



Beneficial Effects of Metal- and Metalloid-Based Nanoparticles on Crop Production

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11.1 Introduction

Because of the ever-increasing number of people on the planet, the demands for their nutrition are increasing (Population Institute 2017). On the other hand, increasing urbanization, industrialization, and pollution have led to the fact that the number of hectares of arable land, the quality of the soil, the amount of water resources, and the amount of rainfall decreased, and adverse effects such as drought, high temperatures, exhalation, etc. weaken plants that are increasingly being attacked by various pests including molds, bacteria, or insects, resulting in an overall crop decrease. In addition, excessive fertilization with chemical fertilizers in order to increase the fertility of the depleted soil is counterproductive (Bread for the World 2018; World Hunger Education Service 2018). Some of the abovementioned problems can be partially solved locally by using transgenic plants (Ahmad et al. 2012; Raven 2014; Ahanger et al. 2017); however, the overall antagonism against genetically modified crop plants gives space for other possible modern solutions, namely, the application of nanomaterials (FAO 2010, 2013; Sekhon 2014; Jampílek and Kráľová 2015, 2017a, b, 2018a; Prasad et al. 2017; Achari and Kowshik 2018; Agarwal et al. 2018).

Nanotechnology is a fast-growing field – so-called the key technologies of the twenty-first century – that provides for the development of materials that have new dimensions, novel properties, and a broader array of applications (e.g., Sekhon 2014; Jampílek and Kráľová 2015, 2017a, b, c, 2018a, b, c; Prasad et al. 2017;

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Ventola 2017; Achari and Kowshik 2018; Agarwal et al. 2018). Real nanoparticles (NPs) are defined by US National Nanotechnology Initiative in the range 1–100 nm (National Nanotechnology Initiative 2018). According to the Recommendation on the Definition of a Nanomaterial adopted by the European Commission, the term “nanomaterial” means “a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1–100 nm” (European Commission 2018).

NPs, nanoformulations, and nanomaterials can be prepared from inorganic or organic materials or their combinations (e.g., Bhushan et al. 2014; Pisárčik et al. 2017, 2018; Jampílek and Kráľová 2018b), and, in general, nanomaterials in agriculture and food industry have been widely used as nanofertilizers/systems for delivery of nutrients, for crop protection (pesticides, agrotexiles), and for protection of foods (Campos et al. 2016, 2018; Jampílek and Kráľová 2015, 2017a, b, 2018a, c; Achari and Kowshik 2018; Kah et al. 2018, Panpatte et al. 2016). Thus, application of nanotechnology can be considered as an excellent tool for increased crop production. Nevertheless, as mentioned above, nanoscale materials change properties and behavior of all pattern materials, and thus many nanomaterials showed not only benefits but also adverse effects and toxicity. It was observed that NPs are able to generate reactive oxygen species (ROS) and oxidative stress, to interact with cellular components and many enzymatic systems (Dietz and Herth 2011; Dolez 2015; Hossain et al. 2015; Marmioli and White 2016). At exposure to toxic metals, the oxidative stress in plants results in changes in processes at molecular, biochemical, morphophysiological, and whole levels, and therefore plants generate specific, appropriate protective/defensive mechanisms to suppress toxic effects of these pollutants (Wani et al. 2018). ROS also affect the expression of a number of genes and therefore control many processes like growth, cell cycle, programmed cell death, abiotic stress responses, pathogen defense, systemic signaling, and development, and therefore plants have antioxidant defense systems to protect plant cells from oxidative damage by scavenging of ROS, whereby the major sites for the production of $^1\text{O}_2$ and $\text{O}_2^{\cdot-}$ in chloroplasts are photosystem (PS) I and PSII (Gill and Tuteja 2010). Moreover, metallic NPs, similar to toxic metal ions, when applied in excess are particularly harmful to plants causing damage in the structure and function of the photosynthetic apparatus; reduction in concentration of photosynthetic pigments, especially chlorophyll (Chl); and disruption of grana and other malformations in chloroplasts, resulting in reduced photosynthetic efficiency of PSII and decreased net photosynthesis and finally in reduced plant growth (Masarovičová et al. 2010, 2014; Masarovičová and Kráľová 2013; Tighe-Neira et al. 2018; Kráľová et al. 2019). On the other hand, some metal NPs, e.g., TiO_2 NPs, were found to improve photosynthetic efficiency by increasing electron flow between the PSII and PSI in the Hill reaction as well as cause an increase in ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) activity in the Calvin and Benson cycle, whereby enhanced photosynthetic efficiency helps to achieve the sustainable yield (Su et al. 2007; Gao et al. 2008; Hasanpour et al. 2015; Tighe-Neira et al. 2018).

Chemical nature, size, shape, surface charge, and the dose introduced are the major factors responsible for the processes of intracellular NPs penetration (Dykman and Shchyogolev 2017; Burman and Kumar 2018). However, it is necessary exactly to estimate the concentration range for individual plant species, in which the particular metal NPs exhibit plant growth stimulation, while higher concentrations are phytotoxic, and verify it in field conditions. Investigation of transgenerational impact of metal-based NPs on the seed quality and the development of second-generation seedlings is desirable as well (Medina-Velo et al. 2018; Tan et al. 2018).

This contribution comprehensively reviews recent findings related to the beneficial effects of metal- and metalloid-based NPs on crops. Attention is focused on their potential to be used as plant growth-promoting compounds and components of fertilizer preparations and their favorable effects in reducing harmful impact of abiotic stresses (drought, salinity, flooding and waterlogging, soil acidity, temperature, UV light, elevated CO₂, toxic metal pollutants) on plants. The effects of metal-based NPs on crops based on the composition, particle size, particle shape, morphology, surface coating, and concentration of the NPs as well as their mechanism of action are discussed as well.

11.2 Metal-Based Nutrient Elements in Nanofertilizers

Application of fertilizers can significantly increase production up to 35–40%, when the right nutrients are applied at the right rate, at the right time, and in the right place for the selected crop (Mikkelsen 2011). In agricultural practice, the use of slow-release fertilizers delivering the nutrient stepwise or controlled-release fertilizers having plant nutrient in a form that plant cannot immediately absorb, and thus the uptake is delayed after application and plant will receive available nutrients for a longer time, is much-favored (Shaviv 2005; Trenkel 2010; Noh et al. 2015). Plant nutrient management is crucial to many current global sustainability issues, and the responsible nutrient management and sustainable agricultural production must include also consideration of environmental, economical, and social components (Mikkelsen 2011). Ferti-fortification, i.e., fertilizing crops with micronutrients such as Fe, Zn, Mn, Cu, S, and Mo, can largely help in alleviating micronutrient malnutrition in human population. Accumulation of essential elements in the edible tissues of crops using agro-biotechnological techniques (e.g., gene overexpression and activation control), and their direct fortification into formulation of processed foods could increase the concentration and bioaccessibility of these bioactive ingredients (Gharibzahedi and Jafari 2017; Dapkekar et al. 2018). Li et al. (2016a) assessed current foliar fertilizers in terms of their solubility, morphology, and surface properties and presented new screening criteria of new-generation micronutrient foliar fertilizers focusing on design of nanoscale foliar fertilizers and development of long-term micronutrient foliar fertilizers based on the nanotechnology.

Widespread use of chemical fertilizers in order to increase the crop productivity can disturb the soil mineral balance, decrease soil fertility, and cause severe damage to microbial flora and plants. Therefore recently increased attention is devoted to

nanoscale fertilizers that are characterized not only with their size but also with high surface area, sorption capacity, and ability to increase the nutrient use efficiency through mechanisms such as targeted delivery and slow or controlled release resulting in improved crop yields. Nanofertilizers show beneficial impact on seed germination rate, seedling growth, photosynthetic activity, nitrogen metabolism, and carbohydrate and protein synthesis, and their contribution to the pollution of environment is considerably lower than that of chemical fertilizers (Liu and Lal 2015; Solanki et al. 2015; Mani and Mondal 2016; Chhipa 2017; Hatami 2017; Jampílek and Kráľová 2017b; Khan and Rizvi 2017; Dimkpa and Bindraban 2018).

In this context, it could be mentioned that toxic metals accumulated in edible part of crops could threaten human health, and therefore, it is necessary to perform life cycle assessment (LCA), i.e., quantitative assessment of emissions, resources consumed, and the potential impacts on health and the environment that can be attributed to a product over its entire life cycle (Suppan 2017).

At over-application of fertilizers, undesirable effects for plants could occur connected with the loss of these nutrients in runoff resulting finally in environmental pollution (Wilson et al. 2008). As application of chemical fertilizers also could be connected with adverse effects on the environment reflected in pollution of atmosphere and groundwater, soil acidification, eutrophication, reduced soil fertility, loss of biodiversity, and high consuming of energy in synthesis processes, the use of nanosized fertilizers requiring lower amounts of active ingredient to the same or improved effects is at most desirable (Jampílek and Kráľová 2017b; El-Ghamry et al. 2018).

Nanofertilizers could be applied as foliar sprays, by addition to soil or by soaking seeds in nanofertilizer (Duhan et al. 2017; Preetha and Balakrishnan 2017). Benefits of nanotechnology applications as nanofertilizers or nano-encapsulated nutrients used in horticulture on germination and growth of plants were reported by Feregrino-Perez et al. (2018).

Metal/metalloid nutrient elements that are required for growth of plants are as follows: K, Ca, Mg, Fe, Mn, B, Zn, Cu, and Mo; some other such as Ni, Se, V, Na, Si, Co, and Al could be also considered as important elements for plants showing at low doses beneficial effect on plant growth (Liu et al. 2015; Fernández-Luqueño et al. 2015; López-Valdez et al. 2018). Both macronutrients (K, Mg, and Ca) and micronutrients (Cu, Zn, Mn, Fe, Ni, Al, Co, and Na) are indispensable for growth and development of plants being involved in many important processes, including activation of enzymes and catalytic active cofactors or enhancement of resistance to biotic and abiotic stresses (Hänsch and Mendel 2009; Marschner 2012; Dalcorso et al. 2014; Tripathi et al. 2014, 2015a; Hasanuzzaman et al. 2018).

For slow and steady release of potassium, an alkali metal belonging to metal macronutrients, slow-release fertilizers using microporous aluminosilicate minerals, zeolites, are used. Although zeolites' particles often do not occur at nanoscale, their nanostructures are represented by channels and voids with diameters of 0.3–10 nm created by dimensional framework of SiO_4 and AlO_4 tetrahedra, which could be laden, for example, with potassium along with other slowly dissolving ingredients (e.g., Ca) and further minor and trace nutrients (Liu and Lal 2015; Zhou and

Huang 2007). Due to density of negative charge in the structure and the dimensions of interior channels, the natural zeolite can highly selectively adsorb NH_4^+ and K^+ compared to Na^+ or divalent cations such as Ca^{2+} and Mg^{2+} . Retention of these nutrients in the root zone to be used by plants as needed by zeolites contributes to improved plant growth. *Brassica alboglabra* Bailey grown in soil amended with NH_4^+ - and K^+ -loaded zeolite showed an increase in the total harvest weight, whereby high levels of the N and K contents were maintained in the soils (Li et al. 2013), and similar growth responses of hot pepper to application of NH_4^+ - and K^+ -loaded zeolite fertilizer were reported as well (Li et al. 2010).

The K^+ -loaded zeolites as well-suited for plant growth applications were recommended also by Beitollah et al. (2009). Adequate levels of macronutrients (N, P, and K) for plants can be achieved by slow-release fertilizer consisting of NH_4^+ - and K^+ -saturated clinoptilolite phosphate rock media (Allen et al. 1993). Ball-milled clinoptilolite achieving nano-dimension (90–110 nm) that was fortified with Zn by loading ZnSO_4 -released Zn for a period of 1176 h, while the Zn release from the ZnSO_4 lasted only 216 h, suggesting that the nanoscale clinoptilolite could be used as a slow-release Zn fertilizer and improve Zn use efficiency by crops (Yuvaraj and Subramanian 2018).

For the loading of NPK fertilizers, also chitosan (CS) NPs were used (Corradini et al. 2010; Hasaneen et al. 2014). Foliar treatment of *Ocimum basilicum* plants with nanocalcium and nanopotassium chelate fertilizers increased harvest index, grain yield, biological yield, calcium percentage, potassium percentage, and Chl content in plants (Ghahremani et al. 2014).

