example, can attach to the walls and walk against gravity on ceilings and vertical walls. This is possible because of the patterned structure present in these animals that efficiently interact with the substrate.

This is also possible due to the nanosized hairlike structures in their feet which increases the total surface area that enables them to walk on wet surfaces and against gravity as a result of strong surface adhesion mediated by the van der Waals forces of interaction (Moret 2006). Mollusc shells consist of a nanocomposite called nacre. Nacre is a hierarchical nanocomposite which is designed calcium carbonate aragonite platelets of sub-micrometre and micrometre sized which are in turn separated by a bio macromolecular glue. Nacre design is such that it incorporates traits like strength, enhanced stiffness, resistance, and toughness. The $CaCO_3$ form a thin and strong shell as the amorphous mineral transformed by lectin proteins into ordered crystals forms the $CaCO_3$ nanoparticles (Freeman et al. 2010).

4.5 Nanoparticles in Humans

The human body consists of nanostructures like proteins, enzymes, bones, antibodies, and DNA. The functioning of the human body without nanostructures is impossible. There are certain examples of nanostructures which play a crucial role in some of the most important cycles of human body and generally in its functioning as well. Their DNA has a size range of 2.2–2.6 nm, glucose is 1 nm, and haemoglobin is 6.5 nm (Papazoglou and Parthasarathy 2007); proteins ranges from 3 to 6 nm (Milo and Phillips 2015), etc.

4.6 Clay Minerals

Clay minerals are natural nanoparticles comprising of layer silicates, involving three weathering processes, namely, transformation, inheritance, and neoformation by abiotic pathway. The transformation is a process involving the alteration of the interlayer region, while the overall structure remains intact; inheritance as the name suggests the birth of the layers from parent rocks and clay materials, and lastly neoformation is a process of weathering that involves crystallization or precipitation from a solution or gel precursor. Wilson (1999) studied that micaceous nanoscale minerals in the soil are mostly acquired from the parent rock, for example, soil smectites are formed by transformation, inheritance, and neoformation, while kaolinite is a product of neoformation. One of the important functions of bacteria is forming mineral nanoparticles, comprising layer silicates. Bacteria have negatively charged cell walls and a large surface area to volume ratio, which is well suited for mediating mineral formation as they can oxidize and reduce metals and also cause precipitation (Bargar et al. 2008).

4.7 Short-Range-Order Minerals

The principal nanoscale materials in volcanic soil minerals are allophane, imogolite, ferrihydrite, and Al- and Fe-humic complexes. These minerals are formed by rapid volcanic ash weathering, and they are present in abundance in the volcanic soil. Imogolite has fixed chemical composition. Unlike imogolite, allophane does not have the same as the Al/Si ratio may vary.

Ferrihydrite through a solid-state reaction forms hematite, followed by goethite produced via dissolution and precipitation. Ferrihydrite has nanosize (2–5 nm) which is the principal constituent of the juvenile volcanic soils (Schwertmann 2008). The allophanic andisols accumulate organic matter particularly humic substances. The strong association of allophane with humic substances is the reason for its stability in volcanic soils.

Allophane shows a powerful tendency for sorbing phosphate and arsenate, which offers possible evolution of an eco-friendly process of secluding arsenic from potable water and phosphorus in the outflow, for the remediation of arsenic-contaminated soils (Violante and Pigna 2002; Arai et al. 2005; Yuan and Wu 2007). Non-allophanic andisols accumulate aluminium and iron humic complexes which are present in minimal quantity than aluminium complexes as iron forms iron oxides, hydroxides, and oxyhydroxides (Dahlgren et al. 2004).

4.8 Metal Oxides, Hydroxides, and Oxyhydroxides

Soils consist of various oxides, hydroxides, and oxyhydroxides[(hydr) oxide] of Al, Fe, and Mn, which are formed through microbial pathways or by weathering of primary and secondary silicate minerals. Gibbsite [γ-$Al(OH)_3$] is the most widespread aluminium (hydr)oxide, and its production includes the liberation of aluminium from primary alumina silicate minerals, subsequently by hydrolysis and precipitation, whereas the desilication of kaolinite leads to gibbsite formation in many highly weathered tropical soils. Fe (hydr)oxides present in almost all types of soils; some are dynamically coloured, for example, goethite which imparts yellowish-brown colour; during the presence of red hematite, this colour is concealed. Goethite and hematite are the most common species in soil as they are thermodynamically stable, followed by magnetite, maghemite, and ferrihydrite. Soil aggregate stabilization and clay flocculation are encouraged by these nanomaterials which are integral for the adsorption and retention of nutrient anions, for example, phosphate by electrostatic interactions and ligand exchange (McBride 1994; Schwertmann 2008).

Birnessite and vernadite, Mn (III, IV)- (hydr)oxides, occur as poorly crystalline nanoparticles, and they form coverings on mineral surfaces in alliance with iron (hydr)oxides and constituents of soil. Humics are chemically recalcitrant due to their structural complexity; therefore the macromolecular humics are replaced by relatively low molecular weight molecules that are bound by weak dispersive forces and are capable of forming micelles in solution (Sutton and Sposito 2005).

The sorption of Cu and Cd is enhanced by humic acid and allophane complexes (Yuan et al. 2002). In most of the study, it is found that various factors and variables like ionic strength, pH, and contaminant loading influence the contaminant-nanoparticle interaction (Chorover et al. 2007). The sorption of metalloids, organic contaminants, and heavy metals by soil nanomaterials depends on contact time. The rate of sorption is biphasic that occurs in two phases, the initial phase which is rapid that occurs in a few milliseconds while the slow phase takes days due to diffusion, precipitation, and structural rearrangement (Sparks 2018). The bioavailability of contaminants decreases with contact time ("ageing") as a result of the above-mentioned phases (Chorover et al. 2007). The intrinsic complexity of physiochemical processes of the soil urges a broad, multidisciplinary application along with high-resolution modern instrumental techniques for a better understanding of sorption phenomena and nanoparticle interactions. The question that arises here is that if there are so many nanoparticles already present in the environment, then what is the requirement of artificially synthesizing nanoparticles? The answer to this question is given in the next section, that is, synthesized nanoparticles.

5 Synthesized Nanoparticles

The anthropogenic pollution of the lithosphere and hydrosphere due to past and present activities has been one of the biggest concerns for human health and sustainable development all over the world. The day-to-day industrial activities involving production of harmful substances along with abandoned contaminated plants and sites are a potent source of pollution. Therefore, a thorough cleaning of the effluents produced by these industries is crucially required followed by remediation of polluted soil and water. The nanosized zero-valent iron (nZVI) is a potent nanomaterial arising in the field of remediation due to lower expected impact on the environment and its high reactivity with the contaminants. The usefulness of nZVI in processes of removing contamination from soil and water along with modification of material properties for fulfilling specific requirements of application is still being taken up under extensive research. The aim is the removal of contaminants from the soil with various processes like the catalytic activity, efficiently by nZVI and eliminating any harmful effect further on soil biota and plants.

nZVI, nanosized zero-valent iron, is a nanoparticle with various distinct features as compared to iron. nZVI is a key synthetic nanomaterial used for environmental remediation due to good adsorption capacity, its higher reactivity, and lower cost (Machado and Pacheco 2016; Liu and Hong 2017; Phenrat and Lowry 2019; Yan et al. 2013). nZVI has a strong reducing power and reacts with numerous organic and inorganic compounds, consisting of heavy metal ions, halogenated hydrocarbons, antibiotics, organic dyes, etc. They readily react with water and oxygen and also have a high tendency of agglomeration due to such reasons; nanoparticles are usually supported or capped as shown in Fig. 13.1. The nZVI is a core shell nanoparticle which is either capped or supported by inorganic or organic materials like pumice to reduce the immediate reactivity of nZVI with water and oxygen. The support and capping also slows down rapid agglomeration and increases transport properties as well as stability. Capping and support agents increase the stability and properties for transport while reducing reactivity up to some extent, during reaction. The nZVI has high reactivity and strong reducing power towards inorganic (like ammonium ions, heavy metal ions, Cr(VI), etc.) and organic compounds (like polychlorinated biphenyls, fuels, PAH, etc.).The photosensitive core shell nanoparticle adsorbs the contaminants from water and soil after the removal of protective layer by irradiated UV light, which is known as photoinduced precipitation.

The two main drawbacks for catalytic application concerned nZVI are its susceptibility to aggregation and easy passivation on its surface when it comes in contact with air or an aqueous environment. The oxidation of nZVI can be avoided by encapsulating the nanoparticle in the suitable solid matrix avoiding hindrance of the access to catalytic sites. For example, nZVI/reduced graphene oxide (rGO) composite protects the nanoparticle from oxidation and also provided charge transfer to substrate (Goswami et al. 2020). Another example of the same involves the reduction of p-nitrophenol to p-aminophenol using $NaBH_4$, while the reaction is catalysed by nZVI (Bae et al. 2016). The application of nZVI/$NaBH_4$ system for reduction is highly beneficial as sodium borohydride disintegrates nZVI nanoparticles as a result of chemical etching which forms small particles that gives protection

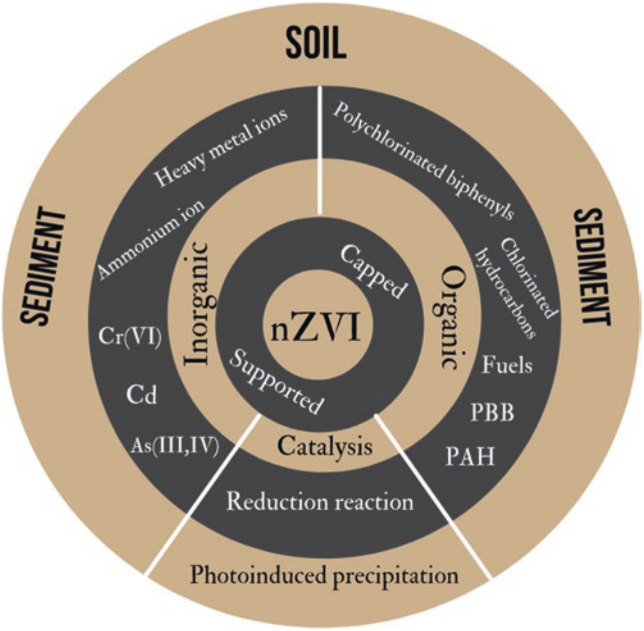

Fig. 13.1 Application of nZVI for environmental remediation

from oxidation and increasing surface area for p-nitrophenol reduction. The nZVI catalyst can be easily recycled and reused and proves to be a sustainable option.

Polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), and carboxymethyl cellulose (CMC) are capping materials that have stabilized nZVI by reducing $FeCl_3$ with hydrazine (Parimala and Santhanalakshmi 2014).

The field application in soil remediation is much more challenging as the nZVI is transported to the contaminants in sufficient concentrations. There are mainly two possibilities in field applications, creation of reactive zones with relatively mobile NPs and that the reactive nanoparticle migrates to contaminated zones. The soil and water pollutants are closely linked with respect to contamination

6 Other Categories of Nanomaterials

(i) *Organic-based nanomaterials*: Organic-based nanomaterials (NMs) are organic matter nanomaterials which are transformed into desired structures like liposomes, micelles, and dendrimers by self-assembly and noncovalent (weak) interactions.

(ii) *Inorganic-based nanomaterials*: These inorganic nanomaterials include metal and metal oxide nanoparticles and nanostructured materials (NSMs). These inorganic-based nanomaterials can be amalgamated into metals such as Ag or Au nanoparticles, metal oxides such as ZnO and TiO_2 NPs, and semiconductors such as ceramics and silicon.

(iii) *Carbon-based nanomaterials*: These NMs contain carbon and are found in morphologies such as ellipsoids or spheres. Graphene (Gr), fullerenes (C60), carbon nanotubes (CNTs), carbon black, carbon nanofibres, etc. are included in this category. These carbon-based fabrications are produced by various methods like laser ablation, chemical vapour deposition (CVD), and arc discharge (Kumar and Kumbhat 2016).

(iv) *Composite-based nanomaterials*: Composite nanomaterials are multiphase NPs and NSMs that are one or more than one phase on the nanosized dimension that combine NPs with other NPs or NPs with bulk-type materials (e.g. hybrid nanofibres) or complex structures, such as a metalorganic framework. The composites are made of combinations of inorganic or organic components, carbon-based, or metal-based NMs embedded in any form of metal, ceramic, or polymer bulk materials at the molecular level to acquire new properties.

7 Nanoremediation and Nanobioremediation

Bioremediation by definition is a process of rejuvenating and cleaning contaminated soil and water. Bioremediation utilizes microbes or microorganisms for that matter which consume the contaminants for making the environment contaminant-free.

The process of nanoremediation is somewhat similar, but, in this process, nanoparticles are used for the process of cleansing. This is one of the widely used applications that is being studied and researched. Phytoremediation coupled with nanotechnology advances the remediation process when the plant fulfills certain parameters like higher biomass, well-developed root system etc. (Ranjan et al. 2021). The nanoparticles are both naturally occurring (natural composites, volcanic ash, clay minerals, etc.) and man-made (e.g. nZVI, Fe_2O_3, Al_2O_3, etc.) which are employed for the remediation. Nanotechnology is potentially beneficial to the environment and is a much more sustainable technology than other techniques. The changes in the environment can be determined via remediation of contaminated molecules and certain chemicals acting as sensors (Neufeld et al. 2006).

Some organic compounds like polychlorinated biphenyls (PCB) and polychlorinated hydrocarbons (PCH)are broken down by nanoparticles. Carbon nanotubes strongly adsorb dioxins compared to conventionally activated carbon. Hydroxyapatite rehabilitates the polluted soils by decreasing bioavailability of heavy metals, copper and zinc, in the soil. The various mechanisms involved in the synthesis of nanoparticles by microorganisms include alteration of solubility, lack of specific metal transport system, toxicity through reduction or oxidation, biosorption, precipitation of metals, efflux system, bioaccumulation, etc. (Fan et al. 2013; Husseiny et al. 2007).

The microbiological reaction rates increase with nanoparticle catalysts present in the cells which stimulate the microbial activity (Shan et al. 2005). A good example describing this is fungi as they have many enzymes in their cells and are easy to handle and they excellently synthesize metal and metal sulphide nanoparticles (Hulkoti and Taranath 2014). It is observed that great number of proteins result in a high productivity of the nanoparticles (Husseiny et al. 2007).

Nanoparticles have various advantages, but their negative impact on the environment is the one to be concerned and cautious about as there is a possibility of release of dangerous compounds as time advances. For example, nanofibres and nanotubes can inhibit cell wall synthesis. These molecules are bactericidal. Much research is being conducted to eliminate any such harmful effects and also for better understanding the transport of nanoparticles and their sustainability and toxicological effects on diverse biological systems, including humans (Zhang et al. 2011; Cameotra and Dhanjal 2010). The Table 13.2 below consists of certain examples of nanoparticles and their effective nanoremediation of the contaminants from the soil.

7.1 Principles of Nanobioremediation

The toxic chemical compounds like polychlorinated biphenyls released every year amount to around ten million tonnes which is a massive amount, and after their release, they may also convert into more reactive forms like polychlorinated dibenzofurans or polychlorinated dibenzo-p-dioxins; those are by-products of chlorine-mediated chemical processes.

Table 13.2 Nanoremediation of contaminants in soil

Nanoparticle	Contaminant	Remark	References
Fe/Ni bimetallic nanoparticles	Tetracycline (TC)	The ageing of Fe/Ni nanoparticles resulted in a decrease in the removal of TC. The ageing products responsible were found to be magnetite and maghemite	Dong et al. (2018)
Fe/Pd bimetallic nanoparticles	Polychlorinated biphenyls (PCB)	After a span of 14 days, a 20% decrease in PCB was seen from the soil	Fan et al. (2013)
nZVI	Cu, Pb, Sb	The soil washing efficiency was increased by the nanoparticle as well as portraying selective removal for Cu, Pb, and Sb	Boente et al. (2018)
Reduced graphene oxide silver nanoparticles (rGO-Ag)	Phenol, bisphenol A, and atrazine	The photocatalytic degradation results in the decrease of these compounds. Significant decline in contaminants is seen promoting oxidative degradation especially when carried under visible light	Bhunia and Jana (2014)
Palladium nanoparticles	Pentachlorobiphenyl	These nanoparticles coupled with supercritical fluid CO_2successfully remove all PCBs from the soil at all temperature ranges and 200 atm	Wang and Chiu (2009)
Manganese oxide nanoparticles	17β-oestradiol	88% of oestrogens were removed from the soil. Increased concentration of nanoparticles elevated the oestrogen degradation along with the decreased injection velocity	Han et al. (2017)

The complications that have arisen for the successful implementation of remediation technologies are due to certain factors like the high chemical and physical variability and cytotoxicity of these chemical compounds, as well as multiple interactions with abiotic and biotic environmental factors (Jeon et al. 2016; Zhu et al. 2017; Hurtado et al. 2017). The final use of nanoparticles and nanomaterials with biotechnologies propose an alteration in remedial abilities, thus increasing the speed of degradation (Kang 2014; Fulekar and Pathak 2017). The major characteristics of these technologies are that they are cost-effective and highly efficient and have a wide range of applications.

Over the years the biological processes are integrated with nanoparticles and nanomaterials to accelerate the toxic compound removal from the environment. Factors like nanotoxicity, the size of the particle, etc. affect the living organism and their entire process. It was reported by Tan et al. (2018) that there are a variety of factors influencing this interaction between the biota, microorganisms, and the nanomaterial like pH, temperature, size, and shape of the nanomaterial, their coating, media, nature of the contaminant and the nanomaterial, etc.