Treatment of peanut (*Arachis hypogaea*) plants grown on sand supplemented with Hoagland solution and CaCO_3 NPs (20–80 nm, 160 mg/L as Ca) considerably improved seedling dry biomass by 15%, and at co-application of CaCO_3 NPs with humic acids (1000 mg/L), even 30% increase in plant biomass was observed (Liu et al. 2005). Application of calcium phosphate nanogel fertilizer composites (CAPNGFC) increased the germination of rice and peanut (Umarani and Mala 2013a) and showed a significant increase in amylase and protease activity as well as weight per fruit in *Abelmoschus esculentus* (Umarani and Mala 2013b). Calcium phosphate NPs (CaPNPs) in combination with both the arbuscular mycorrhizal fungus *Glomus mosseae* and endosymbiont *Piriformospora indica* more effectively stimulated *Zea mays* growth than the combinations of CaPNPs + *G. mosseae*, CaPNPs + *P. indica*, or CaPNPs alone, and the treated plants showed improved Chla content and performance index (Rane et al. 2015).

11.2.1 Beneficial Effects of Essential Metal-Based Nanoparticles on Plant Growth

Beneficial impact of nanoscale metal and metal oxide micronutrients on plant growth was reported by many researchers (e.g., Masarovičová and Kráľová 2013; Masarovičová et al. 2014; Liu and Lal 2015; Tripathi et al. 2015a; Jampílek and Kráľová 2017b; Ruttkay-Nedecký et al. 2017). Seed quality is an important factor

for the successful cultivation of crops. Germination of seeds starts with the uptake of water, followed by rapid imbibition of water by seeds until all of the matrices and cell contents are fully hydrated, which is essential to set in motion the metabolic events in seeds that are metabolically inactive in the mature dry state. In germination process, protein synthesis and respiratory activity initially involve components stored within the mature dry seed, and increases or modifications of hormones, especially gibberellin, also play an important role (Nonogaki et al. 2010). Several metals and metalloids applied in bulk as well as nanoscale forms were reported significantly to improve seed germination (e.g., Prasad et al. 2012; Siddiqui and Al-Wahaibi 2014; Anusuya and Banu 2016; Subbaiah et al. 2016; Guha et al. 2018).

11.2.1.1 Copper and Copper Oxide Nanoparticles

Application of CuNPs through hydroponic solution or as spray enhanced the growth of maize plants by 51% compared to control, and it was found that CuNPs tested in this study could enter into the plant cell, easily be assimilated by plants, and cause plant growth stimulation by regulating the different enzyme activities, showing the highest impact on glucose-6-phosphate dehydrogenase (Adhikari et al. 2016). External Cu microparticles and CuNPs applied to soil at a dose of 0–200 mg Cu/kg did not affect Chl and malondialdehyde (MDA) content and shoot length, while they increased water content (6.9–12.5%) and reduced shoot biomass of *Origanum vulgare* plants (Du et al. 2018). Based on proteomic and physiological analyses of wheat seeds exposed to 25 ppm CuNPs (a concentration causing increased spike length, number of grains per spike, and 1000 grain weight in tested wheat varieties), Yasmeen et al. (2017) estimated increased levels of proteins involved in starch degradation and glycolysis as well as increased sugar content, superoxide dismutase (SOD) activity, and Cu content in CuNP-treated seeds suggesting improved stress tolerance in wheat through CuNPs by mediating the process of starch degradation, glycolysis, and tricarboxylic acid cycle. CuNPs biosynthesized by *Citrus medica* L. fruit extract applied at doses up to 20 µg/mL increased mitotic index in actively dividing cells of *Allium cepa* (Nagaonkar et al. 2015). Lopez-Vargas et al. (2018) reported that following the treatment of tomato plants with CuNPs, the production of fruits with greater firmness, increased vitamin C and lycopene contents, enhanced ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)diammonium salt) antioxidant capacity, increased activity of SOD and catalase (CAT), and decreased APX and glutathione peroxidase (GPX) activity was observed. Biogenic CuNPs with the size 20 nm showed a significant increase in height, root length, fresh and dry weights, and performance index of pigeon pea (*Cajanus cajan* L.) seedlings (Shende et al. 2017).

Cu-CS NPs at a dose up to 0.12% enhanced percent germination, shoot and root length, root number, seedling length, fresh and dry weight, and seed vigor index of maize seedlings and induced the activities of α -amylase and protease enzymes, increased the total protein content in germinating maize seeds, and decreased content of starch suggesting that enhanced seedling growth was connected by mobilizing the reserved food, primarily starch, through the higher activity of α -amylase (Saharan et al. 2016). Beneficial impact of CuNPs absorbed on CS hydrogels on

tomato growth and quality was reported also by Juarez-Maldonado et al. (2016). Cu-CS NPs exhibited promising stimulatory effects on plant height, ear length, ear weight/plot, grain yield/plot, and 100 grain weight of maize also in field experiment, and treated plants showed notable defense response reflected in higher activities of antioxidant enzymes, SOD and peroxidase (POD), and defense enzymes, polyphenol oxidase (PPO) and phenylalanine ammonia lyase, as well as higher Chl content (Choudhary et al. 2017). Both foliar spray and combined application (involving seed coat and foliar spray) of Cu-CS NPs were found to enhance the growth profile of finger millet plants and increased yield, which in the case of combined application resulted in a yield increase approx. by 89%, and increased defense enzymes in treated plants caused the suppression of blast disease (Sathiyabama and Manikandan 2018).

Application of CuNPs in CS-PVA hydrogels increased the yield and nutraceutical properties of the tomato fruits, which was reflected in increased numbers of leaves and clusters, fresh biomass of roots, and dry biomass of stems, leaves and roots of the plants as well as higher lycopene content and total antioxidant capacity in the fruits, whereby using a dose of 0.02 mg CuNPs, the lycopene content increased by 37% (Hernandez et al. 2017). Grafting is a cultivation technique that allows the plant to be more efficient in its utilization of water and nutrients, and CS-PVA hydrogels with CuNPs were found to improve the growth of grafted watermelon by inducing modifications in leaf micromorphology, increasing stoma width and primary stem and root length resulting in improved plant growth (Gonzalez et al. 2017).

Engineered NPs of essential metals have usually both stimulatory and inhibitory effects upon plant performance, whereby, in general, the concentration levels for the stimulatory effects of CuNPs were lower than for those for Fe⁰NPs, but beneficial impact on plant growth showed also AuNPs at concentrations smaller than those of Fe⁰NPs and CuNPs what could be attributed to effects on secondary metabolites (Tolaymat et al. 2017). Investigation of the impact of bimetallic (Cu and Au) alloy NPs in submerge root cultures of *Stevia rebaudiana* on the production of biomass and secondary metabolites showed that in the presence of naphthalene acetic acid (0.5 mg/L), application of 30 µg/L AuCu NPs stimulated biomass accumulation and enhanced total phenolic production, and total flavonoid production in adventitious root cultures of *Stevia rebaudiana* was estimated, best results being observed with AuCu NPs (1:3) (Ghazal et al. 2018).

Addition of crystalline monoclinic cubic CuO NPs with mean size 47 nm to in vitro culture of *Stevia rebaudiana* in Murashige and Skoog (MS) media using a concentration 10 mg/L resulted in notable enhancement of bioactive major steviol glycosides (rebaudioside A and stevioside) and total phenolic content as well as total flavonoid content (Javed et al. 2017a). It was found by Singh et al. (2017) that in contrast to treatments with 100 and 500 mg/L of CuO NPs, respectively, application of a low dose (10 mg/L CuO NPs) slightly increased Chl pigment and sugar content in tomato plants. Foliar application of 200 mg/L CuO NPs to 3-week-old soil-grown cucumber seedlings increased fruit fresh weight (Hong et al. 2016).

CuO NPs and ZnO NPs applied at a dose 10 mg/L were found to stimulate the growth of *Brassica napus* plants, and exposure of germinated seeds of rapeseed to

these NPs caused changes in transcript levels of genes involved in signal transduction pathway including auxin-responsive protein, protein kinase, MPK3, and MPK4 both in root and shoot tissues (Rahmani et al. 2016). CuO and ZnO NPs at doses of ≥ 10 mg metal/kg were found to modify the production of key metabolites involved in plant protection in a root-associated microbe, *Pseudomonas chlororaphis* O6, and reprogramming of root morphology involving increases in root hair proliferation (CuO NPs) and lateral root formation (ZnO NPs) in wheat seedlings, and systemic changes in wheat shoot gene expression causing altered regulation for metal stress resilience as well as the potential for enhanced survival under stress were observed (Anderson et al. 2018).

11.2.1.2 Zinc and Zinc Oxide Nanoparticles

Foliar application of spherical Zn-CS NPs with particle diameters 250–300 nm and zeta potential of +42.34 mV containing 20 mg Zn/g (w/w) on two durum wheat cultivars grown in Zn-deficient sand media performed after anthesis (twice a week, for 5 weeks) resulted in 27 and 42% increase in grain Zn content suggesting that CS-based nanocarriers could be used in agronomic biofortification (Deshpande et al. 2017).

Presence of weathered and fresh ZnO NPs and Zn salt in soil stimulated grain yield in *Triticum aestivum* L. plants by 15% and 29%, respectively, whereby grain Zn content was increased (186% and 229% by weathered ZnO NPs and salt and 229% and 300% by fresh ZnO NPs and salt) and whereby grain Zn did not exist in ion form (Dimkpa et al. 2018). Amendments of ZnO NPs or Zn salt through soil and foliar pathways, under “low” and “high” levels of nitrogen, phosphorus, and potassium (NPK), showed that grain yield of sorghum notably increased by both Zn types; however the effect was insignificant when Zn was soil-applied at low NPK. While at all NPK levels and Zn exposure pathways, both Zn types increased N and K accumulation relative to control plants, P accumulation depended on both NPK level and Zn exposure pathway and enabled higher soil P retention (Dimkpa et al. 2017a).

ZnO NPs seed priming (25, 50, 75, 100 ppm) linearly increased the growth characteristics, photosynthesis, and biomass of wheat, and considerably higher Zn levels were estimated in the roots, shoot, and grains of treated plants compared to control indicating that such treatment could be suitable to reduce Zn deficiency in plants (Munir et al. 2018). Tomato seedlings, roots of which were treated at the 20-day stage of growth with 2–16 mg ZnO NPs/L and then transplanted and grew under natural environmental conditions, showed at the 45-day stage of growth considerably improved growth, photosynthetic efficiency, and activities of carbonic anhydrase and antioxidant systems; the best results, including maximum proline accumulation, were observed with the treatment of 8 mg ZnO NPs/L for 30 min (Faizan et al. 2018).

ZnO NPs (34 nm) applied at concentration 1 mg/L considerably enhanced steviol glycoside production in micropropagated shoots of *Stevia rebaudiana* Bertoni, while at higher concentrations, they were found to be phytotoxic, and strong decrease in the antioxidant activities and formation of secondary metabolites was

observed (Javed et al. 2017b). Considerable increase in biomass, growth tolerance index, Chl contents, and antioxidant enzyme activities of rice seedlings treated with 100 mg/L ZnO NPs compared to control were estimated; however at concentrations >300 mg/L, phytotoxic effects were observed (Chutipajit et al. 2018). Cucumber plants cultivated in soil amended with 5 mg ZnO NPs/kg soil showed enhanced yielding capacity by 36 %, and the fruits had more carotene, Zn, and Fe compared to the control, while accumulation of ZnO NPs in fruits was not estimated (Astafurova et al. 2017).

Seed priming with 100 ppm ZnO NPs for 6 h was shown to be an effective treatment in mitigating the harmful effects of Cu stress on growth as well as contents of Chla, Chlb, soluble carbohydrates, and proteins of the 14-day-old *Vicia faba* seedlings that were irrigated with 150 mM CuSO₄ (Kasim et al. 2017).

Medina-Velo et al. (2018) reported that uncoated and coated ZnO NPs showed low residual transgenerational effects on seed composition, which could be beneficial in agricultural production. While ZnO NPs adversely affected the growth of eggplant in plant tissue culture, they enhanced eggplant growth under greenhouse conditions, whereby the accumulation of ZnO NPs in various parts of eggplant was observed in both plant tissue culture and greenhouse-cultivated seedlings (Thunugunta et al. 2018). Application of ZnO NPs (25 nm size) at 1000 ppm stimulated both seed germination and seedling vigor of peanut plants, which was reflected in early flowering and higher leaf Chl content (Prasad et al. 2012). Low concentrations of ZnO NPs had beneficial impact also on seedling vigor, pigment, and protein and sugar content of tomato plants as well (Singh et al. 2016). Increased Chl content and maximal sugar accumulation were also recorded at treatment of *Brassica juncea* plants with 5 ppm ZnS NPs (Nayan et al. 2016). Germination of cucumber seeds treated with 1600 mg/L ZnO NPs increased by 10% (de la Rosa 2013).