Wang et al. (2014) proved the stability of Au NPs in the buffer and MilliQ water; however, the stability was lost at different pH 4, 7, 8, and 10. Tang et al. (2016) also demonstrated that the thermal stability of Cu nanoparticles was influenced by different synthetic methods. Once the biota and NPs interact, events like adsorption, absorption, dissolution, and photocatalytic reactions might happen, which may further participate in the degradation of contaminants.

7.2 Bioremediation Based on Nanotechnology

Bioremediation based on nanotechnology can be simply described as the pairing of a nanoparticle with a bioagent for the purpose of effective remediation. Kim et al. (2013) studied the effect of polybrominated diphenyl ethers' (PBDEs) degradation by this method using nZVI-*Sphingomonas* sp. through the process of reductive debromination which leads to biological oxidation. This hybrid method causes remediation of heavily polluted sites especially with highly halogenated environmental pollutants. A two-step method involving biosurfactant-enhanced soil washing technology after dechlorination by nZVI removed polychlorinated biphenyls (PCB) from contaminated soil. nZVI enhanced efficiency of soil washing by reducing the interfacial tension between two phases, the oil and soil, and about 90% of PCB was removed by nZVI, and the nanoparticle-bioagent combination had the remediation efficiency of 78–99% with rapid reaction time (Jing et al. 2018). Table 13.3 contains similar examples of nanobioremediation of environmental contaminants and the process by which they are remediated.

8 Examples and Case Studies

nZVI

Soil remediation is a much more challenging task due to matrix complexity. The reagents required for soil remediation are much more than what is required for wastewater purification. Singhal et al. (2012) experimented on malathion decomposition in the soil in vitro. They added Malathion, a widely used insecticide, to the soil which was dried followed by crushing and sieving it. The nZVI, that is, the zero-valent iron nanoparticle, was added along with the dry soil, and it was observed that Malathion degraded effectively to the harmless O-dimethyl phosphorodithioic compound, but the degradation decreased with increase in the size of the nanoparticle.

Similarly, Quinn et al. (2005) included nZVI emulsified with vegetable oil for soil remediation of the soil having contamination with trichloroethane (TCE). Degradation of TCE in significant quantities was studied, but the usefulness of the process of nanoremediation was repressed, because nanoparticles weren't uniformly administered in the target treatment area, as they migrated above the target treatment depth rather than far from points of injection. There was a significant reduction of the TCE concentration in the soil and groundwater, but in turn increased the concentrations of intermediate dechlorination products, namely, cis-dichloroethene

Table 13.3 Nanobioremediation of environmental contaminants

Nanoparticle	Bioagent	Contaminant	Remark	References
nZVI-C-A beads	*Bacillus subtilis*, *E. coli*, and *Acinetobacter junii*	Cr (VI)	About 92% of Cr (VI) was removed showing enhanced removal by the combined technology where calcium alginate beads were entrapped in nZVI	Ravikumar et al. (2016)
nZVI	*Dehalococcoides* spp.	TCE	The dechlorinating bacteria were deactivated by nZVI which after a lag phase could remove TCE while producing by-product ethene. nZVI also stimulated the metabolic activity of methanogens	Xiu et al. (2010)
nZVI	*Paracoccus* sp. *strain YF1*	Nitrate	The higher the concentration, the more reduction in denitrification rate, while lower the conc. Of nZVI; there is enhanced denitrification along with slight microbial toxicity	Liu et al. (2014)
Pd/nFe	*Laccase derived from Trametes versicolor*	Triclosan	Triclosan was remediated by Fe nanoparticles, while laccase derived from *Trametes versicolor* degraded and converted the by-products into nontoxic compounds	Bokare et al. (2010)

(continued)

Table 13.3 (continued)

Nanoparticle	Bioagent	Contaminant	Remark	References
Pd/nFe	*Sphingomonas wittichii RW1 (DSM 6014)*	2,3,7,8-Tetrachlorodibenzop-dioxin (2,3,7,8-TeCDD)	The highly toxic dioxin, recalcitrant in nature, was degrades by the sequential usage of nanoparticles and the bioagent, sequentially	Bokare et al. (2012)
Pd/nFe	*Burkholderia xenovorans* LB400	Polychlorinated biphenyl (PCB) Aroclor 1248	Pd/nFe nanoparticles efficiently dechlorinated the various chlorinated biphenyls into biodegradable followed by degradation by *Burkholderia xenovorans* bioagent	Le et al. (2015)

and vinyl chloride, which were detected in the groundwater. It was studied that the TCE concentration decreased by the nZVI emulsified treatment due to the TCE sequestration into the oil and TCE abiotic degradation in alliance with nZVI. Hence, TCE concentrations were lowered by emulsified nZVI more efficiently than by nZVI alone (Hara et al. 2006).

Similarly, arsenic was successfully immobilized by commercial nZVI as iron oxides adsorbed the arsenate onto their surface covered by the shell. The electrical conductivity or pH of the soil was unaltered due to this application, additionally iron availability increased, and a remarkable reduction in phytotoxicity was witnessed (Baragaño et al. 2020a, b).

Graphene Oxide

According to a study conducted by Baragaño et al. (2020a, b), graphene which is a carbon derivative in the form of nanoparticles is especially effective in the remediation and recovery of soils polluted with arsenic. The study also showed promise in other heavy metal pollutants. Arsenic, which enters the environment from smelting, fossil fuel consumption, and pesticides, was the chief focus of the study. There is a risk of biomagnification through trophic levels which causes immediate negative effects. The currently used approaches exhibit a variety of issues such as slow speed, extensive technology involvement, or simply being an energy negative process. Another condition that is to be kept in mind while designing remedial processes is to ensure that the products formed from the process should not be harmful; otherwise it becomes futile.

Arsenic is a highly dangerous contaminant, toxic to nearly all forms of life. It is also carcinogenic, with reported effects on the lungs, skin, bladder, and other organs (Gopalakrishnan et al. 2015; Wu et al. 2008). It shows acute toxicity in both plants and animals. The central axiom of detoxification and neutralization of this pollutant in the environment is either neutralization or immobilization. Simply put, either the pollutant is made harmless by certain treatments or simply removed from the immediate environment. Using an integrated approach, combining methods such as bio-nano remediation shows much more promising results than individual methods. In this particular case, the particles exhibit high reactivity and specific surface area which allows for the present metal to form complexes. This reduces toxicity, altering the mobility of the ion itself. This result shows some variation depending on the nature of the metal ion.

In the study, both zero-valent iron (nZVI) nanoparticles and graphene oxide (nGOx) nanoparticles were assessed. The former is widely known and applied but less is known about graphene. The results were compared and assessed using various microscopic techniques (atomic force microscopy), X-ray techniques, and dynamic light scattering. When tested, it was observed that using graphene gave significantly better results than nZVIs in various tests with heavy metals in samples such as copper, iron, magnesium, arsenic, and others. This has many implications, starting from opening the gateways to testing out graphene nanoparticles for other pollutants. It also reinforces the paradigm that this is a diverse avenue where so far, only hit and trial can tell us what pollutant can be handled best by what nanotechnology.

Photoinduced Precipitation

The adsorption on nanoparticles is a widely used technology for removal of hydrophobic contaminants from water and soil. The amphiphilic deblock copolymers are used to form photosensitive core-shell nanoparticles, and the irradiation with the UV light removes the protective layer which is responsible for colloidal stability which rapidly gets converted into aggregates. Decreasing the particle size led to enhanced interactions, which was suggested by the aqueous phase separation measuring the partitioning between the nanoparticles and the aqueous phase. Some preliminary in vivo experiments suggested that the treatment with photocleavable nanoparticles reduces teratogenicity significantly of triclosan, bisphenol A, and 17α-ethinyl oestradiol without producing toxic by-products.

The polychlorinated biphenyls, pesticides, and exposure to certain other kinds of chemicals associated with increased disposition led to certain endocrine disorders, cancer, infertility, diabetes, etc. The meticulous influence of these chemicals and agents in the ubiquity of these ailments is still unknown, but it is always recommended and tried to reduce the presence of these substances as much as possible. Sustainable practices will only ensure the safety of the environment and health. Therefore, keeping the soil and water contaminant free is extremely integral. The fast and effective methods offered by nanotechnology provide the appropriate solution to this problem of clean-up. The methods like sequestration and reactive remediation present viable alternatives which are lesser energy intensive. The percolation of the colloidal solutions of amphiphilic nanoparticles through the sediment is also the preferred method of soil remediation, although the most advanced remediation technology is the nanoparticle zero-valent iron or magnesium which we have already discussed in the section above. The nZVI injected in the soil remediates it by reducing the water-metal interface. The two concerns that are being worked on regarding nanoparticles are their persistence and prevalence in the soil and the formation of secondary toxic products. The photoinduced precipitation by nanoparticles for extraction of pollutants from the soil is an effective method that has been proposed and proved.

The paramagnetic iron oxide and titanium oxide core-shell nanoparticles have been proposed for separation. The titanium oxide shell acts as a photocatalyst which degrades organic pollutants, while the iron oxide allows magnetic separation from the dispersion. The biodegradable, photo-responsive core-shell nanoparticles are developed with a combination of several design principles to bind and extract the contaminants from the contaminated soil. The hydrophobic core acts as a "trap" for the hydrophobic molecules, while the hydrophilic structures stabilize the system. The nanoparticles shed their stabilizing layer in ultraviolet irradiation which results in the loss of their colloidal stability and leads to the formation of macroscopic aggregates. The aggregates contain pollutants and can easily be separated by methods like decantation, sedimentation, centrifugation, etc. The use of ultraviolet light helps in disrupting the colloidal stability, that is, it helps in exploiting its stability and large surface area for handling the bulkier material (Brandl et al. 2015).

9 Future Prospects

The applications mentioned above for environmental biotechnology, specifically soil, are some of the best methods for remediation. In addition to these applications, innovations have emerged for other fields involving nanotechnology, like clinical nanotechnology, agricultural nanotechnology, biomaterial energy production, etc. The incorporation of nanobioremediation has provided a new edge for better agriculture as well as improving the health of the soil to uphold more minerals for better flourishment. The distinct nano-based products such as nano-insecticides, nano-pesticides and nano-herbicides can jointly help in management of insects, pests and weeds which are of paramount concern to farmers (Rajput et al. 2021a). A balanced environment makes it feasible for the microorganism and the plants to dwell. These nanoparticles introduced must be biodegradable in nature or must have least to zero participation in producing toxic by-products. The biosystem is enhanced by classic and next-generation biotechnological modifications such as gene editing, protein engineering, or mutagenesis which makes the synthesis of cellulose-based nanomaterials more comprehensible.

The latest research in the field of RNA-based fungicides showcase their feasibility over traditional biochemical fungicides. The RNA-based fertilizers are foliar sprayed on plant parts or fruits which silences the fungal pathogen. The use of nanomaterials such as graphene, gold particles, photonic crystals, etc. as biosensors has now become a major aspect in the field of diagnostics. The biological component in biosensors responsible for recognition incudes enzymes, nanoparticles, microorganism, receptors, antibodies, etc. These biosensors exhibit enhanced selectivity and sensitivity when modified with biorecognition layers using nanomaterials, providing appropriately accurate diagnostics results. The concept of biosensors in healthcare and clinical monitoring has been incorporated with various substances like temporary tattoos, patches, and many more, among others (Kim et al. 2019). However, the workers employed in treacherous environments performing tasks in potentially toxic, radioactive, or enclosed areas can be protected with the advancements in real-time surveillant bio-nano technologies. These innovations can somewhat change the outlook of the healthcare sector starting right the step of timely diagnosis. Nanotechnology is mostly a cost-effective and environmentally friendly alternative, exhibiting efficient results and promising a sustainable future.

10 Conclusion

Nanotechnology is a massive and upcoming field. The advantages listed by the methodologies are alone sufficient to tell their success. The nanoparticles utilized in the remediation of soil have opened new doors to combat soil pollution. Intertwined with soil pollution is water pollution which also is being worked on at a great speed. Natural nanoparticles contribute a lot towards keeping equilibrium in the environment as a whole. But the advancements in the technologies have increased the level of toxicity which cannot be combatted by natural nanoparticles alone. Iron based, titanium based, iron and palladium based nanoparticles, etc. are the advancements required for an efficient remediation. This chapter thus involves the various prospects of such integration and combination of processes along with bioremediation. The nZVI and graphene oxides are some of the most commonly used effective and efficient methods that fulfil the requirement of remediation sustainably. These advances are one of the many successful methods for creating a sustainable environment without hindering the health of the entire ecosystem as whole.

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Chapter 14
Nanoparticles and Their Effects on Growth, Yield, and Crop Quality Cultivated Under Polluted Soil

Urfi Jahan, Uzma Kafeel, Mohd Irfan Naikoo, and Fareed Ahmad Khan

1 Introduction

Nanotechnology is a novel and scientific approach that leads to the development of valuable nanomaterials (NMs) (Mali et al. 2020). It covers several aspects of agriculture, food security, disease treatment, new tools for pathogen detection, effective delivery systems, and packaging materials (Khan and Siddiqui 2020; Raghib et al. 2020). During the last several decades, it has grown to prominence as cutting-edge technology, serving as a convergent science that brings together diverse fields (environmental science, energy, plant science, materials physics, and nanomedicine) and human welfare sectors (Gugliotti et al. 2004). Specifically, nanotechnology has the ability to bring practical answers to varied agricultural issues. According to McCalla (2001), by 2025, the global population could surpass eight billion. Thus, feeding the ever-increasing human population is a significant concern for the twenty-first century. The crop productivity and quality are being confronted by the booming human population, weather instability, shrinking prime agricultural area, and irrigation water (Prasad et al. 2017). Many people of the world directly or indirectly depend on agriculture produce. For addressing the increasing challenges of food security and sustainable production, notable nano-techno advancements have been developed in recent years in the field of agriculture (Usman et al. 2020) (Fig. 14.1).

Nanoparticles can be identified into three main categories based on source, namely, natural, incidental, and engineered or manufactured NPs (Nowack and Bucheli 2007). The first category has existed since the beginning of the earth and is emitted from natural activities like volcanic eruptions, forest fires, dust storms, and photochemical reactions. The second form of NPs is anthropogenic, usually

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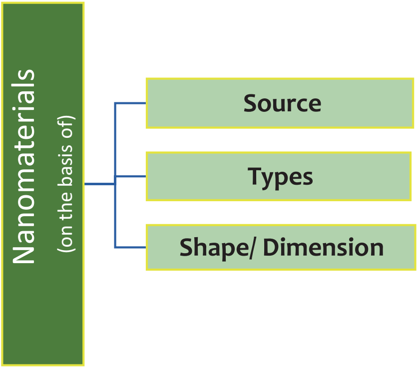
Fig. 14.1 Nanomaterials classified mainly on these bases



emanating from gasoline/diesel exhaust, coal combustion, and industrial exhausts (Uddin et al. 2013). The third form is produced by reducing the metal to its nuclear size. NP synthesis includes a few techniques, such as physical, chemical, and biological (Asanithi et al. 2012; Siddiqi et al. 2018). The synthesis techniques for a variety of NPs were developed and progressed to the molecular level (Gugliotti et al. 2004). Due to the small size of NPs, the ratio of surface area to volume increases (relative to bulk forms), improving the biochemical reactivity and conferring unusual and valuable physical properties. It is a potential rising field of science with brilliant applications in both basic and applied sciences (Ali et al. 2014).

1.1 Nanoparticle Use in Agriculture

The farming sector is the mainstay of any developing country, and crops are among the significant sources of important nutrients for both humans and animals (Rajput et al. 2021b; Ranjan et al. 2021). Nano-technological innovations can boost modern agriculture in a more productive, cost-effective, and eco-friendly way (FAO 2002). Among the various forms of NPs, inorganic NPs (metals: 29%, metal oxides: 26%, CNTs and fullerenes: 6%) constitute over half of total farming uses (Peters et al. 2016).