An experiment performed under field conditions showed that foliar application of ZnO NPs and ZnSO₄ on wheat did not improve the grain yield or quality; however both treatments increased the grain Zn concentration (average increments were 5 and 10 mg/kg for ZnSO₄ and ZnO NPs, respectively), whereby Zn within the grain was always present as Zn phosphate, suggesting that the foliar application of ZnO NPs could be utilized for Zn biofortification (Zhang et al. 2018a). Application of 1500 ppm of ZnO NPs resulted not only in higher germination percentage (80%) and seedling vigor index (1923.20), but it also increased yield of maize by 42% compared to control and by 15% compared to treatment with 2000 ppm of ZnSO₄. Moreover, following treatment with 100 and 400 ppm ZnO NPs, accumulated Zn in grains reached 35.96 ppm and 31.05 ppm, respectively, suggesting successful biofortification with this essential metal (Subbaiah et al. 2016).

Humic acid priming was reported to improve the rice seed germination and seedling growth under ZnO NPs stress to some extent (Sheteiwiy et al. 2017). Growth parameters of two rice cultivars were pronouncedly increased in seed priming with 30% polyethylene glycol (PEG) under ZnO NPs stress, and improvement in the cell structures of leaf and roots was observed as well (Salah et al. 2015).

Green synthesized ZnNPs (8–32 nm; irregular shape) and spherical CuNP (15–30 nm) enhanced the in vitro germination of *Citrus reticulata*, effect of ZnNPs

being more significant (Hussain et al. 2017). Zn–Al layered double hydroxides (ZnAl-LDH) with borate association exhibited controlled-release of Zn and B contents initiating from the anionic exchange of BO_3^{3-} and the transformation of Zn^{2+} from LDH basal plane resulting in improvements in plant growth when used with the NPK fertilizer (Songkhum et al. 2018). Treatment of soybean seeds with Fe, ZnO, Cu, and Co NPs stimulated germination rate and the growth of primary roots and leaves, depending on concentrations of metal NPs used, and an increase of the root mitotic index compared to the control was observed as well (Hoe et al. 2018).

A comprehensive overview related to the beneficial and detrimental aspects of the ZnO NPs exposure toward various terrestrial plants was presented by Pullagurala et al. (2018).

11.2.1.3 Iron and Iron Oxide Nanoparticles

Fe^0 NPs were found to penetrate the peanut seed coats resulting in increased water uptake and stimulating seed germination, and at treatment with 40 and 80 $\mu\text{mol/L}$, they stimulated the plant growth more effectively than ethylenediaminetetraacetate–iron (EDTA-Fe) solution, probably due to the uptake of Fe^0 NPs by the plants (Li et al. 2015a). Priming with low doses of Fe^0 NPs increased root and shoot length, biomass, and photosynthetic pigment content, the highest activities of hydrolytic and antioxidant enzymes, along with root dehydrogenase enzyme, being estimated at a dose of 20 mg/L , and even after 14 days of growth, neither membrane damage nor reduction in proline level and antioxidant enzyme activities were observed (Guha et al. 2018). Combine foliar application of MgNPs and FeNPs solutions to black-eyed pea (*Vigna unguiculata*) resulted in improved photosynthetic efficiency of plants and enhanced uptake of Mg in aboveground plant parts as well as increased seed weight, although reduced yield was observed at treatment with MgNPs alone (Delfani et al. 2014).

Foliar treatment of *Brassica juncea* plants with FeS NPs (4 ppm) solution at the 30th days after sowing showed maximal enhancement in agronomic attributes and higher Fe contents in plant organs, and improved redox status of the treated plants resulted in higher levels of photosynthates, whereby an increase in growth and seed yield was connected also with activation of both Rubisco small and large subunits, glutamine synthetase, and glutamate synthase genes suggesting that at specific growth stage, FeS NPs could activate carbon and nitrogen assimilatory pathways (Rawat et al. 2017).

The foliar application of nanoscale iron oxide on durum wheat plants at a dose 2 g/L was found to be the most effective in increasing Chl a , Chl b , total Chl, protein, Fe, and carbohydrate contents in leaves, as well as grain yield and grain Fe and protein contents (by 38 and 58%, respectively); however these parameters decreased at the higher rate of iron oxide NPs (Ghafari and Razmjoo 2015). Colloidal magnetic NPs of 10.5 nm coated with perchloric acid and applied in form of magnetic fluid (NPs volume fraction of 4.5%) at doses 10–50 $\mu\text{L/L}$ promoted photosynthesis efficacy of maize plants, which was reflected in a small but statistically significant increase of the Chl a /Chl b ratio (Racuciu and Creanga 2007). Superparamagnetic iron oxide NPs (SPIONs) were found to play a crucial role on the enhancement of

Chl content in subapical leaves of soybean; however the photosynthesis efficiency obtained with this treatment was similar to that of conventional growth medium iron chelate (Ghafariyan et al. 2013). Treatment with 0.5 M γ -Fe₂O₃ NPs induced positive changes in the contents of Chl_a, Chl_b, and total carotene in tomato plants and increased the crop yield; treated plants were more resistant to chlorosis (Pavani et al. 2016). The γ -Fe₂O₃ NPs applied at a dose 20 mg/L notably stimulated root elongation by 11.5% and increased germination index and vigor index of maize by 27.2% and 39.6%, respectively; however at higher concentrations, the γ -Fe₂O₃ NPs, which entered plant roots and were mostly situated around the epidermis of root without translocation to shoots, caused oxidative stress exclusively in the roots, and phytotoxic effect was reflected in reduced Chl levels (Li et al. 2016b). Beneficial impact of Fe₂O₃ NPs on root length, plant height, and biomass of peanut (*Arachis hypogaea*) plants by regulating phytohormone contents and antioxidant enzyme activity was observed as well (Rui et al. 2016).

Treatment with 20–100 mg/L γ -Fe₂O₃ NPs increased the Chl contents of watermelon during the duration of exposure lasting 3 weeks, while Chl contents of *Zea mays* exposed to γ -Fe₂O₃ NPs were higher than in control only in the first week of treatment (Hu et al. 2018). Similarly, maize plants exposed to engineered ferrihydrite and hematite NPs showed increased growth and Chl content at doses 1, 2, and 4 g/L (Pariona et al. 2017). With increasing FeO NPs concentration from 0 to 0.75 g/L, Chl contents and the levels of lipids and proteins in soybean plants increased, while in the concentration range 0.75–1.0 g/L FeO NPs reduction of these parameters was observed (Sheykhbaglou et al. 2018). Use of magnetizing irrigation water notably improved growth, pigments, yield, nutritional and amino acids value in seeds, and water-use efficiency of faba bean plants compared to irrigation with normal water and was recommended as appropriate to improve productivity of faba bean under sandy soil conditions (Hozayn et al. 2016).

Based on the differences in root phytohormone production and antioxidant enzyme activity between transgenic and non-transgenic rice plants treated with γ -Fe₂O₃ NP, which were estimated in vivo, it could be suggested that the response of genetically modified crops treated with NPs will differ from that of conventional crops (Gui et al. 2015).

Adding Fe₃O₄ NPs (2000 mg/L) to 1 mM solutions of Pb, Zn, Cd, and Cu notably reduced growth inhibition of wheat seedlings caused by tested heavy metals due to reduction of oxidative stress by increasing the enzyme activity (SOD and POD), and the alleviating effect of Fe₃O₄ NPs was associated with their adsorption capacity of heavy metals (Konate et al. 2017).

In the maize plants fertilized with Fe₃O₄ NPs using half of the recommended dose of Fe in salt preparation (27 vs 54 M), positive effect on morphological features such as height and biomass of plant organs, leaf area, and proline content was observed (Elanchezhian et al. 2017). Maize plants (*Zea mays* L. cv. Merit) grown in calcareous soil foliar-sprayed with Fe₃O₄ NPs at a dose 100 mgFe/g had significantly improved Ca, Fe²⁺, total Fe, and ferritin contents (164%, 200%, 300%, and 200% of the control), whereby enhanced growth of treated maize plants could be attributed, at least in part, to the increased content of ferritin that is decisive in

maintenance of Fe homeostasis and balance of the plant redox system (Jalali et al. 2016). Soaking of *Phaseolus vulgaris* L. seeds in solution of PEG-coated Fe₃O₄ NPs (at 1000 mg Fe/L) did not affect seed germination but increased radicle elongation by 37% what might be related to water uptake enhancement induced by the PEG coating (Duran et al. 2018).

The responses of Fe₃O₄-treated lettuce plants grown in soil and soil bacterial community depended on the applied concentration of Fe₃O₄ NPs. At low concentrations, plant growth stimulation accompanied by the increased abundance of *Xanthomonadales* and the decreased abundance of *Cyanobacteria* and *Sphingobacteria* as well as no significant changes in bacterial alpha diversity indices was observed. Treatment with high doses of Fe₃O₄ NPs inhibited plant growth, decreased the phylogenetic diversity of bacterial community, reduced the abundances of *Xanthomonadales* and *Sphingobacteria*, and increased the proportion of *Cyanobacteria* (Xu et al. 2017).

MnO_x NPs and FeO_x NPs applied at low concentrations (<50 ppm) pronouncedly promoted the growth of lettuce seedlings by 12–54% (Liu et al. 2016). Better germination of maize seeds treated with MgO NPs prepared using aqueous leaf extracts of betel showed better germination, and enhanced plant growth was observed as well, whereby treatment with low MgO NPs concentrations resulted in increased Chl content compared to control suggesting that these NPs could be considered as an alternative source of fertilizers (Jayarambabu et al. 2016).

11.2.1.4 Nickel Nanoparticles

NiNPs (5 nm) at low concentrations (0.01 and 0.1 mg/L) did not affect or stimulated growth of 10-day-aged wheat seedlings and pronouncedly increased the intensity of photosynthesis and transpiration, while at application of 0.01 mg/L NiNPs, also slightly increased content of Chl_a and Chl_b was observed. However, Ni concentration in roots and shoots of NiNPs-treated plants (50.89 ± 1.67 and 14.20 ± 2.38 µg/g d.w., respectively) was considerably higher than in control plants (3.8 ± 0.15 and 0.87 ± 0.025 µg/g d.w.) (Zotikova et al. 2018).

11.2.2 Beneficial Effects of Other Metal- and Metalloid-Based Nanoparticles Stimulating Plant Growth

11.2.2.1 Silver Nanoparticles

In cucumbers exposed to AgNPs at concentrations <200 mg/L, stimulation of root elongation was observed, while at treatment with Ag⁺, stimulation was estimated already at doses <5 mg/L, whereby both radish and wheat plants were more susceptible to the toxicity of AgNPs at the vegetative growth stage than the germination stage (Cui et al. 2014). Golabadi et al. (2015) investigated the effects of AgNPs on flower expression in greenhouse cucumber (*Cucumis sativus* L.) plants. The highest values for the number of male flower, male node, period of male flowering, and the number of male and female flower were obtained at 15-leaf stage. At applying spraying with 200 ppm AgNPs at 15-leaf stage, the highest number of male flower

was produced. Application of AgNPs at concentration 100 mg/L stimulated growth of *Brassica rapa* ssp. *pekinensis* plants, while at concentrations ≥ 250 mg/L, phytotoxic effects were observed (Baskar et al. 2015). Pronouncedly enhanced number of seeds per pod, number of pods per plant, hundred seed weight, biological yield, and green pod yield over control were observed at treatment of *Pisum sativum* seeds and application of foliar spraying with AgNPs (10–100 nm) on pea seedlings using 60 ppm AgNPs (Mehmood and Murtaza 2017). Similarly, using seed soaking and foliage spraying of broad bean with biosynthesized AgNPs (10–100 nm) resulted in improved growth and yield of crops (Rashidi et al. 2016). Priming of maize seeds with 10 ppm AuNPs showed improved promoting emergence percentage, enhanced seedling vigor (threefold over the control), as well as improved physiological and biochemical properties of maize seedlings, whereby Au translocation from seeds into plant vegetative organs was minimized (Mahakham et al. 2016).

Exposure to low AgNPs concentrations (10, 20, 40 ppm) was reported notably to increase the Chl a and carotenoid contents in rice accompanied with enhanced shoot and root growth and biomass of the seedlings what could be connected with AgNPs-induced changes in antioxidative enzyme activities and related gene expression levels, low ROS level, and decreased lipid peroxidation and H $_2$ O $_2$ content (Gupta et al. 2018).

Treatment of chickpea seeds with Ag–CS NPs (20–50 nm; 0.1%, w/v) resulted beside of significant stimulation of seed germination, seedling length, fresh and dry weight also in pronouncedly higher Chl levels and increased activities of enzymes (α - and β -amylase, APX, POD and CAT) in *Cicer arietinum* seedlings (Anusuya and Banu 2016).

The biomass of genetically transformed hairy root cultures of *Cucumis anguria* pronouncedly increased in the presence of AgNPs, and AgNPs-elicited hairy roots produced considerably higher amount of individual phenolic compounds (flavonols, hydroxycinnamic and hydroxybenzoic acids) and total phenolic and flavonoid contents than Ag $^+$ -elicited hairy roots, whereby antioxidant, antimicrobial, and anticancer activities were also notably higher following AgNPs elicitation compared with that observed in Ag $^+$ -elicited hairy roots (Chung et al. 2018).

11.2.2.2 Gold Nanoparticles

An experiment using seeds of a model plant of *Arabidopsis thaliana* showed that treatment with 24 nm AuNPs at a dose 10 μ g/mL resulted in three-fold higher total seed yield compared to control and pronouncedly improved germination rate and vegetative growth, and free radical scavenging activity was observed at application of AuNPs doses 10 and 80 μ g/mL, respectively, whereby microRNAs expression showed correlation with seed germination, growth, and antioxidant potential of plants on AuNPs exposure (Kumar et al. 2013).

Raliya et al. (2016) who delivered various Au nanostructures (30–80 nm) by aerosol application to a watermelon plant found that AuNPs were taken up by the plant through direct penetration and transport through the stomatal opening and translocated from leaf to root by the phloem transport mechanism, whereby the efficacy of translocation expressed by number of particles recovered in root decreased as follows, cube (20,000) > rhombic dodecahedral (15,000) > sphere

(9500) > rod (9000), suggesting improved translocation of low aspect ratio particles. Pronounced stimulation of watermelon root elongation treated with Au nanorods was reported by Wang et al. (2013), although at application of high concentrations, phytotoxic effects connected with oxidative stress were observed.

In hydroponically cultivated seedlings of rice, radish, and pumpkin, the positively charged AuNPs (6–10 nm) were most readily taken up by plant roots, and also when translocation to stems and leaves was found to be more efficient for negatively charged AuNPs, none of the AuNPs accumulated in the shoots of radish and pumpkin plants, while in rice shoots, accumulation of 1.1–2.9 ng/mg AuNPs was estimated (Zhu et al. 2012). Foliar spraying of *Brassica juncea* plants under field conditions with AuNPs (10, 25, 50, and 100 ppm) showed beneficial impact on plant height, stem diameter, number of leaves per plant, number of branches, number of pods, and seed yield and improved the redox status of the treated plants, the dose of 10 ppm being most effective, whereby an increase in reducing sugar as well as total sugar contents was observed up to 25 ppm AuNPs (Arora et al. 2012).

11.2.2.3 TiO₂ Nanoparticles

Foliar spraying of 14-day-old mung bean plants with 10 mg/L TiO₂ NPs caused pronounced improvement in shoot length (17.02%), root length (49.6%), root area (43%), root nodule (67.5%), Chl content (46.4%), and total soluble leaf protein (94%) in plants, and in 6-week-old plants, an increase in activities of enzymes over control was observed, which was 67.3% for acid phosphatase, 72% for alkaline phosphatase, 64% for phytase, and 108.7% for dehydrogenase (Raliya et al. 2015). Hydroponically grown cucumber (*Cucumis sativus*) plants treated with TiO₂ NPs (0–4000 mg/L) pronouncedly increased root length (>300%), and it was found that Ti was transported from the roots to the leaf trichomes, which could be considered as possible sink or excretory system for the Ti (Servin et al. 2012).

Treatment with TiO₂ NPs increased shoot length of rice plants cultivated in phosphorus-deficient soil up to 14.5%, and application of 750 mg/kg of TiO₂ NPs resulted in 2.6-, 2.4-, and 1.3-fold increase of P contents in rice roots, shoots, and grains (Zahra et al. 2017). Low concentrations (0.5–2 g/L) of TiO₂ NPs enhanced the growth of hydroponically cultivated *Solanum lycopersicum* plants approx. by 50%, and treatment with TiO₂ NPs was connected with approx. threefold increase of glutathione synthase and glutathione *S*-transferase expressions in both roots and leaves suggesting significant role of thiols in detoxification of TiO₂ NPs in tomato. Moreover, considerable increase in photosynthetic parameters such as quantum yield, performance index, and total Chl content as well as induced expression of PSI gene was observed in tomato plant exposed to 0.5–2 g/L of TiO₂ NPs with respect to untreated plants, while treatment with 4 g/L TiO₂ NPs had adverse impact on plant growth and photosynthetic performance of plants. It could be mentioned that application of TiO₂ NPs pronouncedly affected distribution of essential elements in tomato plant organs resulting in threefold higher P levels and 25% reduction in Fe contents (Tiwari et al. 2017). In *Brassica napus* L. plants treated with TiO₂ NPs (500, 2500, and 4000 mg/L), improved morphological (root length, plant height, fresh biomass) and physiological (photosynthetic gas exchange, Chl content, nitrate

reductase activity) parameters and enhanced activity of antioxidant enzymes (SOD, POD, CAT) were estimated, whereby intact and typical grana and stroma in thylakoid membranes of chloroplast suggested that treatment with TiO₂ NPs did not induce the stressful environment within chloroplast (Li et al. 2015b).

Application of nano-anatase TiO₂ increased the activity of Rubisco activase also accompanied by conformational changes what resulted in strong stimulation of Rubisco carboxylation and the high rate of photosynthesis and was reflected in improved growth of *Spinacia oleracea* plants. Moreover, at treatment with nano-anatase TiO₂, Chl content was 17-fold higher, and photosynthetic rate showed a 29% increase compared to control (Gao et al. 2008). Nano-anatase TiO₂ markedly improved whole-chain electron transport, photoreduction activity of PSII, and O₂-evolving and photophosphorylation activity of spinach chloroplasts under visible light and UV light illumination. Moreover, nano-anatase h⁺, which photogenerated electron holes, captured an electron from water, which accelerated water photolysis and O₂ evolution (Lei et al. 2007). Nano-anatase TiO₂ application was found to modify PSII microenvironment and increase absorbance for visible light, improve energy transfer among amino acids within PSII protein complex, and accelerate energy transport from tyrosine residue to Chl_a resulting in enhanced photochemical activity of PSII and oxygen-evolving rate in spinach (Su et al. 2007). According to Hong et al. (2005), nano-anatase TiO₂ might bind to the PSI reaction center complex and intensify the function of the PSI electron donor, although it does not change the configuration of the PSI reaction center complex.

TiO₂ NPs applied at a dose of 10 ppm significantly reduced the mean germination time of wheat seeds to 0.89 days compared to control (1.35 days), and treatment with 2 and 10 ppm of bulk TiO₂ and TiO₂ NPs as well stimulated shoot and seedling lengths, effects of TiO₂ NPs being more pronounced; however treatments with high TiO₂ NPs doses caused inhibitory effects (Feizi et al. 2012). Although germination of *Triticum aestivum* was not affected by TiO₂ NP exposure (5, 50, and 150 mg/L), enhanced seedling shoot length at 3rd day was estimated, while at 20th day, it was reduced, whereby TiO₂ NPs phytotoxicity was more severe after longer exposure periods and higher applied doses, causing more severe damage in shoots than in roots (Silva et al. 2017). Exposure of wheat and rapeseed plantlets to TiO₂ NPs (14 nm or 25 nm anatase) in hydroponics conditions induced increased root elongation but did not affect germination, evapotranspiration, and plant biomass. Both TiO₂ NPs were accumulated in plantlets upon root exposure, Ti content being higher in rapeseed than in wheat, but TiO₂ NPs were able to accumulate in plantlets also upon leaf exposure (Larue et al. 2012). While application of 100 mg/L TiO₂ NPs and wastewater significantly inhibited maize seed germination and seedling growth and caused accumulation of phenolics in maize plants, treatment with 25 mg/L resulted in considerable increase of shoot fresh weight, shoot dry weight, root fresh weight, root dry weight, root area, and Chl_a, Ch, and carotenoid content, and also the adverse effects caused by wastewater on growth of maize plants were pronouncedly improved in the presence of this TiO₂ NPs concentration (Yaqoob et al. 2018). In maize plants sprayed with 0.01% and 0.03% TiO₂ NPs at the reproductive stage (appearance of male and female flowers), considerable increase of Chl_a Chl_b,

total Chl ($a + b$), Chl a /Chl b , carotenoid, and anthocyanin content was observed (Morteza et al. 2013). In wheat plants grown in soil spiked with 60 mg/kg TiO₂ NPs, Chl content increased by 32.3% compared to control; however at higher TiO₂ NPs concentration (100 mg/kg), a lower Chl content by 11.1% was estimated (Rafique et al. 2018), while exogenous application of TiO₂ NPs (100–800 mg/L) to Chainat 1 rice cultivar did not affect photosynthetic pigments Chl a , Chl b , and carotenoids (Samart et al. 2018). Spraying of *Phaseolus vulgaris* L. plants with TiO₂ NPs showed beneficial impact on Cha and seed protein content, biological yield, grain weight, and grain yield, the most appropriate concentrations varied in the range from 0.02% to 0.05% and depended on the stage of plant growth in that spraying was applied (rapid vegetative growth, flowering and pod fill), and at foliar application, the TiO₂ NPs can reduce the effects of photo-oxidative stress and prevent the chloroplast destruction and Chl degradation of leaf tissue (Ebrahimi et al. 2016).

11.2.2.4 CeO₂ Nanoparticles

Treatment of barley plants with 125 mg CeO₂/kg soil resulted in a 331% increase in shoot biomass compared with the control, while application of a double dose caused an increase in grain Ce accumulation (by 294%) with concurrent notable increases in P, K, Ca, Mg, S, Fe, Zn, Cu, and Al as well as enhanced methionine, aspartic acid, threonine, tyrosine, arginine, and linolenic acid contents in the grains (Rico et al. 2015).

CeO₂ NPs (25 nm) at a dose of 50 mg/kg soil enhanced the fresh biomass accumulation of radish plants, root expansion being 2.2-fold higher compared to control, and relative Chl content was enhanced by 12.5, 12.9, and 12.2% when compared to control on the 40th day of cultivation in *Raphanus sativus* seedlings cultivated in soil amended with 10, 50, and 100 mg/kg CeO₂ NPs (<25 nm) (Gui et al. 2017).

Coriandrum sativum L. plants grown in soil amended with 125 mg/kg CeO₂ NPs produced longer roots, pronouncedly increased CAT activity in shoots and APX in roots, and changed the chemical environment of carbohydrates in cilantro shoots suggesting changed nutritional properties of cilantro by CeO₂ NPs (Morales et al. 2013). CeO₂ NPs at doses up to 4000 mg/L stimulated shoot elongation in maize, cucumber, and tomato, while root growth was promoted only in cucumber and maize (Lopez-Moreno et al. 2010).

11.2.2.5 Al₂O₃ Nanoparticles

Exposure of model plant *Arabidopsis thaliana* to 98 μM Al₂O₃ NPs stimulated root weight and length by 48% and 39%, respectively, had no adverse effect on photosynthesis and plant growth, and did not induce lipid peroxidation. Favorable impact of Al₂O₃ NPs was connected with an increase in the transcription of several genes involved in root growth as well as in root nutrient uptake (e.g., upregulation of the root hair-specific gene family and root development genes) (Jin et al. 2017). Similarly, low concentrations of Al₂O₃ NPs stimulated growth of *Brassica oleracea* var. *capitata* seedlings and also enhanced pigment, sugar, and protein contents of cabbage seedlings and induced activities of antioxidant enzymes (SOD, CAT, putidaredoxin), while higher concentrations exhibited negative effects. Consequently it

could be assumed that at lower Al_2O_3 NPs concentration, the metabolic processes in cabbage were supported resulting in attenuation of toxic effects of Al^{3+} ions (Amist et al. 2017). In contrast to Al^{3+} ions, the Al_2O_3 NPs did not affect adversely the growth and did not induce oxidative stress in *Vigna radiata* seedlings, and due to adsorption/restriction of Al_2O_3 NPs on root surface, translocation of Al in exposed seedlings was low and Al in shoots was not detected (Shabnam and Kim 2018).

High abundance of proteins involved in oxidation–reduction, stress signaling, and hormonal pathways related to growth and development in soybean plants exposed to Al_2O_3 NPs stress estimated using proteomics could be responsible for optimum growth of Al_2O_3 NPs-stressed plants (Hossain et al. 2016).