Numerous nano-agricultural products are presently being made to eliminate the conventional toxic chemical usage. Metals, containing NPs like Fe, Mg, Zn, Cu, and Mn, are put forward as fertilisers at low doses and as pesticides at higher doses (Liu et al. 2016) as these metals are necessary for cellular function but toxic above a threshold (Marschner 2011). For instance, ZnO and CuO NPs render potential as fertilisers as they provide bioavailable essential metals and as pesticides because of dose-dependent toxicity (Alamri et al. 2022; Rajput et al. 2021a, c; Shende et al. 2021). Over the recent decade, many nano-enabled patents and products have been produced to control plant disease and increase crop yields, namely, nanopesticides, nanosensors, and nanofertilisers, also nano-enabled remediation strategies for contaminated soils (Mali et al. 2020). Gogos and his team (2012) studied the use of NPs

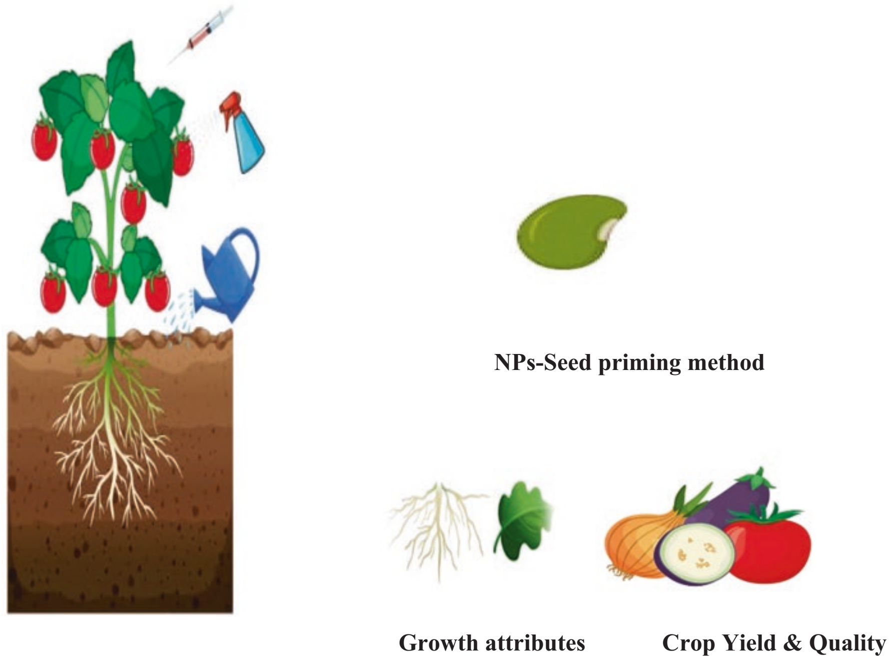


Fig. 14.2 Common NP treatment applications (inoculation based, foliar spray, soil irrigation, seed priming) and altering growth, yield, and quality attributes

in plant protection, and nutrition found that NPs could assist deliver pesticides, fertilisers and also detect plant disease and pollutants (Fig. 14.2).

There are various methodologies by which plants can be exposed to NPs, such as the direct injection of NPs into plant tissue (Corredor et al. 2009), amendment of NPs in the form of biosolids (Fayiga and Saha 2017), soil amendment, or irrigating plants with NP suspensions (Raghib et al. 2020). NPs can infiltrate living tissues, migrate to various parts of the plant system, and accumulate in underground and aerial parts. In the soil matrix, NPs move via the apoplastic or symplastic area to enter the epidermis of roots, pass through the cortex, and ultimately translocate to the stem and leaves through the xylem and phloem (Pérez-de-Luque 2017), therefore often causing a widespread impact on the plant system.

The NP absorption, translocation to different aerial parts, and their toxicity on plant system depend on bioavailability, solubility, exposure time, plant species, chemical composition, surface structure, aggregation dose, type, concentration, shape, and size of NPs (Ruttkay-Nedecky et al. 2017). Therefore, different plant species have a different response to the same NPs and may vary significantly with plant growth stages and treatment methods (Rastogi et al. 2017). Moreover, NP interaction with the plant cell results in gene expression modification and related biological pathways, which ultimately alter plant growth and development (Ghormade et al. 2011). Plants are a crucial part of all ecosystems, and their interaction with NPs is a critical aspect of the risk assessment (Yang et al. 2017). Once entered into the soil system, NPs may alter soil quality by affecting nutrient release in target soils, soil organic matter, and soil biota, and they can be utilised by the successive crops due to their gradual nutrient release. ENMs (engineered nanomaterials) and organic contaminants transferred and accumulate from the soil to the edible parts of crops (Deng et al. 2014). Da Silva (2014) also reported NPs affecting terrestrial plants in conjunction with metals.

1.2 Pollutants/Contaminants in Soil

Soil is a valuable resource as it serves numerous vital tasks such as life support, food production, carbon storage, water purification, and biodiversity preservation (Blum 2005).

Safe and healthy soil is necessary for the sustainable development of human society. However, our soil is under grave threat. Rapid industrialisation and different human activities, such as industrial waste discharge, sewage irrigation, and improper use of chemical pesticides and fertilisers, have resulted in an increased build-up of toxic metals/metalloids and persistent organic pollutants in soil over the past decades (Naikoo et al. 2021) (Fig. 14.3).

1.3 Use of Nanoparticles in Soil Pollution Remediation

The advancement of nanotechnology has provided new inspiration and ideas for polluted soil phytoremediation. NPs can help with phytoremediation by eliminating contaminants directly, enhancing pollutant phytoavailability, and boosting plant development. For example, nanoscale zero-valent iron (nZVI) particles have been employed to remove a variety of contaminants from the soil. Fullerene NPs can increase pollutant phytoavailability (Song et al. 2019). Therefore, the immobilisation or remediation of toxic HMs from polluted agricultural fields is regarded as a profound, imperative, and imperious issue (Dar et al. 2017). Therefore, soil remediation using plants and NPs in combination primarily involves two factors. One factor is to absorb heavy metals or metalloids from the soil while another affecting the internal structure of plants in order to promote growth (Deng et al. 2017). There is a variable influence of NPs on metal and metalloid uptake because of the type and application method as well as the plant and HM species involved (Usman et al. 2020). Ag NPs mitigate the deleterious effects of HMs in crop plants and may assist in the bioremediation of contaminated environments by enhancing remediating plants growth (Azeez et al. 2019; Deng et al. 2017).

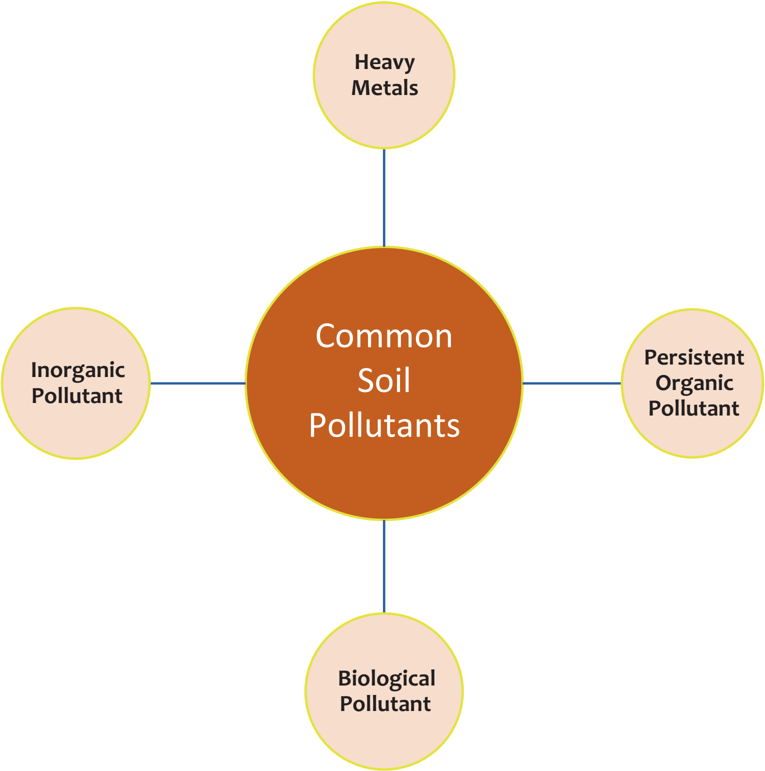


Fig. 14.3 Common soil pollutants

2 Effect of NPs on the Growth of Crop Plants

Nanotechnology serves as a platform to deliver agrochemicals and several macromolecules needed to boost plant growth and stress tolerance (Mali et al. 2020). Various NPs documented both enhancive and inhibitive effects on plant development (Yang et al. 2017)**.** In agriculture, nanobiopolymers have found massive use, such as soil health maintenance, reduction of agrochemical doses (after seed coating), and acting as a growth promoter (Baker et al. 2017). Many studies reported the application of NPs promoting earlier plant germination and enhancing plant production. Plant metabolism was boosted by NPs due to their unique properties (Nair et al. 2012). The extent to which NPs in soil promote or restrict plant growth appears to be related to plant type, NP type, and concentrations (Yoon et al. 2019). The exposure period to NPs is also an influencing factor for plant growth. Plant growth is aided by NPs, although some NPs show toxic effects as well. Increased water uptake by CNTs (carbon nanotubes) can boost plant growth and seed germination. CNTs (carbon nanotubes) can boost plant growth and seed germination by increasing water uptake. Their key role as nanofertiliser can improve the farming sector, although the harmful effects of CNTs may decrease the variety of agricultural-wise essential microorganisms and enhance the bioavailability of toxic metals in agro crops (Vithanage et al. 2017). The unique characteristics of NPs allow them a specific adsorption effect which leads to unrestricted plant growth in soil polluted with HMs. Excessively high NP concentrations, on the other hand, can impair plant growth (Chen et al. 2017).

2.1 Positive Aspects Concerning the Growth

The soybean crop treated with TiO_2 NPs in cadmium-contaminated soil depicted an increase in photosynthetic rate, growth, and biomass, as well as application till 300 mg kg^{-1}enhanced the biomass (Singh and Lee 2016). Tomato plant growth was improved by amendment of sewage sludge containing nano-TiO_2 (Bakshi et al. 2019). Zand et al. (2020a) observed enhanced shoot biomass of *Sorghum bicolor* crop grown under Sb-contaminated soil exposed to TiO_2 NPs, most significant increment at 500 mg kg^{-1} TiO_2 NPs treatment. With the addition of 100–500 mg kg^{-1} TiO_2 NPs, total plant biomass increased marginally. Likewise, adding 5 g kg^{-1} nHAP (nano-hydroxyapatite) to the soil can raise soil pH, fix Pb, and increase the biomass, thus promoting *Lolium perenne* growth (Ding et al. 2017). In addition to this, Fe NP treatment accelerated plant growth when grown in Cd-contaminated soil. Wheat morphological characteristics and dry biomass of shoots, roots, spike husks, and grains were improved by exogenous administration of Fe NPs (Hussain et al. 2019). Exogenous and soil application of ZnO NPs boosted growth and photosynthesis in *Triticum aestivum* cultivated in Cd-contaminated soil (Hussain et al. 2018; Raghib et al. 2020). Similarly, ZnO NPs showed significant improvement in the development of the sunflower in soil irrigated over a longer duration with polluted wastewater than the control (Seleiman et al. 2020). Mustard and cabbage crops with nZVI treatment promote plant growth by increasing biomass of roots, stems, and leaves in Cr-contaminated soil (Su et al. 2016). In like manner, nZVI-treated soils exhibited better growth of barley plants in arsenic polluted soil. Studies have shown nZVI at 10% concentration has the best immobilisation effect and limited arsenic availability, hence favouring the growth of *Hordeum vulgare* (Gil-Díaz et al. 2017).

Under cadmium-contaminated soil, nano-ZVI similarly enhanced dry weight of leaf, stem, and root of *Boehmeria nivea* (Gong et al. 2017). A low concentration of nZVI (100–500 mg kg^{-1}) effectively promotes growth by enhancing shoot biomass in *Lolium perenne* L. under Pb-polluted sediment (Huang et al. 2018). Si NPs improved the dry biomass of shoots, roots, spikes, and grains by 24–69%, 14–59%, 34–87%, and 31–96% in foliar spray and by 10–51%, 11–49%, 25–69%, and 27–74% in soil-amended Si NPs, respectively, in *Triticum aestivum* growth under Cd-polluted soil (Ali et al. 2019a).

Furthermore, colloidal silica NPs preserve soil fertility by ensuring homogeneous distribution of groundwater within the soil, and several metallic NPs, such as

CNTs, improve seed germination, resulting in healthy plant growth (Rai et al. 2018). *Moringa oleifera* growing in Cd- and Pb-polluted soil exposed to Ag NPs promoting germination and tolerance indices, also improved growth and vigour index (Azeez et al. 2019). Graphene oxide (GO) NPs applied to *Triticum aestivum* cultivated under arsenic-polluted soil slightly increased the germination rate and the root number (Hu et al. 2014).

2.2 Negative Aspects Concerning the Growth

The high dose of TiO_2 NPs (1000 and 1500 mg kg^{-1}) markedly inhibits seedling emergence and *S. bicolor* growth (Zand et al. 2020a). Likewise, a higher concentration of TiO_2 NPs showed a reduction in fresh and dry biomass, chlorophyll content, and plant height (Singh and Lee 2016). Huang et al. (2018) reported that a higher concentration of nZVI (1000 and 2000 mg kg^{-1}) caused a decline in total chlorophyll content, leaf physiological structure, and root biomass, thus inhibiting *Lolium perenne* growth in lead-polluted sediments. Plant growth is hindered by the presence of Ag in the soil.

Despite the limited transfer of Ag NPs, the high- and low-dose treatments significantly reduce root development of both monocot and dicot crop species, viz. wheat and rape, compared to the control (Pradas del Real et al. 2016). *Brassica rapa* sown in arsenic-polluted soil when treated with CNTs reported a reduction in fresh and dry biomass (Awad et al. 2019). *Triticum aestivum* showed adverse effects when exposed to As (V) soil and GO (graphene oxide) NPs. GO NPs directly affected the shoot length, and As (V) enhanced the impact of GO. Thus, it induced a significant reduction in fresh weight and chlorophyll contents (Hu et al. 2014).

2.3 No Effect Concerning the Growth

The addition of nano-HAP on *Lolium perenne* L. and celery (*Apium graveolens*) showed no significant growth rate (Ding et al. 2017; Yang et al. 2020). The treatment of nano-CeO_2 to *Helianthus annuus* plant in spiked boron soil did not produce a significant effect on plant biomass (Tassi et al. 2017). Similarly, *Glycine max* in cadmium-contaminated soil showed no significant change in root biomass to CeO_2 NPs (Rossi et al. 2017). Also, the application of silver and silver sulphide NPs (present in biosolids) to *Lactuca sativa* showed no significant differences in the aerial biomass (Doolette et al. 2015) (Table 14.1).

Table 14.1 Effect on crop growth

NMs/NPs type	Crop type	Soil pollutant/ contaminant	Effect on crop growth	References
GO NPs	*Triticum aestivum*	Arsenic	Moderately increased germination rate and root number; reduced fresh weight, shoot length, and chl contents	Hu et al. (2014)
Silver and silver sulphide NPs	*Lactuca sativa*	Biosolids	No significant changes	Doolette et al. (2015)
nZVI	Cabbage, mustard	Hexavalent chromium	Accelerated growth and biomass	Su et al. (2016)
TiO_2 NPs	Soybean	Cadmium	Increased plant biomass, photosynthetic rate and growth till TiO_2 NPs (300 mg kg^{-1}); reduction in plant heights, chl content, and fresh and dry biomass at higher levels	Singh and Lee (2016)
CNTs	*Brassica rapa*	Arsenic; lead; heavy metals	CNT-HM enhanced growth; CNT-As decreased growth	Awad et al. (2019)
CeO_2 NPs	*Glycine max*	Cadmium	Total dry weight slightly higher	Rossi et al. (2017)
$nCeO_2$	*Helianthus annuus*	Boron	No significant effect on plant biomass	Tassi et al. (2017)
nZVI	*Lolium perenne*	Lead	Chl content decreased with the increase of nZVI; low nZVI (100–500 mg/kg) favours growth, but high nZVI (1000 and 2000 mg/kg) inhibits the growth	Huang et al. (2018)
ZnO NPs	*Triticum aestivum*	Cadmium	Increased photosynthesis and growth	Hussain et al. (2018)
ZnO NPs	*Oryza sativa*	Cadmium	Improved growth; high dose increased total biomass	Zhang et al. (2019)
Ag NPs	*Moringa oleifera*	Cadmium; lead	Promoted germination and tolerance indices; enhanced growth; improved vigour index; increased chl a, b, and carotenoid contents	Azeez et al. (2019)
nHAP	*Apium graveolens*	Cadmium	No significant effect on growth	Yang et al. (2020)
TiO_2 NPs	*Sorghum bicolor*	Antimony	TiO_2 NPs (100–500 mg kg^{1}) increased plant biomass and slightly altered total chl contents**;** TiO_2 NPs (1000 and 1500 mg kg^{-1}) inhibited germination and growth	Zand et al. (2020a)
nZVI	*T. repens*	Cadmium	nZVI (600 mg kg^{-1}) boosted shoot biomass and Chl a/Chl b ratio; inhibitory effect on germination and growth at higher dose	Zand et al. (2020b)

Chl denotes chlorophyll; PBDEs denotes polybrominated diphenyl ethers

3 Effect of NPs on the Yield of Crop Plants

Nanotechnology products, like nanopesticides, nanoherbicides, nanobionics, etc., increase crop production. Nanobiotechnology offers new tools for manipulating and improving crop output using NPs. Smart delivery of agrochemicals enhances the yield by optimising water and nutrient conditions (Mali et al. 2020). Advancement in nanoscience has implemented new methods for the molecular management of diseases, increasing the yield through nanofertilisers/nanoinsecticides with efficient resource (water and soil) use (Peters et al. 2016). Modern farming has been using enormous pesticides to boost productivity. However, according to the UN's Food and Agriculture Organization (FAO), pests and diseases rob 20–40% of global crop production each year, despite the application of about two million tonnes of pesticides (King 2017).

Further, NP-mediated gene transformation and delivery of macromolecules that activate gene expression in plants can be used to improve agriculture even more (Mali et al. 2020). NPs could potentially act as a magic bullet, containing substances such as beneficial genes, herbicides, and organics that target specific plant parts to boost yield (Marchiol et al. 2014). However, other works reported that NPs enhance yield characteristics in plants. Seed priming with mineral NPs has the potential to alter the nutrient content of seeds, hence impacting yield (Rui et al. 2018).

3.1 Positive Aspects Concerning Yield

Nano-titanium dioxide (present in sewage sludge) enhanced tomato fruit yield (Bakshi et al. 2019). The uptake of copper NPs and iron NPs improved wheat yield. Besides, Cu NP uptake enhances stress tolerance in wheat variants, consequently leading to better yield of wheat crop (Yasmeen et al. 2017). Foliar application of iron NPs improved wheat productivity when cultivated in cadmium-contaminated soils (Hussain et al. 2019). Under a similar environment, the highest dry weight of grain reported at 100 mg/kg of Fe NPs (Adrees et al. 2021). Moreover, the exogenous and soil-applied zinc oxide NPs can promote wheat productivity in Cd-polluted soil (Hussain et al. 2018; Khan et al. 2019). Likewise, ZnO NPs application to sunflowers significantly improved the yield in soil watered with polluted effluent for a lengthy period of time.

Foliar application with Zn NPs enhanced the seed yield ha^{-1}, 100-seed weight, the number of seeds per head, the head diameter, and sunflower oil yield by 19.2%, 6.7%, 9.2%, 5.7%, and 214 kg ha^{-1}, compared to the untreated plants. Additionally, ZnO NPs can mitigate the harmful influence of toxic metals on sunflower productivity (Seleiman et al. 2020). Moreover, applying silicon NPs by seed priming, foliar spray, and soil amendment methods may increase the productivity of wheat (*Triticum aestivum*) cultivated under cadmium-contaminated soil (Ali et al. 2019a). Fluoride contamination in soil reduces yield by suppressing grain development, thereby

Table 14.2 Effect on crop yield

NMs/NP type	Crop type	Soil pollutant/ contaminant	Effect on crop yield	References
Silver and silver sulphide NPs	*Lactuca sativa*	Biosolids	No significant differences in dry weight of plant at harvest	Doolette et al. (2015)
ZnO NPs	*Triticum aestivum*	Cadmium	Increased yield	Hussain et al. (2018)
Ag NPs	*Moringa oleifera*	Cadmium; lead	Improved productivity	Azeez et al. (2019)
ZnO NPs	*Oryza sativa*	Cadmium	No difference found at ripe and harvest process	Zhang et al. (2019)
Ag NPs	*Capsicum annuum*; *Lactuca sativa*; *Raphanus sativus*	Sludge	Reduced lettuce and radish yield and no change in chilli yield	Li et al. (2020)

inhibiting reproduction and panicle development in rice crops. Thus, nano-Si-priming efficiently restored the harvest of grains (Banerjee et al. 2021). Besides, nano-silicon-mediated stimulation of yield has observed in *T. aestivum* and *Z. mays* seedlings exposed to cadmium-contaminated soil and insect infestation, respectively (El-Naggar et al. 2020). Root exposure with Ag NPs in sludge-amended soil throughout a life cycle declined the lettuce and radish harvest by 42% and 61% (Li et al. 2020).

3.2 *Negative Aspects Concerning Yield*

The application of silver NPs containing sludge could negatively influence crop production of both wheat and rape crops (Pradas del Real et al. 2016).

3.3 *No Effect Concerning Yield*

No significant differences reported in aerial biomass of *Lactuca sativa* at harvest as transformed silver NPs (present in the applied biosolids) had very little bioavailability to lettuce plant (Doolette et al. 2015) (Table 14.2).

4 Effect of NPs on the Quality of Crop Plants

According to a United Nations directive, global nutritional security and climate change measures in the agriculture sector must be taken in the twenty-first century (King 2017). So far, several types of NPs have been examined, with encouraging results in terms of improving quality. Further enhancement in terms of quality can be accomplished using NP-mediated gene transformation and delivery of macromolecules that induces gene expression in plants (Mali et al. 2020). Besides affecting morphology and biochemistry, it also influences the nutritional content of both natural and transgenic crops.

Nanotoxicity in crops can be visualised as a reduction in plant hormone concentration when specific NPs, such as CeO_2 NPs and CNTs, interact with them (Hao et al. 2016). Furthermore, crop nutrients (e.g., amino acids, proteins, fats, and sugars) are essential components of nutritional quality and are also influenced by different NPs (Yang et al. 2017). The use of nanotechnology to develop new foliar fertilisers could help synchronised agro crop nutrient management (Li et al. 2016). The NPs function as a magic bullet, hence serving as a smart delivery system for agricultural administration, explicitly about crop nutrition (Marchiol et al. 2014). Nutrient management and synchronised release and uptake of nutrients in agriculture crops are possible using nanofertilisers, reducing nutrient losses (Rai et al. 2018). The NP application for agricultural practice becomes even more challenging under the condition of accumulation in edible plant parts like fruits and seeds and modulation in nutrient composition (Yang et al. 2018).

4.1 Positive Aspects Concerning Quality

The unique photocatalytic and antimicrobial qualities of titanium dioxide make it effective for controlling and suppressing plant diseases, indirectly responsible for quality improvement. For example, cucumbers showed a reduction in infection when exposed to TiO_2 (Cui et al. 2009; Servin et al. 2015). The uptake of copper and iron NPs in wheat boosted the quality, reflected through increased sugar content (Yasmeen et al. 2017). The application of iron NPs on wheat crop in cadmium-contaminated soil demonstrated alleviation of toxic effects of Cd and reduced Cd contents in grains and tissues, while enhanced grain Fe biofortification in a dose-additive manner application of Fe NPs (Hussain et al. 2019). Same as reported earlier, Fe NPs augmented the quality of wheat grains. The highest concentration of Fe and least Cd content is found in the root, shoot, and grain at 100 mg/kg of Fe NPs (Adrees et al. 2020). In addition, the use of zinc oxide NPs and iron NPs reduced the amount of Cd in roots, shoots, and wheat grains.

The amount of Cd in grain was found to lower the Cd threshold level when exposed to higher NP treatment. Both ZnO NPs and Fe NPs increased the Zn and Fe amount in plants, especially in grains depicting use in cereals' biofortification. Hence, it will improve the nutrient content in seeds eliminating hidden hunger (Rizwan et al. 2019). Both foliar and soil application of ZnO NPs showed a simultaneous decline and increment of Cd and Zn content in tissues and grains. The amount of Cd in wheat grains declined by 30–77% and 16–78% with foliar and soil amendment of ZnO NPs, respectively. Overall, the zinc NPs play a significant role in increasing nutrients and decreasing Cd toxicity in the wheat crop, as reported by many studies (Hussain et al. 2018). ZnO NPs possess the potential to simultaneously reduce both arsenic and cadmium in rice grains cultivated in As- and Cd-co-contaminated rice paddies (Ma et al. 2020).

The ZnO NPs amendment to Cd-polluted soil has the potential to increase Zn while minimising Cd accumulation in tissues and grains by lowering the bioavailable soil Cd. About 78%, 64%, and 103% greater Zn concentrations observed in shoots, roots, and grains at the highest NPs (100 mg/kg), respectively, and the same exposure resulted in minimum Cd content in the wheat crop (Khan et al. 2019). Sunflower cultivated in polluted soil when exposed to ZnO NPs significantly boosted quality by enhancing the sunflower oil percentage, oleic acid, and oleic/linoleic acids ratio. It also showed a reduction of Cd, Cu, Cr, and Pb contents and significantly enhanced Zn and Fe (Seleiman et al. 2020). Similarly, foliar spray of 100 mg/L ZnO NPs significantly diminished the Cd content in rice crop by 30% and 31% in shoot and root, respectively, and enhanced Zn concentrations in tissues (Ali et al. 2019b). Likewise, foliar exposure of ZnO NPs (100 mg/L) showed the lowest Cd and highest Zn contents; therefore, the amount of Zn increased by 56%, 101%, and 106% in roots, shoots, and grains, respectively, at 100 mg/L of ZnO NP exposure.

The amount of Cd in grain decreased by 26%, 81%, and 87% when exposed to ZnO NPs at 25, 50, and 100 mg/L. Consequently, it could minimise Zn deficiency, thus improving the wheat crop quality (Adrees et al. 2020). Si NPs with higher concentrations were effective in lowering Cd levels in grains. The foliar spray of Si NPs diminished the Cd level in shoots, roots, and grains by 16–58%, 19–64%, and 20–82%, respectively, whereas soil-applied Si NPs declined the Cd contents in shoots, roots, and grains by 11–53%, 10–59%, and 22–83%, respectively. Thus, Si NPs reduced Cd and increased Si contents in matured grains of wheat (Ali et al. 2019a). Fluoride contamination resulted in an excessive build-up of fluoride in the spikelet sap, which prevented rice grains from hardening.

The addition of Si NPs increased the bioavailability of nutrients such as silicon, potassium, zinc, copper, iron, nickel, manganese, selenium, and vanadium boosted seedling health even during prolonged fluoride stress. Thus, by lowering fluoride bioaccumulation, Si NPs effectively alleviated molecular damage and restored quality, especially in edible grains (Banerjee et al. 2021). High concentration graphene oxide (GO) NPs (10 mg/L) reduce arsenic uptake in wheat crops (Hu et al. 2014). The addition of nZVI decreased Cr content in cabbage mustard tissues (Su et al. 2016). A low level of nZVI accelerated Fe translocation by the shoot of *Lolium perenne* grown in Pb-polluted sediment (Huang et al. 2018). The amount of Cd and Pb uptake significantly reduced in *Moringa oleifera* when exposed to Ag NPs (Azeez et al. 2019).

4.2 Negative Aspects Concerning Quality

The use of nano-TiO_2 particles increased Cd bioaccumulation in soybean plants (Singh and Lee 2016). Also, high Ti concentrations in plant tissues lead to competition between Ti and Fe for ligands and proteins, resulting in Ti phytotoxicity (Lyu et al. 2017). Thus, a higher concentration of Ti NPs likely caused iron deficiency symptoms in a plant, leading to poor quality. Simultaneous impacts of antimony and excessive TiO_2 NPs in soil showed increased toxicity and enhanced Sb accumulation capacity in plants. More significant Sb accumulation found in shoots than roots suggested that *S. bicolor* aerial parts were the preferential Sb storage organ (Zand et al. 2020a)**.** Also, CeO_2 NPs had no effect on Cd accumulation, although Cd boosted Ce accumulation in soybean plant tissues, especially roots and older leaves (Rossi et al. 2017).

Higher levels of nano-CeO_2 resulted in a detrimental effect on the boron nutritional status in sunflowers (Tassi et al. 2017). Further, K and Mg content in leaves of lettuce declined when exposed with Ag NPs (present in sludge), suggesting unintended residual transgenerational effects (Li et al. 2020). Nano-ZVI increased the accumulation capacity for Cd in *T. repens* (Zand et al. 2020b)**.** Besides, the addition of a high amount (500 mg kg^{-1}) of ZnO NPs in the low Cd-polluted soil could facilitate Cd accumulation, exceeding the permitted Cd concentration limit in Chinese rice (0.2 mg kg^{1}) (Zhang et al. 2019). The translocated CNTs bound with Pb or As in cabbage plants led to toxicity (Awad et al. 2019). Low concentration (0.1 and 1 mg/L) GO NPs boosted As uptake in the wheat plant (Hu et al. 2014). A high concentration of nZVI caused Fe absorption suppression because the iron uptake pathway and translocation from root to shoot were reported to be blocked by nZVI. It also increased the potential of *Lolium perenne* to accumulate Pb (Huang et al. 2018).

4.3 No Effect Concerning the Quality

No detrimental effect on boron's nutritional status in the plant, indicating a counteraction by nano-CeO_2 showing a reduced NP availability for plant uptake when high levels of boron were present in soil (Tassi et al. 2017). Barley in arsenic-polluted soils, when treated with nZVI, did not show any adverse effects regarding the nutrient content (Gil-Díaz et al. 2017). Bakshi et al. (2019) reported no significant Ti accumulation and no nutrition change in tomato fruits. The nano-HAP application showed no change in Cd concentrations in the celery plant (Yang et al. 2020). Also, exposed to Ag NPs (present in sludge) retained their nutritional status (Ca, K, Mg, P, Fe, Mn, and Zn), including protein and amino acid levels in chilli fruits and radish roots (Li et al. 2020) (Table 14.3).

Table 14.3 Effect on crop quality

NMs/NP type	Crop type	Soil pollutant/contaminant	Effect on crop quality	References
GO NPs	*Triticum aestivum*	Arsenic	Low dose (0.1 and 1 mg/L) improved whereas high dose (10 mg/L) declined As uptake	Hu et al. (2014)
nZVI	Cabbage; mustard	Hexavalent chromium	Decreased Cr content in tissues and accelerated Fe absorption	Su et al. (2016)
TiO_2 NPs	Soybean	Cadmium	Higher Cd uptake and bioaccumulation	Singh and Lee (2016)
CNT	*Brassica rapa*	Arsenic; Lead	Enhanced toxicity	Awad et al. (2019)
nZVI	*Lolium perenne*	Lead	Increased accumulation capacity of Pb; high dose of nZVI suppressed Fe absorption, while low dose accelerated Fe translocation by shoot	Huang et al. (2018)
ZnO NPs	*Triticum aestivum*	Cadmium	Increased and decreased concentration of Zn and Cd, respectively	Hussain et al. (2018)
Ag NPs	*Moringa oleifera*	Cadmium; lead	Uptake of Cd and Pb reduced	Azeez et al. (2019)
nHAP	*Apium graveolens*	Cadmium	No significant change	Yang et al. (2020)
ZnO NPs	*Oryza sativa*	Cadmium	High dose increased bioavailable Cd	Zhang et al. (2019)
Ag NPs	*Capsicum annuum*; *Lactuca sativa*; *Raphanus sativus*	Sludge	Nutritional quality is minimally affected in chilli fruits and radish roots, whereas K and Mg declined in lettuce leaves	Li et al. (2020)
nZVI	*T. repens*	Cadmium	Accumulation capacity increased for Cd	Zand et al. (2020b)
TiO_2 NPs	*Sorghum bicolor*	Antimony	Accumulation of Sb in shoots which enhances the toxicity	Zand et al. (2020a)

5 Conclusion and Future Outlook

Nanotechnology offers farmers better solutions to their problems by ensuring ecological sustainability and economic stability. Globally, many countries have anticipated that nanotechnology has the ability to maximise harvest and agricultural efficacy in an eco-friendly manner, even in an adverse environment. The usage of nanotechnology would be critical in nourishing a burgeoning population with diminishing natural resources. However, before NPs are widely used, their adverse effects must be assessed and addressed.

The number of publications dealing with NPs has increased exponentially, although research about the impact of single NPs on plants explicitly dominates.

Increased anthropogenic activities have resulted in harmful pollutants being released into the agro-environment, either intentionally or unintentionally. An increase in production (yield) with the least and efficient use of NPs in an already polluted terrestrial environment is now the main cynosure of agriculture scientists. The present chapter summarises the research progress by using several NPs via seed priming, foliar spraying, and soil amendment. We also listed the outcomes of different NPs on plants and reviewed progress mainly from three aspects: positive, negative, and no change under polluted soil. Several studies implied NPs could competitively adsorb the bound contaminants from soil and increase pollutants' concentrations, causing accumulation in crops. As a result, they are significantly affecting morphology, harvest, and quality.

These might also depend on soil property, plant variety, and the property of NPs. Most previous studies only focused on the interaction of plants with NPs or soil pollutants alone. However, the knowledge regarding their combined effects on the quality of crops is still minimal and henceforth is undoubtedly a new research direction. Researchers have found both beneficial and adverse impacts of NPs on higher plants, but very little work has been done to assess this under polluted soil. Various studies reported positive effects of low dosage, which showed a non-significant control effect, while excessive dosage enhances the harmful effects in crops. Besides, the increasing number of research demonstrates the negative impact of NPs, such as inhibited germination, growth and delayed ripening, etc. Micronutrient content in NP-treated crops suggested they could significantly alter the crop quality and yield. Future studies should address the following, considering polluted soil environment:

(a) Toxicity of NPs
(b) Lack of soil or field-based studies with NPs and more studies required in various types of contaminated fields as the behaviour of NPs differs significantly in laboratory conditions and the natural environment
(c) Limited nanoresearch with essential crop nutrients
(d) More extended growth experiments till harvest/maturity would be necessary to investigate the outcome of crop yield
(e) To study more cultivars as the responses found to be different among species and cultivars, and probing the role of NPs with varied crops, still await the acquisition of information
(f) Simultaneous potential accumulation of NPs and contaminants in crops

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Chapter 15
Role of Nanoparticles in Remediation of Contaminated Soil

M. Trivedi, S. Kedari, and G. C. Nikalje

1 Introduction

Technology and inventions has led to the industrial development all over the world. Meanwhile, this expansion of industrialization has led to release of various hazardous contaminants like carbon monoxide, chlorofluorocarbons, lead (Pb), arsenic (As), cadmium (Cd) and others in the environment (Mandeep and Shukla 2020). The improper disposal of these materials has reduced the quality of soil, water and air (Cechin et al. 2016). Maintaining the quality of these natural resources has become difficult causing pollution and a risk to the human health as well as environment (Mueller and Nowack 2010). To overcome these problems, several methods of remediation are being introduced, viz. bioremediation, phytoremediation and chemical and physical remediation. Bioremediation and phytoremediation use living organisms like microbes, fungi and plants, respectively. Both these methods are time-consuming and take longer time for treatment; hence they cannot be applied for immediate remediation (Sarkar et al. 2019). In addition, utilization of nanotechnology for bioremediation, i.e. nanobioremediation, is emerging.