11.2.2.6 Selenium Nanoparticles

Selenium in proper concentration is beneficial for the health of humans and animals, and it is supplied to the human organism with food; however due to low level of Se transfer from soil to the food chain, the agronomic biofortification of Se is necessary. As plants are the main source of this element, it is important to increase its levels in plants. Se at low concentrations acts as an antioxidant and through its antioxidative mechanism can serve to counter abiotic stresses. As excess of Se can be phytotoxic causing adverse effects such as inhibition of plant growth, wilting and drying of leaves, reduced protein synthesis, and death of immature plants, the use of nanomaterials in fertilization of plants with Se could be advantageous (Brodowska et al. 2016). Production, biological effects, and use of SeNPs in agroecosystems were summarized by El-Ramady et al. (2014).

Anion-responsive carbon nanosystem fabricated using polyethylenimine modified hollow/mesoporous carbon NPs, in which selenate could be effectively loaded, was reported to be suitable for controlling Se fertilizer release and improving Se utilization efficiency in vegetables (Zhang et al. 2018b).

SeNPs at concentrations 265–530 μM significantly stimulated the organogenesis and the growth of root system (approx. by 40%) by tobacco callus cultures in contrast to selenate, which showed inhibitory effects at the same dose. Moreover, using medium supplemented with 530 μM SeNPs, the roots of regenerated plantlets accumulated even $2,947 \pm 99$ mg Se/kg d.w. (Domokos-Szabolcsy et al. 2012). Se enrichment in perennial onion plants *Allium nutans* L., *A. schoenoprasum* L., and *A. obliquum* L. after spraying with SeO_4^{2-} , SeNPs, and SeO_3^{2-} containing the same Se concentration (2.34 mg Se/L or 32 μg Se per plant) was observed and the ratio $\text{Se}_{\text{leaves}}/\text{Se}_{\text{roots}}$ (indicator of Se migration intensity) decreased in the following order $\text{Se(VI)} > \text{SeNPs (Se(0))} > \text{Se(IV)}$. Total Se content in leaves of perennial onions as a result of foliar fortification with SeNPs, Se(IV), and Se(VI) was 720, 410, and 1085 $\mu\text{g/kg}$ d.w. in *A. nutans*; 1109, 565, and 2169 $\mu\text{g/kg}$ d.w. for *A. schoenoprasum*; and 1108, 267, and 1215 $\mu\text{g/kg}$ d.w. for *A. obliquum*, while in control plants, it was only 82, 91, and 153 $\mu\text{g/kg}$ d.w. (Golubkina et al. 2012). Fortification of Chinese cabbage with Se using a nutrient containing SeNPs was described by Bi et al. (2010).

Spherical chitooligosaccharide–Se NPs with average particle size 100 nm and weak positive charge on the surface when used in the booting stage of rice seedlings

were found to enhance rice production by 8–15%, total antioxidant capacity by 30–60%, and Se content by 3–10-fold suggesting that they could be used as plant nutrient regulator. The ability of these NPs to release Se slowly, especially in plant, contributes to increasing the effect of enrichment and stability in the rice endosperm (Tong et al. 2008). Stimulation of germination of wheat seeds using treatment of water-soluble composition of SeNPs in sodium alginate with concentration 1.0–3.0 mg/L (by Se) was patented by Jurkova and Omelchenko (2016).

11.2.2.7 SiO₂ Nanoparticles

Beneficial effects on morphological, physiological, and biochemical characteristics of plants *Hyssopus officinalis* L. and *Nigella sativa* L. and field crops *Zea mays* L. and *Phaseolus vulgaris* L. were observed at treatment with 400 mg/L SiO₂ NPs (Sharifi-Rad et al. 2016). Treatment of wheat plants with 500 and 1000 mg/L of mesoporous SiO₂ NPs caused enhancement of seed germination and resulted in increased plant biomass, total protein and Chl content, as well as photosynthetic activity of seedlings; oxidative stress or cell membrane damage was not observed even at 2000 mg/L SiO₂ NPs (Sun et al. 2016). SiO₂ NPs applied at concentrations 25, 50, and 100 mg/L increased fresh and dry weights, length and number of branches, and Chl in explants of apple rootstock MM106 in tissue culture, concentration of 100 mg/L being the most effective (Avestan et al. 2016). In maize plants grown in soil, an amendment of SiO₂ NPs to soil at a dose of 15 kg/ha positively impacted besides Chl content also proteins and phenols (Suriyaprabha et al. 2012). Application of 8 g/L SiO₂ NPs (12 nm) significantly improved seed germination percentage, mean germination time, seed germination index, seed vigor index, fresh weight, and dry weight of tomato seedlings (Siddiqui and Al-Whaibi 2014). Pre-sowing of sunflower seeds in low concentration SiO₂ NPs solutions (0.2 and 0.4 mM) considerably reduced days needed to 50% germination and mean germination time and improved root length, mean daily germination, seedling vigor index, and final germination percentage suggesting beneficial effect of SiO₂ NPs nanoprimering on *Helianthus annuus* plants (Janmohammadi and Sabaghnia 2015).

Potato (*Solanum tuberosum* var. Agria) plants treated with four different silicon compounds (nanosilica, sodium silicate, nanoclay, and bentonite) in greenhouse conditions using doses 1000 and 2000 ppm, respectively, enhanced all root characteristics, and application of 1000 ppm bentonite enhanced leaf dry weight up to 18%, and increased stem diameter up to 17% was observed after treatment with 1000 ppm of nanoclay and bentonite. Moreover, treatment with Si improved mini-tuber quality characteristics as well (Soltani et al. 2018). Co-application of NPK fertilizer in combination with NanoChisil (fertilizer CS NPs and SiO₂ NPs) and NPK fertilizer with nanosilica (fertilizer SiO₂ NPs) increased plant height, number of leaves, wet weight, and dry weight of *Zea mays* L. plants, the best results being observed for the ratio 25% NanoChisil: 75% NPK (Pertaminingsih et al. 2018).

The results of seed germination and root elongation experiments showed that Al₂O₃ and TiO₂ NPs notably reduced the germination percentage of maize seeds and inhibited root elongation, while SiO₂ NPs and microparticles (MPs) enhanced them. The tested metal oxide NPs penetrated seeds showing greater seed uptake compared

to MPs, which decreased in the order $\text{SiO}_2 > \text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{ZrO}_2$, whereby ZrO_2 NPs and MPs did not affect germination and root growth (Karunakaran et al. 2016).

Foliar and soil application of nanosized Si and Zn to rice plants in a field experiment resulted in considerably higher yields compared to the control, although yields did not differ significantly between the fertilized treatments, whereby co-application of nanosized Si and Zn increased the grain and straw yields, yield components, and Si, Zn, and N concentrations in rice grain and straw (Kheyri et al. 2018).

11.3 Coating

The coating process of nanomaterials is reflected in modified surface properties, and thus, a negative or positive charge on the surface obtained due to coating agents affects interaction of nanomaterials with the environment and could increase or decrease their impact on plants. Metal-based nanomaterials are usually coated with natural organic compounds including CS, dextran, alginate, or citric acid (Lopez-Moreno et al. 2018).

Zou et al. (2017) compared the effects of Ag^+ ions as well as citrate- and adenosine triphosphate (ATP)-coated AgNPs on *Wolffia globosa* and found that Ag^+ and ATP-coated AgNPs inhibited Hill reaction activity, reduced soluble proteins, and caused depletion of sugars; considerable increase of SOD and POD activity as well as inhibition of P and K uptake and stimulation of Fe and Cu was observed as well. On the other hand, in the presence of the citrate-coated AgNPs, Hill reaction activity was not affected; however accumulation of sugars and stimulation of Cu uptake were estimated. Based on these findings, it was assumed that at exposure to ATP-coated AgNPs, ATP would act as an exogenous energy source of plant metabolisms, while at treatment with citrate-coated AgNPs, citrate could serve as the substrate for the tricarboxylic acid cycle, and accumulated sugar may stimulate pentose phosphate pathways.

Biosynthesized AgNPs capped with phytochemicals present in the plant extract of kaffir lime leaf (5 and 10 ppm) pronouncedly improved germination performance of aged rice seeds and seedling vigor compared to control or conventional hydropriming. These AgNPs enhanced α -amylase activity, resulting in higher soluble sugar content for supporting seedling growth, and promoted the upregulation of aquaporin genes in germinating seeds, while higher ROS production was observed in seeds treated with AgNPs nanopriming. According to researchers, nanopriming-induced seed germination could be connected with creation of nanopores for improved water uptake, rebooting ROS/antioxidant systems in seeds, and generation of OH radicals for cell wall loosening, and AgNPs could serve as nanocatalyst for fastening starch hydrolysis (Mahakham et al. 2017).

Phytochemical-capped AuNPs prepared using rhizome extract of galanga plant (*Alpinia galanga*) and applied at concentration 5 ppm as nanopriming agent to activate the germination and early seedling growth of maize aged seeds exhibited the best effects on promoting emergence percentage (83%) compared to unprimed control (43%) and hydroprimed groups (56%) and enhanced seedling vigor index by

threefold over the control. Although the AuNPs were found to be internalized into seeds, they were not present in both shoots and roots, suggesting that the Au translocation from seeds into plant vegetative organs practically did not occur (Mahakham et al. 2016). Citrate- and tannate-coated AuNPs (10, 30, and 50 nm) bioaccumulated in hydroponically cultivated *Nicotiana tabacum* L. var. Xanthi nc., but no bioaccumulation of these NPs was observed in *Triticum aestivum* plants (Judy et al. 2012).

Investigation of phytotoxicity of CuO NPs to rice seedlings in the presence of humic acid (HA) showed that HA coatings on NPs surfaces, which resulted in enhanced electrostatic and steric repulsion between the CuO NPs and the plant cell wall/membrane, thus reducing contact between NPs and plant, were reflected in reduced oxidative damage in plant cells (Peng et al. 2015).

Investigation of the effect of bare and PEG-coated Fe₃O₄ NPs on the germination and seedling development of *Phaseolus vulgaris* L. showed that seed soaking in the solution of PEG-coated Fe₃O₄ NPs (at 1000 mg Fe/L) increased radicle elongation by approx. 37% (which could be connected with the enhancement of water uptake induced by the PEG), while ionic iron forms Fe²⁺/Fe³⁺ and bare Fe₃O₄ NPs showed growth-inhibiting effect. Moreover, treatment with PEG-coated Fe₃O₄ was found to be the least harmful to α -amylase (Duran et al. 2018). In sunflower seedlings treated with sodium oleate-coated magnetite and cobalt ferrite NPs, inhibition of Chl biosynthesis was observed, while zinc ferrite NPs with the same coating enhanced the Chl and carotene levels at some concentrations, although diminished Chl ratio estimated at exposure to all three types of magnetic NPs suggested slight adverse effect on the light harvesting complex II (LHC II) from the chloroplast membranes reflected in impaired photosynthesis efficiency (Ursache-Oprisan et al. 2010).

Investigation of transgenerational effects of TiO₂ NPs in basil plants performed by Tan et al. (2018) was focused on the evaluation of the impacts of successive exposure to TiO₂ NPs with different surface properties, whereby seeds from plants exposed or re-exposed to pristine, hydrophobic, or hydrophilic TiO₂ NPs were cultivated for 65 days in soil unamended or amended with 750 mg/kg of the respective particles. The researchers found that sequential exposure to hydrophobic or hydrophilic TiO₂ NPs resulted in more adverse effects on photosynthesis but in positive effects on plant growth, compared to pristine TiO₂ NPs.

Different responses of hydroponically cultivated wheat seedlings exposed to 20 mg/L CeO₂ NPs (approx. 4 nm) functionalized with positively or negatively charged or neutral dextran coating were observed. Independently of CeO₂ NPs surface charge, in both roots and leaves a reduction (15–20%) from Ce(IV) to Ce(III) was observed; however positively charged NPs adhered to negatively charged cell walls most strongly. On the other hand, treatment with uncharged and negatively charged CeO₂ NPs resulted in higher Ce leaf concentrations compared with positively charged ones. While in plants treated with negatively charged NPs allocation of Ce was estimated mostly in the leaf veins, in plants exposed to uncharged CeO₂ NPs Ce was found in clusters in the nonvascular leaf tissue suggesting that NP coatings can be designed to target NPs to specific parts of plants (Spielman-Sun et al. 2017). In the soil poor in organic matter, the organic citrate coating of CeO₂ NPs significantly enhanced the phytoavailability of the Ce by forming smaller aggregates, thereby facilitating the transport of NPs to the roots of tomato (Layet et al.