Nanotechnology is the design, production and application of structures, devices and systems by manipulation of size and shape at the nanometre scale. They have a high surface to volume ratio, making them a budding candidate for environmental cleanup. From the past few years, green technology being in vogue, synthesis of

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nanoparticles has become a crucial part to be explored. The use of nanoparticles in the environment can be for remediation, treatment, sensing pollutants and their prevention. The nanoparticles have few peculiar properties like their at least one dimension measuring between 1 and 100 nm, having high surface to volume ratio and catalytic and magnetic properties which make them worth for the use of remediation technology (Koul 2019). In order to remove heavy metals from wastewater, carbon nanoparticles (CNTs) are widely used. They don't create any kind of secondary pollution and can be used to remove heavy metal from contaminated sites. The enzyme-mediated remediation is gaining boom with the use of nanoparticles in it as they provide an inert microenvironment that doesn't interfere with the nature of enzymes; also the biological activity remains specific (Baruah et al. 2019).

The various industrial sectors like mining, agriculture and chemical factories have contributed to a great extent for causing the environmental pollution. The use of plants and microbes has been an inexpensive, eco-friendly and cost-effective approach in cleanup technology since Romanian times. Various species from bacteria and fungi have capability to remove heavy metals and convert them to less toxic compounds, for example, fungi from *Aspergillus*, *Allescheriella* sp., *Klebsiella oxytoca*, *Phlebia* sp. and *Stachybotrys* sp. (Dixit et al. 2015)

2 Biosynthesis of Nanoparticles

Microbes are the nano-factories for green synthesis of cadmium, gold, platinum, palladium, silver and titanium nanoparticles (Benjamin et al. 2019). The presence of certain enzymes in the bacteria helps in catalysing the reaction leading to synthesis of nanoparticles. Fungi are also a good source for synthesis of nanoparticles as they secrete more amounts of proteins as compared to bacteria for the synthesis of nanoparticles. These can be further purified by filtration. It provides a simple, rapid, eco-friendly and stable method (Yadav et al. 2017).

Another approach for green synthesis of nanoparticles is the use of plants called phyto-nanotechnology. It is a single-step biosynthesis of nanoparticles, using plants. Plants can be grown easily as well by using plant tissue culture, for yearlong availability. Plants also facilitate the nanoparticle synthesis at industrial scale (Kharissova et al. 2013). The plant-derived nanoparticles can be used in the environmental and biomedical sector. In addition, by using genetic engineering approaches, nanoparticle synthesis can be enhanced in both plants and microbes at large scale.

3 Nanobioremediation

In the past few decades, a large number of contaminants including organic and inorganic pollutants have been persisting in the soil and water ecosystem. Organic pollutants include pesticides, aromatics, hydrocarbons and chlorinated solvents, while heavy metals contribute to the inorganic pollutants in the soil. Various materials like graphene-based materials, nanoparticles and bio-sorbents have been developed for remediation of soil (Chugunov et al. 2000; Wang and Yuan 2014; Gu et al. 2016). Nanobioremediation is the removal of pollutants (e.g. heavy metals, organic and inorganic toxins etc.) by enhancing microbial activity using nanoparticles synthesized by plants, fungi and microbes with the assistance of nanotechnology (Singh et al. 2016). Nanoparticles utilized for bioremediation of water and soils are summarized in Table 15.1. A combined approach of nanotechnology and biotechnology could be more effective in remediation by consolidated effect of microbes and plants together. Many nanomaterials such as bimetallic nanoparticles, carbon fibres, enzymes, nanotubes and zeolites have been successfully used for remediation purpose (Khin et al. 2012).

Soil is one of the valuable assets on this earth, which is now contaminated with heavy metals and agrochemicals. Such contamination leads to loss in biodiversity and affects the geochemical cycles. The irreversible agglomeration of calcium peroxide nanoparticles can be avoided by a simple surface modification technique which is based on hydrolysis-precipitation using calcium chloride as precursor (Khodaveisi et al. 2011). This technique involves use of polyethylene glycol 200 as surface modifier. In addition, it has ability to synthesize new reagents in nanosize with enhanced quality of in situ chemical oxidation. The need for cost-effective new technologies for the decontamination of contaminated sites has increased. In this regard, nanoscale zerovalent iron (nZVI) is widely used for degradation of chlorinated pollutants in soil as an alternative to, e.g. permeable reactive barriers or excavation. A study conducted by El-Temsah et al. (2016) compared two types of nZVI (type B made using precipitation with borohydride and type T produced by gas phase reduction of iron oxides under H_2) for efficient degradation of DDT, as well as the ecotoxicity of soil and water was tested on plants (barley and flax), earthworms (*Eisenia fetida*), ostracods (*Heterocypris incongruens*) and bacteria (*Escherichia coli*). Both types of nZVI effectively degraded DDT in water and had a negative impact on the tested organisms, with nZVI-T giving least adverse effects.

Another entity used for decontamination of soil and groundwater is zerovalent iron (ZVI). The development of stable nanoscale ZVI (nZVI) products has gained a boom. In a study conducted by De Gisi et al. (2017), the effectiveness of nZVI treatment for the decontamination of marine sediments polluted by heavy metals, using the commercial product Nanofer 25s, was evaluated. Two kinds of experiments labelled as (i) sediment at low dosage (2, 3 and 4 g nZVI per kg of SS) and (ii) sediment at high dosage (5, 10 and 20 g nZVI for every kg SS) were performed on sieved sediment with a size <5 mm. According to their results, nZVI is more suitable to be used for specific element removal rather than to be applied for a generalized contamination, meaning that a mix of techniques can be suggested for whole sediment remediation.

It was supposed that when hydroxyapatite (HAP) was used for remediation of heavy metal-contaminated soils, its effectiveness seemed likely to be affected by its particle size. In the study by Li et al. (2014), a pot experiment was conducted to evaluate the efficiency of two particle sizes of HAP: nanometre particle size of HAP

Table 15.1 Applications of nanoparticles for bioremediation of toxic contaminants

Contaminant	Nanoparticles	Results	References
14C-2,4-DCP	CNTs	CNTs inhibited 14C-2,4-DCP mineralization and degradation in soil; SWCNTs had a higher effect than MWCNTs on 14C-2,4-DCP biodegradation	Xia et al. (2010)
2,4-Dichlorophenoxyacetic acid (2,4-D)	Fe_3O_4	These nanoparticles combined with soil indigenous microorganisms induced higher 2,4-D degradation efficiency; they also reduced the half-lives of 2,4-D and resulted in the increased soil microbial populations	Fang et al. (2012)
Aroclor 1242	PAA-coated nZVI	The soil microflora was changed with the PAA-coated nZVI that reduced chloroaromatic mineralizing microorganism's activity	Tilston et al. (2013)
Arsenic	GO	Arsenic uptake was enhanced by GO and amplified which could be proved by phytotoxicity in wheat indicated by decreasing plant biomass and root numbers and increasing the oxidative stress	Hu et al. (2014)
Cd	GO	GO enhanced Cd toxicity with increased ROS production, suppressed plant growth in the *Microcystis aeruginosa*	Tang et al. (2015)
	TiO_2 NMs	TiO_2 NMs increased plant Cd uptake, decreased Cd stress in the plants in soybean In *Chlamydomonas reinhardtii* TiO_2 NMs reduced free Cd ion contents, lowered Cd bioavailability, alleviated Cd-induced growth inhibition	Singh and Lee (2016), Yang et al. (2012)

(continued)

Table 15.1 (continued)

Contaminant	Nanoparticles	Results	References
Chlordane and DDx	MWCNT and C60	C60 increased chlordane accumulation in *Solanum lycopersicum* and *Glycine max* and suppressed DDx uptake, while MWCNT decreased chlordane and DDx accumulation in all the plants	De La Torre-Roche et al. (2013)
Cr	Silicon NMs	Silicon NMs reduced the Cr accumulation, and ROS production in the *Pisum sativum* silicon NMs improved plant growth, protein, nitrogen, carotenoids and chlorophyll contents and antioxidative enzymes activities	Tripathi et al. (2015)
	CMC-stabilized nZVI	These nanoparticles suppressed Cr uptake in rape and Chinese cabbage by 61 and 36%. Also reduced Cr leachability, bioaccumulation and bioavailability	Wang et al. (2014)
Diuron	CNT	Diuron bioavailability was increased by CNTs; stronger diuron toxic effect on the photosynthetic activity of *Chlorella vulgaris* was observed	Schwab et al. (2013)
Phenanthrene	MWCNTs	MWCNTs adsorbed phenanthrene MWCNTs increased the phenanthrene biodegradation	Xia et al. (2010)
Phenol	Ni/Fe	The *Bacillus fusiformis* growth was prompted by nZVI and Ni/Fe nanoparticles aided in the biodegradation of phenol	Kuang et al. (2013)
PCE	Air-stable nano iron	Dechlorination of tetrachloroethane was demonstrated in synthetic aqueous medium and in polluted groundwater	Andreas et al. (2009)

(continued)

Table 15.1 (continued)

Contaminant	Nanoparticles	Results	References
DDT	Nanosized zerovalent iron: type B and type T	Both types of nZVI effectively degraded DDT in water, but showed lower degradation of aged DDT in soil. Both types of nZVI had negative impact on the tested organisms. Negative effects were mostly due to oxidation of nZVI, resulting in O_2 consumption and excess Fe(II) in water and soil	El-Temsah et al. (2016)
Pb, Zn, Cu and Cr	Hydroxyapatite (HAP): nanosized (nHAP) and micro-sized (mHAP)	Both nHAP and mHAP were able to reduce the bioavailability and reduced the uptake of Pb, Zn, Cu and Cr. Also convert them from nonresidual to residual forms	Li et al. (2014)
Pb and Cd	nZVI, nZVI-bentonite, nanoalginite and nano carbon	The tested nanoparticles proved high efficiency in immobilizing Cd and Pb in polluted soils. The best nanomaterials recommended to be used for remediation of Cd- and Pb-polluted soils are nZVI, bent-nZVI and nanoalginite, with special preference for nZVI	Helal et al. (2016)
Polychlorinated biphenyls (PCB)	Iron oxide, V_2O_5/TiO_2 nanoparticles	Iron oxide and V_2O_5/TiO_2 are very good oxidation catalysts, and maximum destruction of PCBs was obtained with iron oxide as catalyst in the presence of air	Varanasi et al. (2007)
Pb and Cd	nZVI	nZVI and cellulosic waste were used to reduce the bioavailability of Pb and Cd in a contaminated soil. Application of nZVI showed higher heavy metal removal efficiency than cellulosic waste	Tafazoli et al. (2017)
Cd	CMC stabilized and non-stabilized nZVI	Both nanoparticles showed maximum removal of Cd at pH 6 in 45 min	Nasiri et al. (2013)

(continued)

Table 15.1 (continued)

Contaminant	Nanoparticles	Results	References
Estradiol	CMC-stabilized MnO_2 nanoparticles	CMC-stabilized MnO_2 nanoparticles hold the potential to degrade various emerging contaminants soil and groundwater	Han et al. (2015)
Polycyclic Aromatic hydrocarbons (PAHs)	Amphiphilic polyurethane (APU) nanoparticles	APU particles have the ability to enhance PAH desorption and transport	Tungittiplakorn et al. (2004)
PAHs	nZVI particles	Both the micro- and nanoscales of ZVI were capable of removing the target compound in soil, but the higher removal efficiencies were by nanoscale ZVI because of the massive specific surface area	Chang and Shu (2005)
Zn and lindane	nZVI particles	The application of nZVI reduced lindane and extractable Zn concentrations following a dose-dependent pattern	Anza et al. (2019)
Zn^{2+}, $Cu^{2+}$and Cr^{3+}	NiO and MgO nanoparticles	NiO-MgO silica-based nanoparticles can be employed for the adsorptive of these metals repeatedly without impacting the adsorption capacity indicating their sustainability	Abuhatabab et al. (2020)
Pesticide-metolachlor	Zerovalent iron	Zerovalent iron can be used for on-site, field-scale treatment of pesticide-contaminated soil	Comfort et al. (2001)
Chlorinated pesticide	nZVI	Use of NZVI has capability for partial or complete dehalogenation of the organochloro pesticides	Singh et al. (2009)
Trichloroethylene (TCE) and Cr(VI)	Nano zerovalent iron (nZVI), emulsified nano zerovalent iron (EZVI), micro zerovalent iron (MZVI)	nZVI achieved a higher reduction of TCE than the other two particles	Jagupilla et al. (2009)

(nHAP) and micrometre particle size of HAP (mHAP) induced metal immobilization in soils. Both mHAP and nHAP were assessed for their ability to reduce lead (Pb), zinc (Zn), copper (Cu) and chromium (Cr) bioavailability in an artificially metal-contaminated soil. The results indicated that both mHAP and nHAP had significant effect on reducing the uptake of Pb, Zn, Cu and Cr by pakchoi (*Brassica chinensis L.*). Furthermore, both mHAP and nHAP were efficient in covering Pb, Zn, Cu and Cr from non-residual into residual forms. The results suggested that mHAP had the better effect on remediation of multiple metal-contaminated soils than nHAP and was more suitable for applying in situ remediation technology.

The ecosystem can be balanced by mine soil reclamation that minimizes adverse environmental impacts and also creates additional lands for agricultural use which indirectly enhances the carbon (C) sequestration (Liu and Lal 2014). A study by De Gisi et al. (2017) proposes a practical and economical approach to apply nanotechnology for mine soil reclamation which suggests adding small amounts of nanoparticles to the conventional soil amendment materials and then applying the mixtures for soil quality improvements.

4 Mechanism of Nanobioremediation

Nanotechnology is a new emerging field with numerous applications in environmental cleanup. Recently, it is being used in the decontamination of various contaminated sites (Pérez et al. 2018). The behaviour of nanoparticles depends on their size, surface area, chemical composition and its reactivity. The morphology, particle size distribution, specific surface area, surface charge and crystallographic characterization are the important characteristics that help to understand the behaviour of the nanoparticles (Thome et al. 2015). Before applying nanomaterials for bioremediation of soil ecosystem, their interaction with soil and pollutants needs to be understood. The nanomaterials used for cleanup are selected depending upon their reactivity with different pollutants present on the contaminated site.

The process of remediation involves various steps: synthesis of nanoparticles; transport of nanoparticles to the site; and injection of nanoparticles and their reaction with the target pollutant. Due to their small size, nanoparticles can easily penetrate into the porous medium like soil and reach the pollutants. The small size of nanoparticles allows to be easily transported in the subsurface, via injection or direct push in slurry form to contaminated zones under pressure or gravity in the view of treatment (Caliman et al. 2010; Noubactep and Care 2010). For a successful remediation, it is necessary for nanoparticles to reach the contaminants. But nanoparticles have clustering tendency and agglomerate rapidly; hence the distribution to the target zone is uneven. The surface of NPs is modified, by coating it with a stabilizer like polymer, e.g. CMC (carboxymethyl cellulose), which reduces the agglomeration and enhances dispersion and transport. The key mechanism for heavy metal removal by zerovalent iron nanoparticles is adsorption and redox reaction which converts toxic heavy metal to less toxic in nature (De Gisi et al. 2017).

4.1 Adsorption

Adsorption is a surface-based phenomenon where solutes adhere to the surface of the adsorbent and form a thin film (Bushra et al. 2017). Nanoparticles have higher surface area to volume ratio which makes them a good adsorbent for remediation. Whereas iron oxides can adsorb heavy metal from soil, hence nanoscale iron oxides are added to the soil. Iron oxide nanoparticles can bind to arsenic and adsorb it from soil. The nanoscale magnetite particles can effectively immobilize phosphate from soil by adsorption (Pan et al. 2010). However, the adsorption depends upon the pH, size of particles and surface morphology. A study of adsorption of phenol from aqueous solution was carried out by using alginate stabilized silver nanoparticle (AgNP) and gold nanoparticle (AuNP) beads as adsorbents.

This study showed that the adsorption efficiency and removal of phenol depends upon various parameters like initial concentration, contact time, pH and adsorbent dosage. The alginate stabilized AgNP and AuNP beads were found to be good adsorbent for adsorption of phenol from aqueous solution (Pal et al. 2014). The removal of arsenic species including As (III) and As(V) from drinking water using magnetic iron oxide nanoparticles coated on sand (MIONCS) was studied by Afzali et al. (2015). The results showed maximum adsorption capacity of arsenic is 0.285 mg g^{-1} at pH 7, which is higher than most of the available arsenic adsorbents. It concluded that the adsorption property of MIONCS has a higher efficiency for arsenic removal from drinking water. Mehrizad et al. (2012) investigated removal of 4-chloro-2 nitrophenol (4C2NP) from pharmaceuticals and pesticide industries using titanium dioxide nanoparticles as an adsorbent. The adsorption capacity was increased as the concentration and temperature of 4C2NP increases. Titanium dioxide nanoparticles recorded a maximum capacity of 86.3 mg.g^{-1} at optimal conditions.

4.2 Redox Reaction

Redox reaction involves reduction and oxidation in which electrons are transferred from one compound to other which results in oxidizing one compound and reducing the other (Tandon and Singh 2015). This transfer of electrons results in change in the oxidation state of the element. Redox reaction can stabilize or immobilize toxic contaminants and convert them to non-toxic or less toxic form which is the motive of remediation. Iron is a strong reducing agent and most commonly used for remediation. ZVI effectively dechlorinates many halogenated hydrocarbon compounds (Gillham and O'Hannesin 1994). The degradation is based on redox reactions, in which iron donates electrons to the contaminants, reducing them to fewer toxic compounds (Mueller and Nowack 2010). The reactivity of nZVI is more than ZVI; hence it is widely used for removing heavy metals like mercury (Hg), nickel (Ni), cadmium (Cd), lead (Pb) and chromium (Cr) from soil (Fig. 15.1).

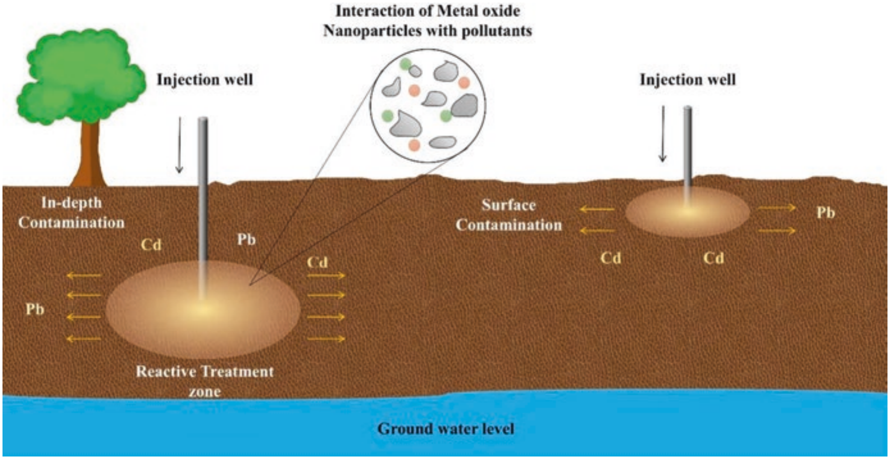

Fig. 15.1 Nanobioremediation of soil. Stabilized nanoparticles are transported in the form of slurry for proper distribution to the contaminated area. For in-depth contamination, the NPs are injected at deeper layers via injection well. For topsoil contamination, the nanoparticles are injected on the surface layer of soil. A reactive zone is created near the injection point through which the soil and pollutants interact with the nanoparticles. The incorporation of NPs with toxic heavy metal pollutants like lead (Pb), chromium (Cr) and cadmium (Cd) converts them to nontoxic or less harmful

5 Factors Affecting Reactivity of Nanoparticles

5.1 Mobility

Nanosize particles are much more mobile than larger sizes. The mobility of particles is less in solid medium like soil compared to aqueous medium like water; hence the degradation rate is also less. The mobility of natural or synthetic nanoparticles in the natural environment is strongly depend on whether the nanoparticles remain completely dispersed, aggregate and settle or form mobile nanoclusters (Karn et al. 2009). Soil composition also affects the dispersion of particles. For remediation, the particles should reach the contaminant zone, but their movement is disturbed by Brownian motion, density of particles, molecular interactions and also magnetic forces (Scott et al. 2011). Sometimes the particles get deposited on the surface of soil or in soil pores, which blocks the pores thus preventing the particles from reaching deeper layers. Nanoparticles are denser than water; due to this it gets settled in fluid; this also blocks the path (Cechin et al. 2016). To improve mobility, different surface coatings of polymers like carboxymethyl cellulose (CMC), polyethylene glycol (PEG), gum, etc. are being developed. These stabilizing agents promote easy distribution of particles through soil and enhance reactivity. Nasiri et al. (2013) evaluated the effect of stabilized and non-stabilized nZVI on the removal of Cd from soil. This resulted in nZVI being a suitable adsorbent for removal of Cd as both nZVI showed maximum adsorption. However, CMC stabilized nZVI had more colloidal stabilization and diffusion which increased its mobility and sustainability in comparison to non-stabilized nanoparticles.

5.2 Aggregation

Nanoparticles have a self-aggregation property which alters their dispersion. The interaction between soil and nanoparticles depends upon the surface chemistry of particles, ionic strength and porosity of soil and flow velocity (Karn et al. 2009), while the reaction between the nanoparticles and pollutants depends on the contact between them. Stable dispersion of particles in soil is essential for proper delivery in deep layers. But nanoparticles aggregate and form clusters which limit their migration and affect reactivity (Karn et al. 2009). Nanoparticles in concentrated solution aggregate more than in dilute solution; therefore, dilute solution is more stable than concentrated solution (He et al. 2008; Baalousha 2009). To prevent aggregation and loss of reactivity, stabilization of particles is necessary. Coating the particles with a stabilizing agent not only prevents agglomeration but also enhances reactivity and mobility. The principle of these stabilizers is that it creates a negatively charged layer on the surface of particles which induce repulsion with negatively charged soil, thus preventing agglomeration (Mueller and Nowack 2010).

If distribution of particles is achieved, surface reactivity increases thus enhancing the remediation. Polymer coating can also serve as a food or energy source for microorganisms (Galdames et al. 2020). Various natural and synthetic polymers or surfactants are used for coating NPs. Han et al. (2015) synthesized stabilized MnO_2 nanoparticles using carboxymethyl celluloses (CMC) as a stabilizer and tested their effectiveness for degrading aqueous and soil-sorbed estradiol. Non-stabilized MnO_2 particles rapidly aggregated and were unable to travel through soil column thus losing its mobility, whereas CMC-stabilized nanoparticles remained fully dispersed in aqueous solution without aggregating for months. CMC being a low-cost green stabilizer proved to be good for synthesizing birnessite (d-MnO_2) nanoparticles.

5.3 Stabilizers

The challenges like loss in mobility and transport of NPs to the site faced during remediation due to aggregation of particles are overcome by using stabilizing agents or stabilizers. These stabilizers are mostly polymers which can be synthetic or natural. Most of the synthetic polymers are negatively charged poly-electrolytes since they are capable of forming a poly-electrolyte layer that induces strong electrostatic repulsions (Hydutsky et al. 2007; Sirk et al. 2009). Some of the synthetic polymers are polyethylene glycol (PEG), polyacrylic acid (PAA), polystyrene sulphonate (PSS), polyoxyethylene sorbitan monolaurate, poly methacrylic acid and di-/tri-block copolymers which have been used as NZVI coatings and tested against different pollutants (Galdames et al. 2020). TCE (Schrick et al. 2004) and lindane (Román et al. 2013) have been degraded with PAA-coated nanoparticles. De Gisi et al. (2017) studied the efficiency of nZVI for treatment of marine sediments polluted with heavy metals by using commercial product Nanofer 25s coated with polyacrylic acid (PAA).

Natural polymers like carboxymethyl cellulose (CMC), starch, xanthan gum or guar gum have been used for coating which could enhance degradation, they can also serve as a food or energy source for microorganisms involved in bioremediation processes, and also, they are biodegradable (Galdames et al. 2020). Starr et al. (2009) investigated the effects of CMC-stabilized Fe3O4 nanoparticles on four pure cultures of bacteria, i.e. *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Enterococcus faecalis*. They hypothesized that CMC prevents nanoparticle aggregation as well as interactions between cells and nanoparticles. This study showed that stabilized nanoparticles may interact with bacterial surfaces without showing any toxicity or inhibitory effect to the tested organisms, thus concluding CMC-stabilized nanoparticles are non-toxic to bacteria. Table 15.2 shows different polymers used for stabilizing nanoparticles.

5.4 Longevity

Ageing is the factor for loss of reactivity of nanoparticles. Nanoparticles have limited lifespan; due to this, the reaction rate gets lesser day-by-day. Remediation with nZVI may be inefficient because nZVI particles may react with non-target substances, including dissolved oxygen, sulphate, nitrate and water. This also implies that nZVI will have a limited lifetime in porous media, and multiple injections of nZVI may be required, thereby making the treatment more costly (Tratnyek and Johnson 2006). Zerovalent iron nanoparticles have high surface area and get easily oxidized with the atmospheric oxygen due to which their functioning gets affected and reactivity decreases soon. Rapid oxidation results in formation of oxide layers on particles which may block the nZVP surface active sites and decrease the reactivity (Cullen et al. 2011). Encapsulation of nZVPs in a hydrophobic coating protects the core of nanoparticles from oxidation in air (Andreas et al. 2009).

6 Nanoparticles and Their Associated Risks

Studies have shown that nanoparticles are effective in bioremediation, but during this process there are few risks associated with them, major being impact on the microorganisms. Many studies have reported that nanoparticles have inhibited the growth of *E. coli* and *S. aureus* (Soni and Prakash 2015). Soil is rich in microbes that play vital roles in the biogeochemical cycles. The nanoparticles such as nano-iron can produce reactive oxygen species and disrupt the cell, leading to reduction

Table 15.2 Types of polymers used as stabilizing agents to prevent mobility and aggregation

Type of coating polymer	Polymers	Nanoparticles	Pollutants	References
Synthetic polymers	Polyethylene glycol 200 (PEG 200).	Amphiphilic polyurethane (APU) nanoparticles	Polycyclic Aromatic hydrocarbons (PAHs)	Tungittiplakorn et al. (2004)
	Polyethylene glycol 200	nZVI	Lindane	Román et al. (2016)
	Polyacrylic acid (PAA)	nZVI	Lindane	Román et al. (2013)
	Trichloroethylene (TCE)			Schrick et al. (2004)
	Polyvinylpyrrolidone (PVP)	nZVI	Trichloroethylene (TCE)	Sakulchaicharoen et al. (2010)
Natural polymers	Carboxymethyl cellulose (CMC)	nZVI	DDT	El-Temsah et al. (2016)
	CMC	Magnetite nanoparticle	Phosphorous	Pan et al. (2010)
	CMC	nZVI	Chromium	Chen et al. (2020)
	Chitosan	nZVI	Methylene blue (synthetic dye), aniline (aromatic primary amine)	Sravanthi et al. (2018)
	Xanthan gum	nZVI	–	Xue and Sethi (2012)
	Guar gum	nZVI	Trichloroethylene (TCE)	Sakulchaicharoen et al. (2010)

in beneficial microbes of soil (Morrison et al. 2002). Nanoparticles from heavy metals can hinder the movement of essential ions via the membrane indirectly inhibiting the growth of the microbe (Mashrai et al. 2017). The organic polymers can be coated to nanoparticles in order to reduce their toxic effects (Zhang et al. 2012). Very limited studies have been conducted till date on the impact of nanoparticles on the fungal growth, with most of them advocating a neutral effect on their growth (Tratnyek and Johnson 2006).

The smaller size of nanoparticles makes them an ideal candidate for bioremediation, but at the same time decrease in particle size and more reactivity make a substance more toxic. There are various studies related to the toxicity of nanoparticles. Nanoparticles may be ingested, inhaled or taken up through the skin (Oberdörster et al. 2007). Factors like the particle aggregation/disaggregation potential, partition coefficient, water solubility, composition, structure, molecular weight, the melting/boiling point, etc. (Vishwakarma et al. 2010) also play role in imparting toxicity to the nanoparticles; however toxicity studies need to be conducted on the mammals and the environment for the same.

A significant reduction in glutathione in the gills and lipid peroxidation in the brain was reported in largemouth bass (*Micropterus salmoides*) which was exposed to nC60 (1 ppm) (Oberdorster 2004). A study by Beddow et al. (2014) demonstrated nanosilver had an impact on *Nitrosomonas* sp. and *Nitrosococcus* species reflected by the inhibition to their nitrification rates. In another study on nitrifying bacteria, the impact of AgNPs [50-nm uncoated and 15-nm polyvinylpyrrolidone (PVP)-coated AgNPs]) to soil nitrification kinetics was studied. The results showed uncoated AgNPs exhibited more toxicity to nitrifying bacteria (Masrahi et al. 2014). The nickel manganese cobalt oxide (NMC) nanoparticle in quantity as low as 5 mg. L^{-1} is lethal for growth and respiration of soil bacterium *Shewanella oneidensis* MR-1 (Hang et al. 2016). Based on the toxic effects of various nanomaterials on the microbes, there is an urgent need to develop an alternative assessment procedure which is more efficient for evaluation. Further computational methods to predict properties, reactivity and mechanisms of actions for various molecular systems. Methods such as molecular dynamics simulations and quantum chemical calculations can be used to manage the potential risks associated with nanomaterials.

7 Conclusion and Future Prospects

Nanoparticles can profoundly be used for the remediation of soil. The small particles are highly reactive and have great absorption capacity. However, there are still a few challenges, such as the delivery of the particles to the target area, that need to be addressed. There are also concerns regarding the human and ecological toxicity caused due to these particles that requires extensive toxicity studies. Currently use of biosensors is viable option for soil bioremediation. Biosensors based on electrochemical properties such as high sensitivity and detection of heavy metals in real time can be developed in the form of nanowires, nanospheres and nanorods. Further whole-cell biosensors can be synthesized having better sensitivity with the help of eukaryotes for detection of heavy metals and agricultural chemicals that contaminate the soil. Such biosensors can be useful for monitoring of in situ pollution.

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Chapter 16
Risks and Concerns of Use of Nanoparticles in Agriculture

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1 Introduction

The act of agribusiness also called “farming/cultivating” is the most common way of cultivating food, feed, fiber, and various other desired items by the development of specific plants and the raising of animals/livestock (Acharya and Pal 2020). Farming is the foundation of most under-industrial/developing nations, and it gives food to people, straightforwardly and indirectly (FAO 2002; Patrick and Jeffrey 2015; Qadri 2018). The entire world populace will develop to an expected 8 billion individuals by 2025 and 9 billion by 2050, and it is broadly perceived that worldwide agricultural productivity should augment to take care of a quickly developing total populace (Ghasemzadeh 2012; Prasad et al. 2017). The FAO of the UN predicts that yearly meat production of 200 million tons will be needed by 2050 to fulfill the food needs achieved by expanding worldwide populace, and this anticipated expanding interest for meat put further pressure on horticultural/agricultural land because farmers need to develop crop yields to deliver animal feed (Ghasemzadeh 2012; Pandey 2018). Farming as a source of food is turning out to be progressively significant in a universe of decreasing assets and a steadily expanding

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worldwide populace (FAO/WHO 2010). Given the rising total populace, it is important to utilize the cutting-edge innovations like nanotechnology and nanobiotechnology in horticultural and food sciences. Nanotechnology has an enormous potential to revolutionize farming and associated fields, together with hydroponics and fisheries (Rajput et al. 2021a, b; Faizan et al. 2020; Usman et al. 2020a, b).

Nanoagriculture centers presently around targeted cultivating techniques that includes the utilization of nano-sized particles with novel properties to help in boosting of yield and animals' efficiency. The nanoscale is the size range from around 1 to 100 nm. At this size range, the laws of material science work in new ways that decides both the limitations and the chances of nanotechnologies and nanoscience in agribusiness and different allied branches (AE 2007; Ulbrich et al. 2016; Pathak 2019; Das and Pattanayak 2020; Das et al. 2020). The potential scopes/chances related to nanotechnologies have prompted critical venture by government organizations, public research centers, colleges, and firms all through the world (Cobb and Macoubrie 2004; Scott 2007; Forsberg and de Lauwere 2013). Nanotechnologies incorporate the creation, formulation, synthesis of different nanoparticles, and their application to physical, chemical, and biological systems (Roco 2007, 2011). Horizon 3 estimates guarantee infinite utilizations of nanotechnology as an empowering innovation in different enterprises. As reported by Roco et al. (2010), the improvement of nanotechnology will have progressive impact on instrumentation, user facilities, computing resources, in silico assets, etc. in agriculture and allied areas (Fig. 16.1).

There is a various meaning of nanotechnology (NCI 2018): according to the National Cancer Institute "innovation improvement at the nuclear, atomic, or macromolecular capacity of about 1–100 nanometers to make and utilize designs, gadgets, system and frameworks that have novel properties." Thus, the National Cancer Institute described nanotechnology as "innovation or technology on the nanometer scale." The nanotechnology primarily defined as "invention and technology that is constructed from single atoms and which relies upon individual atomic particles for its work (enzyme)." In case the enzyme's quality changed, the transformed compound could conceivably work (Wolfenden and Snider 2001; Scott and Chen 2002;

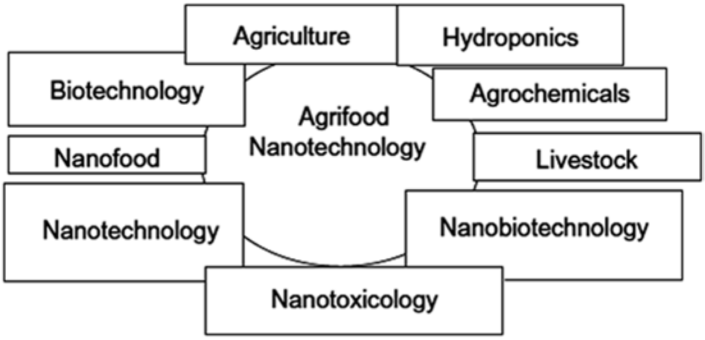

Fig. 16.1 Multidisciplinary nature of agriculture-food nanotechnology

NEHI 2008). Interestingly, whenever eliminated a couple of molecules from a mallet, it actually will work comparably well. This is a significant differentiation that has commonly been lost as the publicity about nanotechnology and utilized as a popular word for "little" rather than a particularly unique innovation (Chaudhry et al. 2005; Wu et al. 2020; Zhao et al. 2021).