2017). CeO₂ NPs coated with citrate acid (CA) at 1:7 ratio applied at a dose of 200 mg/L to radish (*Raphanus sativus*) produced significantly more root biomass, increased water content, and reduced the Ce uptake by 94% compared to bare NPs suggesting that this coating decreased CeO₂ NPs toxicity to plants (Trujillo-Reyes et al. 2013). Both uncoated and citrate acid (CA)-coated CeO₂ NPs applied at a dose of 500 mg/kg increased shoot length of tomato plants (approx. by 9 and 13%, respectively) and did not affect the homeostasis of nutrient elements in roots, stems, and leaves or CAT and APX in leaves, and pronounced increase of total Chl, Chla, and Chlb was observed only at exposure to 250 mg/kg CA-coated CeO₂ NPs. The surface coating reduced Ce uptake by roots but did not affect its translocation to the aboveground organs (Barrios et al. 2016). Coating of CeO₂ NPs with citrate reduced the impact on microbial enzymatic activities but triggered variability in the bacterial community structure near the rapeseed roots (Hamidat et al. 2016). The soil moisture content affected the physiological impact of positively charged CeO₂ NPs and negatively charged CeO₂ NPs with polyvinylpyrrolidone (PVP) coating on soybean plants whereby positive effect on plant photosynthesis was observed at the moisture content >70% (Cao et al. 2018). Treatment of soybean seedlings with both types of CeO₂ NPs using concentration 100 mg/kg resulted in stimulation of plant growth and photosynthesis rate (by 54% for bare and 36% for PVP-coated CeO₂ NPs) and improved Rubisco activity was estimated as well. On the other hand, higher concentration of CeO₂ NPs (500 mg/kg) inhibited net photosynthesis rate, and further increasing of CeO₂ NPs concentration resulted in inhibition of Rubisco activity (Cao et al. 2017). Alginate surface coating increased the uptake of Ce in *Zea mays* plants treated with CeO₂ NPs (Zhao et al. 2012).

Superhydrophobic surface on controlled-release fertilizers that was prepared using bio-based polyurethane derived from liquefied wheat straw modified with organosilicon and SiO₂ NPs to increase the nanoscale surface roughness and reduce the surface energy making it in such way superhydrophobic improved their controlled-release characteristics (Zhang et al. 2017).

11.4 Beneficial Effects of Metal- and Metalloid-Based Nanoparticles on Plants Under Abiotic Stress

Plants as sessile organisms are exposed to different abiotic stresses, i.e., environmental conditions that reduce growth and yield below optimum levels. Drought, heat, cold or chilling, flooding/waterlogging, salinity, UV light, toxic metal pollutants, and high soil acidity are abiotic stresses which represent major threat to food security due to the constant changes of climate and deterioration of environment caused by anthropogenic activities (e.g., Macedo 2012; Calanca 2017; Sha Valli Khan et al. 2018). However, abiotic stresses could also affect the amount and composition of secondary metabolites in crops and modify their nutritional value and health benefits (e.g., Szabó et al. 2003; Ramakrishna and Ravishankar 2011; Javed et al. 2017a, b; Masarovičová et al. 2019). Abiotic stress tolerance in plants is a complex process, involving many different metabolic pathways and cellular and molecular components, and improving crop tolerance is a major goal of crop

improvement programs (e.g., Shanker and Venkateswarlu 2011; Onaga and Wydra 2016; Bechtold and Field 2018; Sha Valli Khan et al. 2018). Recently it was shown that also metal and metalloid NPs could be successfully used to alleviate detrimental impact of abiotic stresses on crops (e.g., Khan et al. 2017).

11.4.1 Drought

Drought is a physiological form of water deficit, where soil water available to the plant is inadequate, which adversely affects the plant's metabolism and can significantly reduce crop productivity. Water stress induces a decrease in leaf water potential and in stomatal opening resulting in the downregulation of photosynthesis-related genes and reduced availability of CO₂, loss of turgor, and changes in membrane fluidity and composition, solute concentration as well as protein–protein and protein–lipid interactions. Endogenous abscisic acid (ABA), which is rapidly produced during drought, triggers a cascade of physiological responses, including stomatal closure, which is regulated by a signal transduction network. During water stress, enhanced ABA accumulation in plants is observed, which plays also an important role in the tolerance against dehydration. In response to a water deficit stress, ion and water transport systems across membranes function to control turgor pressure changes in guard cells and stimulate stomatal closure (Chaves et al. 2003; Osakabe et al. 2014; Kumar et al. 2018). Plants could adapt to water by morphological, physiological, and biochemical responses, e.g., reduced leaf area, efficient rooting system, reduced transpiration, better water-use efficiency, stomatal activity, and accumulation of proline, polyamine, and trehalose (Haworth et al. 2013; Kumar et al. 2018). A comprehensive chapter focused on plant drought stress, its effects on plant's resistance mechanisms, and management strategies to cope with this global challenge was presented by Kumar et al. (2018). Findings related to the mechanisms of gene regulation and the roles of protective metabolites in drought stress tolerance and the progress in genetic or metabolic engineering for enhanced drought tolerance in crop plants were summarized by Valliyodan and Nguyen (2006).

A decrease of adverse effects of drought upon plants of steppe ecotype *Acveduc* at application of CuNPs and ZnNPs was manifested mainly in enhanced activity of antioxidative enzymes reducing the level of accumulation of thiobarbituric acid-reactive compounds, stabilizing the content of photosynthetic pigments, and increasing relative water content (RWC) in leaves, while in the forest-steppe wheat (*Stolichna*) ecotype, the degree of improvement of these characteristics was lower (Taran et al. 2017). Using foliar application of ZnNPs under drought stress produced by interrupted irrigation during flowering stage of wheat, it was found that treatment with ZnNPs had beneficial effect on pronouncedly reduced grain yield and its components, plant height, RWC, and Chl content caused by water deficit stress, whereby application of 2 g/L ZnNPs in flowering stage of plants was found to be most efficient (Ghassemi and Farahvash 2018).

Besides application of salicylic acid (SA) that could compensate adverse effects of drought stress on strawberry plantlets and improve their growth parameters under

in vitro culture, the efficiency of tissue culture and in vitro culture of strawberries was found to be improved also by application of iron NPs suggesting that combined treatment with SA and iron NPs could ensure higher quantity and quality in the in vitro culture of strawberries and could be used for adapting strawberry plants to drought before transplanting them in the field (Mozafari et al. 2018).

Under drought condition corresponding to 50% field moisture capacity (causing a decrease of soybean shoot growth by 27% and grain yield by 54%), application of nanoscale ZnO, B₂O₃, and CuO and their salts (ZnSO₄·7H₂O, H₃BO₃, and CuSO₄·5H₂O) to soil or foliar application 3 weeks after seed germination of soybean reduced drought effects by increasing shoot growth by 33% and grain yield by 36%, and a pronounced increase in levels of N, K, Zn, B, and Cu in shoots and grains was estimated as well. At foliar application, the effects of NPs and salts were similar, but application of salts to soil mitigated drought stress more effectively than foliar application (Dimkpa et al. 2017b). Nanomaghemite (NMH; Fe₂O₃, γ-Fe₂O₃) addition to soil stimulated the growth of sunflower primarily due to the insolubilization of pore water Zn in the soil, thus reducing its availability to the plants, and in contrast to plants growing on soil without NMH amendment, during the water stress, it did not cause an increase in the accumulation of proline or total amino acids in the plants. Consequently, NMH could be a useful soil amendment during phytoremediation procedures, since it can immobilize trace elements in the soil without disrupting the plant water balance (Martinez-Fernandez et al. 2015).

Foliar pretreatment of cotton plants with TiO₂ and SiO₂ NPs increased the pigment content, total soluble sugars, total phenolics, total soluble proteins, total free amino acids, proline content, total reducing power, total antioxidant capacity, and antioxidant enzyme activities and caused enhancement of yield characteristics, which were reduced by drought stress, concentrations 50 ppm of TiO₂ and 3200 ppm of SiO₂ being the most effective (Shallan et al. 2016). Water stress induced by PEG-6000 reduced germination percentage and germination rate (GR) of tomato (*Lycopersicon esculentum* Mill cv. 'Falcato') as concentration increased from -2 to -8 bars, while treatment with SiNPs at a dose of 1 or 2 mM, respectively, was able to improve GR under PEG-induced stress at -4 and -8 bars (Haghighi et al. 2013). Silicon application was reported to be useful in the improvement of the drought tolerance of sorghum through the enhancement of water uptake ability (Ahmed et al. 2011).

Foliar-sprayed CeO₂ NPs (10 mg/L) considerably reduced leaf O₂^{•-} (41%) and H₂O₂ (36%) levels and decreased cell membrane lipid peroxidation (37%) in *Sorghum bicolor* (L.) Moench plants under drought imposed at the booting stage by withholding water for 21 days. Moreover, treatment with CeO₂ NPs caused an increase in leaf carbon assimilation rates (38%), pollen germination (31%), and seed yield per plant (31%) in drought-stressed plants compared to controls suggesting protection of sorghum plants from oxidative damage resulting in higher grain yield (Djanaguiraman et al. 2018a).

11.4.2 Flooding and Waterlogging

Flooding may occur as an overflow of water from waterbodies (rivers, lakes, or ocean), due to an accumulation of rainwater on saturated ground in an areal flood or when the flow rate exceeds the capacity of the river channel (Meteorology glossary 2012). In plants growing in areas prone to flooding, the roots cannot respire due to excess water in the soil profile resulting in insufficient oxygen in the pore space of plant roots. Thus, maintenance of a functional root system upon flooding is essential, because roots are vital for plant function (Sauter 2013).

Treatment of soybean under flooding stress with AgNPs was found to have beneficial effect on plant growth. In early-stage soybean plants exposed to flooding that were treated with 15 nm AgNPs at 2 ppm, enhanced growth and differentially changed 107 root proteins predominantly associated with stress, signaling, and cell metabolism were estimated. Time-dependent increase of abundances of glyoxalase II 3 and fermentation-related proteins under flooding stress decreased at addition of AgNPs, and alcohol dehydrogenase 1 and pyruvate decarboxylase 2 genes, upregulated under flooding stress, were downregulated in response to AgNPs. Moreover, in AgNPs-treated plants lower amount of cytotoxic by-products of glycolysis was estimated. Better growth performance of AgNPs-treated soybean plants under flooding stress could be connected with reduced oxygen deprivation stress (Mustafa et al. 2015). Proteomic analysis of soybean root exposed to varying sizes of silver nanoparticles under flooding stress showed that different sizes of AgNPs might affect the soybean growth under flooding by regulating the proteins related to amino acid synthesis and wax formation. Treatment with AgNPs of 15 nm promoted soybean growth under flooding compared to 2 and 50–80 nm AgNPs, and exposure to 15 nm AgNPs also resulted in the increase of ribosomal proteins, while these decreased in the presence of other NP sizes. Based on *in silico* protein–protein interaction, β -ketoacyl reductase 1 as the most interacted protein under AgNPs of 15 nm (while least interacted under other sizes) was upregulated in the presence of 15 nm AgNPs, and its enzyme activity was decreased (Mustafa et al. 2016).

In the waterlogging environment, when roots cannot respire due to excess water in the soil profile, the deposition of iron plaque on plant roots affects the fate of metal-based NPs. For example, at treatment with 100 mg/L CuO NPs, iron plaque dramatically reduced the Cu contents in rice roots and shoots by 89% and 78%, respectively, compared to control iron plaque; however lower percentage of CuO but higher proportion of Cu(I) in shoots was estimated in plants exposed to CuO NPs with the formation of iron plaque. From low amounts of CuO NPs absorbed by roots via root hairs or lateral roots, which were translocated to shoots and in leaf veins of rice plants with iron plaque, >90% of total Cu(II) was reduced to Cu(I)–cysteine and Cu₂O (Peng et al. 2018). However, treatment of flooded paddy soil with CuO and TiO₂ NPs (100, 500, and 1000 mg/kg soil) adversely affected soil microbes and reduced the composition and diversity of the paddy soil microbial community, toxic effect of CuO NPs being more strong, whereby CuO NPs may also indirectly affect soil microbes by changing nutrient bioavailability (Xu et al. 2015).