Luckily genuine nanotechnologies are underway from the European Union-supported NanoHand project and reported that "nanotechnology contains the arising utilization of nanoscience" (ECCR 2004; EC 2009). The nanoscience is dealing with functional systems either dependent on the utilization of sub-units with specific size-dependent properties or of individual or joined functionalized sub-units (Brune et al. 2006; Raliya et al. 2013; Jeevanandam et al. 2018). The National Nanotechnology Initiative (NNI) thinks about "nanotechnology" just when nanotechnology instruments and ideas are utilized to concentrate on science, biology, and engineered biomolecules. The functionality of these synthesized particles is altogether different from those they have in nature and natural environment. The manipulation of these biological entities is finished by techniques more exact than should be possible by utilizing sub-atomic organic biomolecules, artificially synthesized or manufactured substance, and/or biochemical methodologies approaches that have been utilized for quite a long time in the biology research community (NCI 2018).

Somewhere else, nanotechnology is commonly defined as any innovation managing objects inside the 1–100 nm scale range (Elsabahy and Wooley 2012; Nicolas et al. 2013). Yet, without knowing what sort of items are 1–100 nm long, many individuals have a struggle in relating nanotechnology to its most efficient applications (Yadav and Upadhyay 2020a, b).

Nanotechnology shows a solid level of assembly with numerous different disciplines including information technology, biotechnology, animal husbandry, biomedicines, imaging, diagnostics, and food and agri-science (Groves 2008; Garcia et al. 2010; Ditta 2012; Pillai 2014; Pathak 2019; Singh et al. 2021a). With approaches and items emerging from innovation unions or technology convergences, it is enough hard to forecast and predict about its potential to transform and disturb ordinary living things. In the future, nanotechnology will not only ensure better livelihoods, but will help in solving problems nationally and internationally (Yadav et al. 2016, 2020; Yadav and Upadhyay 2020b).

Nanotechnology is becoming significant in fields like microelectronics, medical services, healthcare sectors, engineering, construction, and agriculture/farming (Joseph and Morrison 2006; Scott 2007; Singh et al. 2021a, b, c, d, e, f). The organic and naturally existing nanoparticles (nanoclay, tomato carotenoid lycopene, numerous synthetics obtained from soil natural matter, lipoproteins, exosomes, magnetosomes, viruses, ferritin) have different designs with multifacial biological role and natural jobs (Stanley 2014; Aggarwal et al. 2021; Tuli et al. 2021; Upadhyay et al. 2021a, b). Bio-nanoparticles are regularly biocompatible and have reproducible organization. The most possible and efficient biomedical utilizations of normal and modified bio-nanoparticles have been accounted by many schools in yesteryears (Singh et al. 2018, 2019, 2020a, b, c, d, e). "What would come about if we could put together the atoms individually the manner in which we need them?" asked Richard Feynman, in a deliberation of the American Physical Society held on 29 December 1959. This thought in the long run turned into an exploration field known as nanotechnology (Feynman 1960; Drexler 1992; Lewis 1993).

Nanotechnology deals with controlling, assembling, synthesizing, and rebuilding materials and gadgets on the size of particles and atoms of nanometer (Dan et al. 2020, 2021a, b; Rana et al. 2021). To know the feeling of the nanoscales, the width of the human hair is 80,000 nm, and the smallest things apparent with the exposed natural eye are 10,000 nm across. At nanoscales, the fundamental guidelines of chemical and physical science are not appropriate, and the same material may work entirely different. One suitable example of this innovation is the carbon nanotube invented in 1991, which is a couple of nanometers in dimensions but can conduct power better compared to copper, multiple times more grounded than steel, however just a 1/6th of its weight. Therefore, nanotechnology is a multidisciplinary field and portrayed as complementary integral, not cutthroat or competitive innovation (Lewis 1993; Jia 2005; Oberdörster et al. 2005; Priest 2006; Maynard 2007; Sozer and Kokini 2009; Raliya et al. 2013). As per an estimate, USD $40 billion were spent on various technologies and research related to nanotechnology by various agencies globally which further increased to USD $9.75 in 2009 (Gao et al. 2016; Harper 2017). Despite the huge speculation from government, private venture is relied upon to surpass public venture focusing on areas like semiconductors, drug and medical care, aviation, security, food, and agribusiness. BCC Research assessed that the worldwide market for items fusing nanotechnologies was roughly USD $15.7 billion by 2010, with figures to develop to USD $26.7 billion by 2015 with a compound annual growth rate (CAGR) of 11.1% from 2010 to 2015 (Harper 2017).

However, the worldwide market for nano-conductive materials should augment from $1.3 billion of every 2020 to $2.7 billion by 2025, at an accumulate yearly development rate (CAGR) of 15.3% during the time of 2020–2025 (BCC 2021). These estimates well established commercial nanomaterial applications, for example, nanocatalyst flimsy chips and membranes for catalytic converters, just as recent advances, for example, as nanoparticulate fabric treatments, rocket fuel additives, nanolithographic tools, and nanoscale electronic memory, health, energy, and the environmental remediation markets.

The agriculture and horticultural area are managing huge challenges like fast climatic changes, rapid diminishing soil characteristics, macro- and micronutrient deficit, and overuse of chemical fertilizers and pesticides, along with the presence of heavy metal in the soil (Chibuike and Obiora 2014; Prasad et al. 2017; Pandey 2018; Acharya and Pal 2020; Alengebawy et al. 2021). However, the worldwide populace increment has subsequently escalated food demand. Nanotechnology has colossally added to maintainable and sustainable farming by upgrading crop production, reestablishing and further development in soil quality (Pramanik and Pramanik 2016; Shang et al. 2019; Mali et al. 2020; Mittal et al. 2020). Nanotechnology is applied in different parts of farming, agriculture, viticulture, and horticulture as (a) nanopesticide applications for targeted delivery; (b) slow and controlled delivery of nanoparticles containing biofertilizers; (c) transport of hereditary materials for crop advancement; and (d) application of nanobiosensors for quick diagnosis of phytopathogens and other biotic and abiotic stresses. This article focuses on the risks and concerns of use of nanoparticles, nanosensors, nanotubes, nanofibers, and nanotechnology in agriculture.

2 Applications of Nanotechnology in Agriculture

The worldwide populace is projected to arrive at 8.5 billion by 2030, and the world should create basically half more food, to take care of around 9 billion individuals by 2050, as per the United Nations reports (Wiens 2016). Conversely, biodiversity, agri, and horticultural domains, seas, forests, and different types of natural resources, are being exhausted at an exceptional rate (Dewulf et al. 2015). Thus, expanding agricultural productivity, rural usefulness, and improving postharvest handling are fundamental to take care of a developing populace. For a long time, farmers have been endeavoring to increment agriculture yields by utilizing regular fertilizers, pesticides, and hybrid seeds. Worldwide environmental change is likewise causing a decrease in agricultural usefulness, due to the colossal modern growth (Bockstaller et al. 2008). Environmental effects on agribusiness can be evaluated utilizing agri-ecological markers to quantify the unfavorable impacts of editing and cultivating, for example, water and soil contamination, soil disintegration, and outflow of nursery gases.

Because of these natural emergencies, the expense of fundamental staples and the expansion in new food costs are unstable in nature, which will keep disturbing the normal populace. The world's food security will be at extraordinary danger, except if, what's more, until we advance agricultural practices and deal with our normal assets sustainably (Dasgupta et al. 2015). The nanotechnology had inescapable efficiency to give a valuable influence on a few areas, agribusiness, food handling, ranger service, natural issues, water industry, energy creation, and, also, economical use of waste resources. As of late, a wide scope of nanotechnology applications has been anticipated in agribusiness, in this manner drawing in serious innovative work rehearses at both scholastic and modern levels (Parisi et al. 2015). Nanotechnology has huge freedoms in different parts of agriculture going from production, assurance, reaping, and post gathering applications. In the accompanying area, uses of nanotechnology in agriculture are being examined.

2.1 Nanofertilizers

Advancement and application of modern sorts of synthetic manures utilizing inventive nanotechnology will possibly be powerful choices of altogether upgrading the worldwide agrarian creations expected to fulfill the future needs of the developing populace (Lal 2008). Moreover, the utilization of traditional fertilizers is hampered by the low effectiveness (simply 30–50%) and hardly any choices to improve the rates (Fageria 2009). Various studies shows that some designed nanomaterials can upgrade plant development in specific focus runs and could be utilized as nanofertilizers in farming to increment agronomic yields of harvests and additionally limit natural contamination. Nanofertilizers are classified as macronutrient nanofertilizers and micronutrient nanofertilizers, nutrient-loaded nanofertilizers, and plant growth-enhancing nanomaterials (Faizan et al. 2018).

Macronutrient nanofertilizers are artificially contained at least one macronutrient components (e.g., N, P, K, Mg, and Ca), in this way having the option to provide the requisite fundamental mega nutrients to floras. Enormous amounts of major fertilizers (primarily nitrogen and phosphorous composts) are utilized for yields of fundamental productivity. Smil (2002) assessed that nitrogen composts have shared an around 40% increment in proportionately food creation in yesteryears, demonstrating the basic job of the said synthetic manures in worldwide food creation. Besides, because of the low productivity (30–35%) and high utilization of these macronutrient composts, huge measures of these supplements (N and P) are shipped into surface and groundwater bodies, disturbing oceanic biological systems and undermining well-being of human and amphibian life. Consequently, a critical and basically fundamental exploration heading is to grow profoundly effective and harmless to the ecosystem ensuring safer climate.

Small-scale nutrients of plants incorporate Fe, Mn, Zn, Cu, and Mo. These nutrients are required in little amount for the profound growth and development of plants that in turn responsible for efficient and augmented plant productivity. These trace elements are usually amalgamated to the principal macronutrients as solvent salts for plant uptake. In any case, plant accessibility of the applied micronutrients might turn out to be low, and lack of micronutrient might happen in certain soils of alkaline pH, rough surface, or that containing lower soil matter (Fageria 2009). Apparently, theses trace elements along with nanofertilizers possibly enhance the bioavailability of necessary supplements to plants considerably under these most pessimistic scenario situations.

The NM-improved composts are characterized as those nanomaterials, which, when expanded with plant nutrient(s), can increment plant uptake proficiency of the nutrient(s) as well as diminish the unfriendly effects of customary fertilizer application; however those NMs neither contain nor give the designated nutrient(s). The main illustration of this kind is supplement of expanded zeolites. Zeolites' particles regularly don't happen at nanoscales. Yet, the arrangement of Al and Si in the three-dimensional system of SiO_4 and AlO_4 tetrahedra of zeolites makes channels and voids that are inside nanoscales (0.3–10 nm). Subsequently, zeolites are materials with nanostructures. It is a direct result of their extraordinary nano-permeable properties that zeolites frequently have incredibly high explicit surface region and high cation trade limit and are profoundly particular toward plant macronutrients (Liu and Lal 2015). These fundamental components might be traded onto zeolite trade destinations, where the supplements can be gradually delivered for plant take-up. There are a few reports archiving that utilization of some different sorts of NPs could likewise improve plant development somewhat, in spite of the way that these particles didn't contain any fundamental plant supplements. Commonplace instances of this sort are TiO_2 nanoparticles (Ti-NPs) and carbon nanotubes.

2.2 Nanopesticides

The help of nanotechnology in plant assurance items has dramatically expanded to accomplish higher yield. Over the years, crops were protected using huge amount and dose of fungicides, herbicides, and insecticides. Unfortunately, most of the pesticides get mixed with environment through various roots and leads to pollution and sometime even fails to control the pests (Pandey 2018). Indiscriminate use of pesticides not only financially burdens the farmers but also leads to environmental degradation. For optimum crop protection and maximum yield, pesticides should be active at their minimum concentration. Future research should be focused on these lines for optimum use of pesticides. One such technology is use of nanoparticles formulated with pesticides of choice. Nanoformulated pesticides are pesticides coated on nanoscale particles of various materials showing effective pesticide properties (Rai and Ingle 2012). The internal structure of the nanoparticles is known as core having effective concentration of pesticide, and capsulation materials are known as external phase (Fraceto et al. 2016). The advantage of nanoformulated pesticides is that this structure leads to sustained release of pesticides at requisite site without impacting the environment and other non-targeted crops. Nanobased pesticides have also other advantages like better transport, better solubility, better hardness, increased permeability, thermal stability, solubility, crystallinity, and also biodegradability essential for sustainable agro-environmental system.

Besides abovementioned advantages/promises, they also showed some concerns which need to be addressed properly. Copper-based nanopesticides like ($Cu(OH)_2$) have shown ill effects on spinach plants leading to change in there metabolic profiles and decreased level of antioxidants (ascorbic acid, α-tocopherol, 4-hydroxybutyric acid, ferulic acid) in plants with low amount of phenolic compounds also (Zhao et al. 2017). On the opposite, Petosa et al. (2017) reported that nanoformulations of pesticides lead to enhanced growth of plants with higher yield due to better transport of pesticides to target area. Further they reported that nanoformulations joining polymeric nanocapsules and the pyrethroid bifenthrin (nCAP4-BIF) show sustained release over the period of time and improved vehicle potential even upon the expansion of fertilizer in loamy sand soil immersed with artificial pore water containing Ca^{2+} and Mg^{2+} cations. This implies that nCAP4 could be a promising conveyance vehicle of pesticides like pyrethroid in plant security. This might be actually because of the expanded capability of scattering and wettability of nanoformulations that decrease natural dissolvable overflow and undesirable pesticide development. Besides, nanomaterials in pesticide detailing show some valuable properties like expanded firmness, porousness, warm dependability, dissolvability, crystallinity, and furthermore biodegradability fundamental for manageable agro-natural framework (Lu et al. 2002).

Further, numerous examinations have given proof that pesticide-based nanoparticles work best for plant-based systemic acquired resistance against pests. Enhanced capacity of pesticides to enter systemically in plant and reach up to cell sap has been reported by use of silica-based nanoformulations. These types of methods will help control biting- or sucking-type bugs like aphid (Li et al. 2007). Moreover, such nanoparticle-based and pesticide-based show enhanced protection against environmental factors like sunlight, etc. Further they have showed promising results for weed and disease management in agriculture. Various inorganic nanoparticles like, ZnO, Cu, SiO2, TiO_2, CaO, MgO, MnO, and Ag NPs play an important role toward control of microbial disease. Recently, ZnO nanoparticles successfully used to control fungal diseases caused by organism such as *Fusarium graminearum*, *Penicillium expansum*, *Alternaria alternata*, *F. oxysporum*, *Rhizopus stolonifer*, *Mucor plumbeus*, and *A. flavus* along with bacterial diseases caused by *Pseudomonas aeruginosa* (Servin et al. 2015; Shang et al. 2019). Hence, the nanomaterials in pesticides, fungicides, and herbicides have a huge extension in practical farming.

2.3 Nanobiosensor Use in Agriculture

Biosensors are electronic devices having receptor and transducer system with suitable biological component, being used to detect the various analytes (Sun et al. 2006). Nanobiosensors are latest edition of biosensor which are more versatile, connected to sensitized component to distinguish particular analyte at very low level through a physico-substance transducer. Nanobiosensors can help in early and rapid detection of analytes which may help to improve crop yields by appropriate management of water, land, fertilizers, and pesticides. High surface to volume proportion, fast electron-move kinetics, and high affectability and stability with longer life offer upper hands to nanobiosensors over regular and old age sensors (Mishra and Kumar 2009). They contain materials at miniscule level that perform as bioreceptor on a transducer which give signal to recognition component to recognize single or multiplex analyte. The major features of nanobiosensor are fictionalization, immobilization, and scaling down that incorporate biocomponents of a transduction framework into complex design to work on the scientific exhibition of NMs (Usman et al. 2020a, b). Their work dependent on turns off/on mechanism identifies analyte fixation inside parts per trillion (ppt) and limits the dissected network dependent on nano-definition.

Further, nanotechnology might be shaped and directed for constant observing of a varied range of pollutants of various origins including physical, chemical, and biological origins (Chen and Yada 2011). The continued use of chemicals to kill pests and insects in different farming exercises had made it important to investigate the new synthetic and physical composition of nanomaterials to foster creative devices for insecticide buildup location. These sensors made up at nanoscale are expected as scientific gadgets that will be requiring something like one detecting measurement no >100 nm, manufactured for checking physical as well as chemical properties on site for inaccessible locations and will provide more prominent affectability, small-scale detection, preciseness, quick recognition, and more versatility than regular discovery strategies (Fraceto et al. 2016; Kumar et al. 2015).

Besides rapid and accurate detection of pollutants at miniscule level, they can also be used measuring various parameters like moisture levels; soil and water pH; maturity index; climatic characteristics; nutritional status of crops, etc.; and amount that impacts the yields and quality of crops in order to support sustainable agriculture and enhanced productivity (Rai et al. 2012). The utilization of an organization of sensors, worldwide situating, and data frameworks through a farming region could instrument and write about various distinctive ecological, yield, and nuisance factors. Regulatory authorities and legislation can give the guides and rules to economical utilization of nanomaterials to identify, approve, and decrease their poisonous impacts in the entire environment (Iavicoli et al. 2017).

2.4 Nanotechnology for Bioremediation

Environmental contamination is perhaps the utmost complications faced by human race today (Das et al. 2015). Earth and water found beneath the earth surface are degraded by noxious contaminations by one or another natural or manmade sources at concentrations fit for presenting incredible danger to social well-being or the climate (Fu et al. 2014). Nanoscience has been seen as conceivably giving reasonable answers for these worldwide difficulties. Nanoscience-based procedures are state of art and economical techniques for the elimination of various contagions like heavy metals/metalloids, dyes, and organic contaminations (Li et al. 2016; Iavicoli et al. 2017; Thomé et al. 2015). Remediation through nanomaterial leads to detoxification of contaminations or change the contaminants to harmless level. These materials have exceptionally good strengths and adaptability for both on-site and uses at outdoor locations. NPs might have the option to get to tiny spaces in the subsurface and stay suspended in groundwater, accomplishing a more extensive appropriation contrasted with bigger, macrosized particles (Li et al. 2016). Remediation with use of nanoparticles can be effectively utilized for cleaning up of large-scale contaminated sites economically; not only it will clean the sites, but it will also reduce the time of cleanup processes. Further it will also help in elimination of need for treatment and disposal of contaminated soil.

A wide range of materials have been utilized effectively for remediation of various contaminants at nanoscale level. Out of these materials, zero-valent iron nanoparticle (ZVI-NP) has been generally examined, primarily because of its low poisonousness and minimal expense underway (Fu et al. 2014). These are electron-contributor particles that are primarily used for degradation of chlorinated compounds and the decrease of substantial metals through redox responses (Tosco et al. 2014). Further, they have been investigated for the removal of heavy metals like cadmium from aqueous solutions and chromium [Cr (VI)] from soil contaminated with tannery waste and wastewater (Singh et al. 2012). Not only from waste water were nanoparticles successfully used to increase the phytoremediation proficiency of heavy metals in tainted soils. Cadmium has been removed successfully from soybean plants using nanoparticles. TiO_2-based NPs have been successfully utilized for removal of Cd from plants and found to decrease the oxidative stress caused by Cd on soybean plants. Removal of lead by ryegrass (*Lolium temulentum* L.) from contaminated soils by using nano-hydroxyapatite and nano-carbon tubes has been reported by Liang et al. (2017). Similarly, various metal oxide-based NPs have been utilized for the expulsion of a few heavy metals and organic compounds. Iron oxide NPs have been largely utilized in the environmental field as anticipated adsorbents because of their redox cycle, particle trade, high proclivity for impurities, and attractive properties. Magnetite (Fe_3O_4), another member of the iron oxides, has been utilized for bioremediation (Lee et al. 2010).

Similarly, NPs can successfully be used in bioremediation of organic pollutants from soil. Further, impurities adsorbed to the NPs could be effectively taken up by plants all together with small-sized nanoparticles. Furthermore, modified membrane selectivity due to phytotoxic NMs may also work with take-up of natural toxins (Kah et al. 2019). De La Torre-Roche et al. (2012) studied the effect of fullerene introduction on accumulation of DDE (a metabolite of DDT) in plants like winter squash (*Cucurbita pepo* L.), soybean, and tomato (*Solanum lycopersicum* L.). Exposure of fullerene leads to increased uptake of DDE from 30% to 65%. They proposed co-take-up of NMs and pollutants as one of the potential instruments of improved take-up, as well as influencing the bioavailability/bioaccumulation of organic pollutants. After impurity removal, nanomaterials can be conveniently recuperated from liquefied media, making the cleaning system more practical. Despite the fact that likely valuable impacts on the eradication and change of noxious foreign substances have been proposed for nanomaterials, there is a still absence of data about their retrieval and reusability. The attention on materials life-cycle used for formulating nanoparticles starting from their entry into the environment not reported, how they are going to remove toxic substances etc., what will be their impact of various biological systems (Usman et al. 2016). All these concerns should be investigated on both the laboratory and pilot scale.

3 Fate of Nanoparticles in Soil and Transport in Plant

As NPs were added to soil for various purposes, they start connecting with soil particles, other materials in soils, and root exudates through the process of biotransformation (Shende et al. 2021; Rajput et al. 2018, 2021b). After establishing the connection, they move toward the aboveground parts of the plant. After entering soil, NPs can go through chemical and/or biological changes relying upon their tendency and on their communications with different soil parts (natural and inorganic). Various organic and inorganic particles including minerals and colloids intermingle with NPs which would prompt their segregation in solid and aqueous phase of soil system (Ben-Moshe et al. 2010). Accumulation is the chief interaction which happens unexpectedly when NMs are brought into the soil climate. Accumulation lessens the accessible exterior space of NMs which influences their usefulness. In addition, expansion in size of total will diminish their versatility in aqueous media and will influence overall purpose of NMs. There are two particular types of aggregation/accumulation which NPs face: aggregation between similar NMs known as homo aggregation and aggregation among NMs and one more molecule in environment (heteroaggregation), e.g., natural colloids, etc. known as heteroaggregation (Lowry et al. 2012). Restricted information is available with regard to destiny and conduct of NPs in the soil framework as the vast majority of the examination has been done in water frameworks and further investigation is required in this area.

Information available suggests that NP mechanisms like osmotic pressure and capillary forces help the NPs to enter into plant roots, or sometimes they directly enter root epidermal cells as root epidermal cells are semipermeable because of the presence of pores, but they stop the passage of NPs larger than 20 nm of size (Lin and Xing 2008). But larger NPs sometimes can initiate development of more novel and bigger pores in the epidermal cell which help their entry into plant system (Lin and Xing 2008). Once NPs cross the barrier of cell wall, they are apoplastically shipped through extracellular spaces to central vascular system and finally reach xylem. But it has been reported to reach up to central vascular system of plant; NPs have to cross the casparian strip barrier simplistically using the process of endocytosis, pore formation, and transport by binding to carrier proteins of the endodermal cell membrane (Tripathi et al. 2017).

Khodakovskaya et al. (2009) suggested that aquaporins and cell channels having pore sizes <1 nm that doesn't allow the NPs; notwithstanding some reports suggest that nanoscale tubes can control aquaporin pore size for penetration in plant cells. However, it has been suggested that aquaporin pore size can be regulated by carbon nanotubes for entry in plant cells. After their entry into the cytoplasm, NPs travel from one cell to another through the plasmodesmata (Tripathi et al. 2017). NPs which fail to enter into vascular system are reported to stay back at the casparian strip. NPs that have entered in the xylem are shipped to the shoots and consequently back to the roots by means of the phloem. Aggregates of NPs taken up by plants which have entered into the plants are found to be located inside the walls of epidermal cells and cytoplasm of cortical cells and furthermore in the nuclei (Reddy et al. 2016). Straight uptake of NPs can happen in seeds through parenchymatous intercellular spaces of the coat followed by dispersion in the cotyledon.

Organic matter, minerals, soil organisms, pH, temperature, and redox status of the soil are important parameters that impact the destiny of NPs applied through the soil route. Covering of NPs by parts of natural organic matter with reactive functional groups like carboxyl, amino, hydroxyl, and sulfhydryl; disintegration of NPs and release of ions; complexation and chelation with minerals and soil particles; and aggregation of NPs and degradation by soil microflora are a portion of the broadly detailed changes of NPs happening in soil. Reactions between the applied NPs and NPs normally framed in soil can contribute toward the adequacy of NPs as nanofertilizers, nanopesticides, etc. (Pérez-de-Luque 2017).

4 Risks and Uncertainties of Nanotechnology

Deliberate and greater contribution of nanotechnology into farming systems poses a number of queries in regard to the ecological fate and transportation of these materials into the climate that actually must be replied. Multifaceted applications of nanoparticles and its buildup and assimilation through everyday items have stressed the researchers and toxicologists. Noxious impacts basically rely upon nano-size measurement and cell association (Yang et al. 2017). It might lead to change in the genetic makeup and may influence the proteomic structure. As per one report, persistent use of ready to serve food varieties with NPs might apply imbalance on gut environment and may cause dysbacteriosis (Fröhlich and Fröhlich 2016). Other noted influences are reactive oxygen species (ROS) creation, DNA harm, genotoxic impacts, crucial organ harms in humans, etc. (Golokhvast et al. 2015). Generation of reactive oxygen species interferes with extracellular networks, bringing about oxidative pressure and toxicity to cell (Iavicoli et al. 2012). Impact of different consumed designed nanomaterials on cell expansion, apoptosis commencement, and pro-inflammatory and inflammatory cytokine release were additionally revealed in vivo, showing cytotoxicity of the liver, kidneys, stomach, and spleen (Ema et al. 2016). Additionally, nanoemulsion with lipophilic center has distinctive rate and degree of processing and adsorption in the gastrointestinal tract, which might make hurtful impacts due its compound nature as surfactant (Cushen et al. 2012). A few in vitro and in vivo examinations have demonstrated its cytotoxic consequences for various human organs; however clinical preliminary information for well-being and viability is as yet anticipated.

Further, clinical and cytotoxic biomarker studies are needed to detail the rules. Warning rules could be given for industrially accessible different food and agri-items with their conceivable hurtful impacts on long-term exposure. Progression of nanotechnology and its uses in food and agribusinesses suggested that nanoparticle ought to be chosen cautiously, dealing with the two, its advantage and disadvantage (Dasgupta et al. 2015). This appears to be a much more earnest issue to challenge seeing the huge number of nanoformulations conceivably utilized in the agricultural practice just as the doubts concerning potential connections with variable ecological components. These might incorporate the as yet unclear impact of normally happening ultrafine particles on the destiny of nano-agrochemicals; the doubts concerning the alterations brought about by maturing, soil, etc.; as well as those induced by the diverse work procedures adopted together with the difficulties in enumerating all these variables into an adequate risk assessment process (Mansoori 2017). In any case, these perspectives ought to be taken into cautious thought since they might influence the physico-substance portrayal of nanomaterials, changing their toxicological profile and consequently word-related dangers. Some of the major risks associated with use of nanotechnology are summarized below:

1. The danger in the area of nanotechnology is blended itself and ecological, health, industrial, and socioeconomic risks.
2. NPs will initiate toxicological consequences for a life form upon contact.

3. Because of the extraordinary potential for application in regions where the nanoparticles can come in direct individuals contact and can cause negative or unwanted harmful impacts.
4. Early exploration too demonstrates that nanoparticles influence various parts of the body where they might apply unfavorable impacts.
5. It is likewise that it could possibly disturb cell, enzymatic, and other organ-related abilities posing health hazards.
6. The nanoparticles are additionally non-biodegradable, and on removal, these arranged off materials may shape another class of non-biodegradable poisons.
7. Nanoparticles or the use of nanotechnology enhances the chance of environmental pollution (water, soil, air) and health hazards.
8. The nanotoxicity studies in agriculture are very limited, and it causes a potential risk to plant, microbes, animals, and even humans.
9. The nanotechnology creates the impression that the utmost danger is to the word-related health of the experts engaged with the formulation, packaging, and transportation of the nanomaterials.

5 Challenges and Barriers in Agro-nanotechnology

There are immense difficulties and constrains to be painstaking that facilitate the accountable commitment of nanotechnologies throughout diverse areas where these guarantees to make a huge commitment to usefulness, output, and effectiveness (Priest 2006; Chaudhry and Castle 2011). Several of these challenges are unified and contain:

- Synthesis and improvement of valuable practices for miniscule processes.
- Administrative, legitimate, governmental, ethical, and moral subjects.
- Contest with reputable miniscale innovations and techniques.
- Permit or grant of verification of nanotools idea, delivery pathways, and their outcomes.
- Intellectual right protection, copyright, patenting, and technology transfer division within organization.
- Potential intramural reluctance to accept nanotechnologies and nanotools within organization premises and businesses.
- Responsibilities and commission for Nanotechnology Research and Development in a pattern which are profoundly, effectively, and evocatively applicable to society and mankind.
- Monitoring of extensive production or price challenges.
- Requirement of interdisciplinary assets and investors.
- Health security, toxicity, and their effectual management of the possible dangers or risks of newly designed and developed nanomaterials.
- Community and consumer apprehension about security and involvement might hinder money-making interest and share in nanotechnology-oriented items.

The Australian Academy of Technological Sciences and Engineering (ATSE) has depicted the nanotechnology cascade significance since beginning with the creation of nanomaterials (nanoscale structures in natural and unprocessed forms) which then become nano-intermediates (transitional items with nanoscale properties) and lastly nano-empowered or nano-enabled items. Technique-based problems to be defeated to empower the formulation and manufacture of nanomaterials include efficient inspection of matters through synthesis, standardization, and effective and maintainable approaches for sequential and substantial production, along with thorough quality confirmation and control programs (ATSE 2008, 2013). The recurrent combination and enduring generations of innovative strategies for synthesis of imaginative, unique, and ground-breaking nano-objects into the prevailing production cycles will also necessitate to be addressed that may give confidence in the scale up of nanotech product synthesis into the coming days (Rose et al. 2007; Yang et al. 2009). Additional progress of material characterization techniques and nanoanalytics projects would too be needed to guarantee the forthcoming advancement of nanotechnologies (Naito et al. 2018; Lespes 2019).

Hodge et al. (2009) proposed that there are various administrative or regulatory difficulties or challenges to whom the society will confront in reference to nanotechnology (Bowman and Hodge 2007; Maynard et al. 2011; Moore 2013). A portion of these include large gaps in information and knowledge across different logical outskirts and technical frontlines. The replies are expected to discourse points raised in reference to the security of nanomaterials, along with the effect of newly designed nanomaterials via the material life-cycle. Considerable multidisciplinary research and investigation will be expected to address this information by nurturing proper metrology and norms for nanotechnologies. Efficient and successful strategies for estimating air, and waterborne nanomaterials are required to instituting and networking adequately the occurrence of administrative gaps and enact to current regulation (Kica and Bowman 2012; Allen et al. 2021). Viably evaluating legislative, administrative and regulatory systems, which might be practically acknowledging and recognizing qualities and shortcomings in various methodologies as well. The balancing financial, regulatory, and legislative assistance of government for nanotechnology are a foundation for future revolution, financial upliftment, policy making, and health security. Guaranteeing apposite spotless and trustworthy is going through all sectors of well-established and emerging nanotechnology guideline structures (Currall et al. 2006; Chaudhry et al. 2007; Siegrist et al. 2007a, b; Taylor 2008; Kumar et al. 2015).

6 Ethics of Nanotechnology in Agriculture

Nanotechnology is perceived as one of the vital technologies which has great possible benefits, and it has to be espoused with a cautionary standard, as that much is not known about its undevised effects on report of being new (Siegrist et al. 2007a, b). Although an excess of claims for nanotechnology in several fields and progressively more assertions are being used in the field of agriculture, and in reality, the common global population appears to know slightly about nanotechnology. Interestingly it was reported that a huge proportion of the US and the European general public have equitably very confined knowledge about the nanotechnology (Siegrist et al. 2008). So, it is clear that if public awareness of nanotechnology in such evolved societies where the literacy rates are relatively high is limited, then the situation is much worse in other parts of world that are also struggling with high illiteracy rates.

Nanotechnology inventions do not evoke arguments as biotechnology; maybe it is significant considering either similar solutions in the copyright law for the nanotechnology should be interject in the future. The nanotechnology is based on the methods and techniques of maneuvering matter on nanoscale, and it makes no difference either it is living or nonliving matter (Chaudhry et al. 2008). Public receptiveness of new technologies is the main feature of their development. The public should be conscious about the potential risks, benefits, and essential measures linked to the usage of nanotechnology. There are a number of reasons why implantation of nanotechnology in agriculture is still comparably at an early stage with other fields. The vital ones include lack of guidelines and unifying regulations on risk evaluation of nanotechnology and potential consumer health possibilities. In the face of potential risk levels that nanotechnology in the field of agriculture pose to the health of public and environment, people doubted that should the industry carry on using these nanosystems in spite of the unpredictability.

Nanotechnology has two greatest threats which are misuse and catastrophic accidents (Sozer and Kokini 2009). Several other ethical issues arise with development of nanotechnology like: Will it provide us more supernatural powers? It may head us to undetectable monitoring, and right to policy can be threaten. It has prospect to eliminate the other ethical issues (e.g., in plants target delivery of active ingredients can be done without damaging non-target plant tissue and also amount of chemical release in environment reduce). Public and related authorities wonder do they have a responsibility to help and provide other countries the technology (Marquis et al. 2009). General debate of people must be held and encouraged in a way to help the people in making an independent viewpoint. A significant role in this procedure should be played by the scientists, elucidating the process, principles, and applications of the nanotechnology among the people. The categorizing of agricultural crops having NPs should be supported to upgrade the free choice of use of these products by the people. It is essential for scientists to make a strong awareness among the people and forces that influence general public and also alert them about benefits and technological risks and failure. As a result, leadership and ethical personal decision-making will be developed in person to solve the problem of technological world (Smolkova et al. 2015).

7 Conclusions

Nanotechnology guarantees to further develop current agriculture practices through the upgrade of the executives and security of contributions to crops and other allied areas. The expected uses and advantages of nano-innovation are gigantic. Usefulness upgrade through nanotechnology-driven farming and expansion of result with minimization of contributions through better checking and designated activity is attractive. Nanotechnology empowers plants to utilize water, pesticides, and composts all the more proficiently. Nanotechnology use might carry possible advantages to growers through food production and to the food business through advancement of inventive items through food handling, protection, and bundling. Expected agri-food nanotechnology applications incorporate nanosensors/nanobiosensors for distinguishing microorganisms and for soil quality and for plant well-being observing, nanoporous zeolites for slow-discharge and productive measurements of water and composts for plants and of supplements and medications for animals, nanocapsules for agrochemical conveyance, making biofuels, nanocomposites for plastic film coatings utilized in food bundling, antimicrobial nanoemulsions for applications in cleaning of food, nanobiosensors for recognizable proof of microbe pollution, and further developing plant and creature reproducing.

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