Proteomic technique was used to investigate the response of soybean plants under flooding exposed to various sizes (30–60 nm) of Al_2O_3 NPs. In the presence of Al_2O_3 NPs in stressed plants increased length of the root, including hypocotyl and suppression of proteins related to glycolysis was observed, whereby the scavenging activity of cells was mediated by regulating the ascorbate/glutathione pathway, and mitochondrion was found to be the target organelle of Al_2O_3 NPs under flooding stress conditions. Al_2O_3 NPs of various sizes affected mitochondrial proteins under flooding stress by regulating membrane permeability and tricarboxylic acid cycle activity (Mustafa and Komatsu 2016). Quantitative proteomic analysis of post-flooding recovery in soybean roots exposed to Al_2O_3 NPs showed that a total of 211 common proteins were changed in abundance during the recovery period after treatment without or with Al_2O_3 NPs. These proteins were related to protein synthesis, stress, cell wall, and signaling, and it was found that *S*-adenosyl-L-methionine-dependent methyltransferases and enolase might be involved in mediating recovery responses by Al_2O_3 NPs. It could be also noted that treatment with 50 ppm Al_2O_3 NPs enhanced survival percentage of seedlings, which showed also improved seedling weight and weight/length of root including hypocotyl during the period of recovery (Yasmeen et al. 2016).

11.4.3 Salt Stress

Soil salinity is established as one of the major environmental problems decreasing crop productivity worldwide, thereby threatening sustainable agriculture. Maize, rice, and wheat having a prominent role in feeding the world's population are sensitive to salinity stress, and their growth and production are significantly retarded by salinization effects (Majeed et al. 2018). Excess salt reduces water potential and causes ion imbalance or disturbances in ion homeostasis and toxicity and adversely affects germination, growth, photosynthetic pigments and photosynthesis, water relation, nutrient imbalance, oxidative stress, and crop yield. Due to the osmotic or water deficit, salinity reduces the ability of the plant to take up water due to presence of salt in soil solution, which results in reduced plant growth, and too high salt concentration in the transpiration stream causing injury to cells in the transpiring leaves contributes to plant growth reductions as well (Parihar et al. 2015). Under salt stress, plants accumulate osmotic adjustment substances and synthesize proline, soluble sugars, glycine, betaine, and other osmolytes to promote osmotic balance at the cellular level. Under high salinity stress, the increase of ROS in the plant leads to lipid peroxidation in the cell membrane (Liang et al. 2018). Strategies to mitigate the salt stress effects on photosynthetic apparatus and productivity of crop plants were reviewed by Mbarki et al. (2018).

Investigation of the impact of 5 mmol/kg of NaCl, KCl, or CaCl_2 and root exudates on transformation and changes of the bioactivity of CuO and ZnO NPs on wheat showed that phytotoxic effect of ZnO NPs reflected in the reduction in shoot and root elongation and lateral root induction was attenuated by the used salts, while NaCl and KCl promoted Zn loading into shoots, in contrast to CaCl_2 , which reduced

it. On the other hand, the effect of tested salts on growth and loading of CuO NPs-treated plants was comparable suggesting major interaction of the plant with CuO rather than Cu ions (Stewart et al. 2015). Salinity stress (25 and 50 mM NaCl) decreased the Chl a , Chl b , and total Chl, photochemical efficiency of PSII, and yield of wheat, while electrical conductivity, soluble sugars, proline content, and activities of CAT, POD, and PPO enzymes showed an increase. Treatment of plants grown at 50 mM NaCl with nanoscale Zn–Fe oxide increased grain yield approx. by 17.40% compared to control plants without NPs application (Babaei et al. 2017). In five tomato cultivars investigated in a callus culture exposed to NaCl, the relative callus growth rate inhibition was observed at 3.0 g/L NaCl, which strongly increased at 6.0 g/L NaCl, and Na content as well as SOD and GPX activities considerably increased with increasing exposure to NaCl. These adverse effects were found to be mitigated by ZnO NPs application, concentration of 15 mg/L being more effective than that of 30 mg/L, although degrees of tolerance to salinity in the presence of ZnO NPs between studied cultivars differed from each other (Alharby et al. 2016).

Priming of rice seeds with 10 mg/L AgNPs (20 nm diameter) resulted in notable increase of root growth when seedlings were cultivated in a nutrient solution containing 85 mM NaCl (Thuesombat et al. 2016). Yadu et al. (2018) reported that treatment with AgNPs could ameliorate also fluoride-induced oxidative injuries in *Cajanus cajan* manifested by accumulations of ROS, MDA and oxidized glutathione, gene expression of NADPH oxidase, and activity of lipoxygenase. A tolerance against fluoride toxicity in *C. cajan* at application of AgNPs was achieved via enhancing the levels of proline, total and reduced glutathione, glyoxalase I and II activities, and expression of pyrroline-5-carboxylate synthetase gene. Hernandez-Hernandez et al. (2018a) reported that CuNPs absorbed on chitosan–polyvinyl alcohol (CS-PVA) hydrogel could activate the enzymatic defense of tomato plants and increase their content of vitamin C and lycopene, respectively, as well and induce mechanisms of tolerance to salinity. The CS-PVA hydrogel and combined application of CS-PVA with Cu NPs enhanced growth of *Solanum lycopersicum* L. plants under salinity stress and also promoted the expression of jasmonic acid and SOD genes suggesting that such treatment could mitigate saline stress through the regulation of oxidative and ionic stress (Hernandez-Hernandez et al. 2018b).

Foliar application of nanoscale Zn fertilizer at a dose of 200 ppm was reported to mitigate the adverse impact of salinity on cotton plants, and it was confirmed that diluted seawater could be used in the irrigation of these plants, although co-administration of phosphorus fertilizer is necessary to avoid P/Zn imbalance (Hussein and Abou-Baker 2018). Priming with ZnO NPs promoted growth of lupine (*Lupinus termis*) plants which were cultivated in pots for 20 days under salinity stress (150 mM NaCl) resulting in the enhancement of the levels of photosynthetic pigments, organic solutes, total phenols, ascorbic acid, and Zn, as well as in increased activities of SOD, CAT, POD, and APX enzymes compared to stressed plants alone. In treated plants, also reduction in MDA and Na contents was estimated compared to salinized plants alone, whereby priming with a dose of 60 mg/L ZnO NPs secured the best improvement in salt tolerance of plants (Latef et al. 2017). In maize plants grown under saline stress, application of ZnO and Fe $_2$ O $_3$ NPs

in form of spray considerably enhanced the root growth, net CO₂ assimilation rate, and sub-stomatal CO₂ concentration (5%) compared to control, and increased concentrations in leaf Fe and Zn were estimated compared with bulk metal oxide treatment, which may be connected with the shape, size, distribution, and characteristics of NPs (Fathi et al. 2017a). On the other hand, in similar experiment with wheat plants that were sprayed with bulk and nanosized ZnO and Fe₂O₃ or their mixture, although the highest plant height and leaf Fe concentration were observed for treatment with Fe₂O₃ NPs, the researchers concluded that the spray of NPs may not be superior compared with bulk forms in alleviation of salinity impacts (Fathi et al. 2017b). Beneficial effects on sunflower plants under saline condition observed with foliar application of bulk FeSO₄ and FeSO₄ NPs were manifested in increased leaf area, shoot dry weight, net carbon CO₂ assimilation rate, sub-stomatal CO₂ concentration, Chl content, maximum quantum yield of PSII (F_v/F_m , where F_v is variable fluorescence and F_m maximum fluorescence), and Fe content, while Na content in leaves decreased. It could be noted that at application of FeSO₄ NPs, the increase in Chl a content and biomass was greater (Torabian et al. 2017). Similar positive results were obtained with application of foliar spray of bulk and nanoscale ZnO on the growth of sunflower cultivars under salt stress (100 mM NaCl), with greater effect of ZnO NPs on biomass production (Torabian et al. 2016).

TiO₂ NPs (anatase) application did not affect germination but notably increased root and stem length and fresh dry weights of *Zea mays* plant organs, especially in co-administration with NaCl (300 mM), whereby treatment of maize plants under salt stress with 0.3% TiO₂ NPs resulted in 1.4-fold increase of root length and 4.8-fold increase of stem length, while fresh weight increased 1.2-fold (Mutlu et al. 2018). Combined treatment of barley plants which were grown under salt stress with TiO₂ NPs and sodium nitroprusside (Na₂[Fe(CN)₅NO]) acting as nitric oxide donor induced salt tolerance in barley, likely associated with increases in some antioxidant enzyme activities, whereby MDA and H₂O₂ concentrations in the shoots of barley were reduced as well (Karami and Sepehri 2018).

In *Brassica napus* plants treated with CeO₂ NPs (200 and 1000 mg/kg dry sand and clay mixture), higher plant biomass and higher efficiency of the photosynthetic apparatus were estimated in both freshwater and saline water (100 mM NaCl) irrigation conditions suggesting changes in canola growth and physiology by CeO₂ NPs application resulting in improved plant salt stress response, although the salt stress could not be completely alleviated (Rossi et al. 2016). In another experiment with *B. napus* plants grown in the presence of CeO₂ NPs applied at a dose of 500 mg/kg dry sand and/or 50 mM NaCl, the researchers found that CeO₂ NPs modified the formation of the apoplastic barriers in *B. napus* roots, whereby under salt stress, they were able to shorten the root apoplastic barriers, thus allowing higher Na⁺ transport to shoots and less accumulation of Na⁺ in plant roots what was reflected in better physiological performance of rapeseed plants (Rossi et al. 2017). Using model plant *Arabidopsis thaliana*, Wu et al. (2018) reported catalytic ·OH scavenging by CeO₂ NPs in *A. thaliana* leaves that pronouncedly improved mesophyll K⁺ retention, a key trait associated with salinity stress tolerance. Leaves treated with poly(acrylic acid)-coated CeO₂ NPs showed approx. threefold lower NaCl-induced

K⁺ efflux from leaf mesophyll cells compared to controls upon exposure to salinity stress, and the ROS-activated nonselective cation channels in the plasma membrane of leaf mesophyll cells were identified as the main [•]OH -inducible K⁺ efflux channels. Long-term catalytic scavenging of [•]OH in *A. thaliana* leaves improved plant photosynthetic performance at saline condition, and consequently plasma membrane channels/transporters could coordinately retain higher levels of K⁺ in the leaf mesophyll cell cytosol (Wu et al. 2018).

Application of Si in bulk and nanoforn enhanced the salt tolerance of the tomato plants, reflected in improved photosynthesis rate, mesophyll conductance, and plant water-use efficiency under saline stress condition, although no considerable difference was found between application of bulk and nanoscale Si (Haghighi and Pessaraki 2013). Almutairi (2016) at investigating the effect of nanoscale Si application on the expression of salt tolerance genes in germinating tomato (*Solanum lycopersicum* L.) seedlings under salt stress found that of the 14 investigated salt stress genes, four genes (AREB, TAS14, NCED3, and CRK1) were upregulated and six genes (RBOH1, APX2, MAPK2, ERF5, MAPK3, and DDF2) were downregulated. Increased germination percentage, germination rate of tomato seeds, and the root length and fresh weight of tomato seedlings were also observed suggesting that SiNPs contribute to improvement of plants' tolerance of salinity.

SiO₂ NPs improved defense mechanisms of squash (*Cucurbita pepo* L. cv. white bush marrow) plants against salt stress toxicity by increasing the net photosynthetic rate, stomatal conductance, transpiration rate, water-use efficiency, total Chl, proline, and carboanhydrase activity in the leaves of plants. Reduction in oxidative damage at treatment of salt-stressed plants with SiO₂ NPs was due to the expression of antioxidant enzymes, such as CAT, POD, SOD, GR, and APX (Siddiqui et al. 2014). Application of SiO₂ NPs at a dose 50 mg/L was found to be the best dose to enhance growth of potato (*Solanum tuberosum*) plants in vitro and mitigate the negative effects of salinity (50 and 100 mM) during a longer period (35 and 90 days) (Salah et al. 2017). High Na⁺ concentrations (up to 5000 mg/L) had detrimental effects on seed germination and the growth of common bean seedlings that were alleviated by treatment with SiO₂ NPs. For example, addition of 300 mg/L SiO₂ NPs increased the final germination percentage, vigor index, and germination speed for seeds, shoot and root lengths as well as root dry masses were enhanced, and low Na content in plant tissues was estimated using irrigation with 5000 mg/L Na⁺ (Alsaedi et al. 2017). Similarly, exogenous application of SiO₂ NPs notably improved germination and growth of *Cucumis sativus* plants even at a dose of 100 ppm and under elevated Na⁺ stress (5000 mg/L Na⁺). Treatment with 200 ppm SiO₂ NPs increased germination rate index by 116%, germination index by 110%, shoot dry mass by 384%, root dry mass by 304%, and K⁺/Na⁺ ratio by 77% (Alsaedi et al. 2018). Beneficial effect of exogenous treatment of soybean plants grown under salt stress with 0.5 and 1 mM SiO₂ NPs was reflected in improved shoot and root growth of seedlings, the increase in K⁺ concentration and antioxidant activities and decreased Na⁺ concentration, lipid peroxidation, and ROS production caused by salt stress (Farhangi-Abriz and Torabian 2018). Treatment of fenugreek plants grown under salinity stress (50, 100, and 150 mM) with 50 ppm SiO₂ NPs alleviated negative

impact of salt on shoot, root, and seedling lengths, and under salinity stress, exposure of fenugreek seeds to 50 and 100 ppm SiO₂ NPs resulted in increased shoot, root, and seedling dry weights compared to bulk SiO₂ application and control treatments, whereby a dose of 50 ppm SiO₂ NPs was more effective than 100 ppm dose (Ivani et al. 2018).

11.4.4 Soil Acidity

Soil acidification is an ongoing natural process that can be accelerated by agricultural practices. It is mainly caused by the release of H⁺ ions during the transformation and cycling of carbon, nitrogen, and sulfur on the soil–plant interfaces and results in declining crop production all over the world (Iqbal 2012). pH belongs to crucial factors governing concentrations of soluble and plant available metals, whereby metal solubility tends to decrease at higher pH values and increase at lower pH, and higher concentrations of toxic metals in soil solution could result in adverse effects on plants (Rieuwerts et al. 1998).

Investigation of the impact of soil properties in a range of soils under both leached and unleached conditions on the toxicity of Ag⁺ to *Hordeum vulgare* L. and *Lycopersicon esculentum* plants confirmed that variations in soil organic carbon and pH were found to be primarily responsible for mitigating Ag toxicity (Langdon et al. 2015). Investigation of CuO NPs dissolution and toxicity to wheat in rhizosphere soil using freshly added CuO NPs (500 mg Cu/kg soil) and CuO NPs aged for 28 days before planting showed that aging of CuO NPs increased their toxicity to *Triticum aestivum* (reduction in root maximal length). The presence of roots in the soil had opposite and somewhat compensatory effects on NP dissolution. The exudates from wheat roots also enhanced soluble Cu in pore water (Gao et al. 2018).

Garcia-Gomez et al. (2018a) compared phytotoxicity of ZnO NPs and Zn accumulation in nine crops (wheat, maize, radish, bean, lettuce, tomato, pea, cucumber, and beet) grown in a calcareous soil and an acidic soil. While in the calcareous soil Zn phytotoxicity was limited due to very low available Zn, in the acidic soil, the high available Zn seriously affected the germination of bean, tomato, lettuce, and beet and the growth of most of the crops (EC₅₀ values ranging from 110 to 520 mg Zn/kg), whereby adverse effects on the photosynthetic pigments and most of the markers of oxidative stress were observed in maize, wheat, bean, and pea. Thus, soil pH and plant species could be considered as key factors affecting the Zn availability and phytotoxicity of ZnO NPs. Zn concentration in the leaves of *Pisum sativum* L. and *Beta vulgaris* L. plants cultivated under greenhouse conditions was 6–12-fold higher in acidic than in calcareous soil, and while in acidic soil the ZnO NPs promoted ROS generation in both plant species with increases from 47% to 130%, in calcareous soil, a 20–65% decrease of ROS levels in treated plants was estimated, obviously due to the supply of zinc in Zn-deficient soils (Garcia-Gomez et al. 2018b). In the acid soil, treatment of wheat with ZnO NPs resulted in the inhibition

of root elongation, while phytotoxicity was mitigated in the calcareous alkaline soil, although uptake of Zn was twofold higher than in control plants. Soluble Zn in the acid soil was 200-fold higher, and shoot levels were 10-fold higher than from the alkaline soil (correlating with phytotoxicity), whereby variation in humic acid between soils was found not to be a major factor influencing plant responses to the NPs (Watson et al. 2015). At comparing the effect of ZnO NPs, ZnO bulk, and ZnSO₄ in the antioxidant defenses of *Phaseolus vulgaris* and *Solanum lycopersicon* plants growing in an acidic (soil pH 5.4) and a calcareous soil (soil pH 8.3), it was found that ZnO NPs showed comparable toxicity to their bulk counterparts and Zn salts, the effects being generally higher in the acidic soil than in the calcareous soil for the bean and the opposite for the tomato, whereby comparable uptakes and toxicities of the different Zn forms suggested that the Zn ions derived from the ZnO NPs exerted a preferential toxicity in plants. On the other hand, based on the results obtained with application of ZnO NPs at a dose of 3 mg Zn/kg, it could be suggested that other underlying mechanisms related to the intrinsic nanoparticle properties may exist, especially at low NP concentrations (Garcia-Gomez et al. 2017).

Investigation of the impact of γ -Fe₂O₃ NPs (6 nm) on root elongation and growth of rice plants grown in pots showed that due to their excessive adsorption onto soil colloids, the observed phytotoxicity was low. However, at application of Fe₂O₃ NPs coated with citric acid, the phytotoxic effect manifested in reduced CO₂ assimilation rate was similar to their bulk counterpart, although bulk citrate-coated iron oxide more effectively inhibited shoot growth due to massive accumulations of Fe plaque on the root surfaces connected with a decline in the pH of rhizoplane soils. This indicated lower phytotoxicity of γ -Fe₂O₃ NPs under reductive conditions compared to microsized iron oxide (Alidoust and Isoda 2014).

11.4.5 Heat Stress

High temperature stress induces morphological, anatomical, physiological, and biochemical changes in plants, including the changes in water relations, decrease in photosynthesis, hormonal changes, and reduced yield in plants (Waraich et al. 2012). Elevated temperatures can directly and effectively change the properties of biological membranes, highly ordered structures consisting of mosaics of lipids and proteins, including their fluidity and permeability, and can induce changes in the lipid composition and/or interactions between lipids and specific membrane proteins (Yue and Yun 2018). During the acclimation process that occurs when the plant acquires resistance to an increase in temperature, plants adjust their homeostasis and steady-state physiology to the new temperatures (Nievola et al. 2017). Investigation of proteomic responses of leaves of 24-day-old rice seedlings to sudden temperature changes in rice seedlings grown at 28/20 °C (day/night) that were subjected to 3-day exposure to 36/28 °C or 44/36 °C (day/night) for high-temperature stress showed that among identified proteins being responsive to temperature stress, 47 proteins were exclusively found at 44/36 °C (day/night) exposure (Gammulla et al. 2011).

Application of AgNPs was found to protect wheat plants exposed to heat stress (35–40 °C) that impaired their morphological growth by interfering in photosynthetic process due to enhanced level of oxidative stress. Beneficial effect of AgNPs under heat stress resulted in improved root and shoot length, root number, plant fresh and dry weight, leaf area, and number of wheat plants (Iqbal et al. 2017). The study of morphogenesis and productivity characteristics of *Cucumis sativus* parthenocarpic hybrids Marinda and Kurazh in ontogenesis grown in greenhouses under thermic films, surface of which was coated with NPs of Cu compounds (film 1) or Ag and Cu compounds (film 2) using magnetron sputtering, showed that application of film 1 improved seed germination, activated plant growth and development, caused shortening of period of the fruiting beginning, and increased productivity of both hybrids. In contrast, the use of film 2 resulted in growth inhibition of both hybrids with subsequent reduction of their productivity (Minich et al. 2016).

Effect of different temperatures (20, 25, and 30 °C) on maize (*Zea mays* L.) germination and root growth under exposure to ZnO NPs (24 ± 3 nm) at 0–1600 mg/L for 15 days was investigated by Lopez-Moreno et al. (2017). While, at 20 and 25 °C, a dose of 400 mg/L ZnO NPs pronouncedly reduced the germination (40 and 53%, respectively) and treatment with 50, 400, and 1600 mg/L ZnO NPs at 20 °C resulted in reduced root growth by 18, 47, and 26% respectively, at 25 °C, root growth increased by 22 and 27% at application of 100 and 800 mg/L ZnO NPs. However, with increasing the temperature to 30 °C, root growth reduction by 42% was observed with a dose of 100 mg/L ZnO NPs, and decreased expression of a protein band with molecular weight of 85 kDa and increased expression of protein of 75 kDa were estimated suggesting that temperature may alter the way the ZnO NPs interact with plants. On the other hand, presence on ZnO NPs in roots was detected at any temperature tested.

Qi et al. (2013) sprayed leaves of tomato seedlings grown to the six-leaf stage with different concentrations of TiO₂ NPs, and then the seedlings were exposed to 35/15 °C (day/night) suggested as a mild heat stress for 7 days in a Chinese greenhouse. At such mild temperature stress in tomato plants exposed to appropriate concentration of TiO₂ NPs, an increase of net photosynthetic rate, conductance to H₂O, and transpiration rate of leaves was observed. Treatment with TiO₂ NPs also significantly decreased the initial minimum fluorescence value (F_0) indicating that PSII is protected from damaging forms of ROS and it increased regulated and decreased non-regulated PSII energy dissipation suggesting beneficial role of these NPs in promoting photosynthesis in tomato leaves under mild heat stress.

Foliar spraying with 10 mg/L SeNPs during the booting stage of sorghum grown under high temperature stress enhanced antioxidant enzymes activity, reduced content of oxidants, contributed to higher levels of unsaturated phospholipids, and improved the pollen germination percentage resulting in considerably higher seed yield. It could be noted that enhanced antioxidant enzyme activities and reduced content of oxidants due to treatment with SeNPs were greater at high temperature (38/28 °C) than at optimum temperature conditions (32/22 °C) suggesting protection of sorghum plants against oxidative damage under high temperature stress by SeNPs (Djanaguiraman et al. 2018b).

11.4.6 Cold Stress

Cold stress is abiotic stress factor that has negative impact on the growth and development of plants resulting in poor germination, stunted seedlings, yellowing of leaves, withering, and reduced tillering. Due to cold stress-induced dehydration, plasma membrane damage occurs resulting in loss of membrane integrity, leading to solute leakage. Moreover, cold stress results in disruption of the integrity of intracellular organelles, leading to the loss of compartmentalization and reduction and impairing of photosynthesis, protein assembly, and general metabolic processes. Both cold acclimation and chilling tolerance of plants involve an array of biochemical, molecular, and metabolic processes, including signal transduction, activation of transcription factors and stress-responsive genes, detoxification of ROS, damage control and repair begin, restructuring of plasma membrane, and acceleration of osmolyte synthesis (Steponkus 1984; Zhu et al. 2007; Yadav 2010).

Cold stress adversely affected *Cicer arietinum* L., which was manifested with increased H₂O₂ and MDA contents and electrolyte leakage index (ELI) causing greater damage in cold-sensitive (C-Sus) compared to cold-tolerant (C-Tol) plants. On the other hand, in chickpea plants under cold stress that were treated with TiO₂ NPs, decreased H₂O₂ levels as well as decreased MDA content and ELI compared to control plants were observed, the changes being more intensive in C-Tol than in C-Sus plants. Protection of plants by the antioxidant enzymes exposed to cold stress was better in C-Tol compared to C-Sus plants and in TiO₂ NPs-treated plants compared to control; lipoyxygenase activity was induced efficiently only in TiO₂ NPs-treated C-Tol plants under cold stress condition. Moreover, stable contents of Chl and carotenoids were observed in TiO₂ NPs-treated plants during cold stress. Thus, an increased tolerance of chickpea plants to cold stress by TiO₂ NPs was reflected in decreasing level of injuries and increasing capacity of defense systems (Mohammadi et al. 2014). The effect of TiO₂ NPs on cold tolerance of C-Tol and C-Sus chickpea plants exposed to cold stress (4 °C) for 6 days was investigated using cDNA-amplified fragment length polymorphism analysis of transcripts induced in plants by TiO₂ NPs during cold stress. Based on differentially expressed transcript-derived fragments (TDFs) of TiO₂ NPs-treated plants, it was found that these could be related to different groups of genes involved in metabolism pathways, cellular defense, cell connections and signaling, transcriptional regulation, and chromatin architecture. Increased transcription level of these TDFs, particularly the first day of cold stress, was critical from the aspect of cold tolerance development resulting in decreased ELI in C-Tol compared to C-Sus plants as well as in TiO₂ NPs-treated plants compared to controls. It could be assumed that TiO₂ NPs could protect the plants against cold stress-induced oxidative stress. Consequently, cold tolerance development could be supported by application of TiO₂ NPs resulting in preventing and controlling the damages also in field conditions and in this way securing increasing crop productivity (Amini et al. 2017). In another experiment with C-Tol and C-Sus chickpea genotypes performed at 4 °C, more permeability to TiO₂ NPs was estimated for the C-Sus plants compared to C-Tol ones, and higher TiO₂ content was estimated during cold stress compared to optimum temperature. Whereas low

temperature increased ELI in untreated C-Tol and C-Sus plants, in plants treated with TiO₂ NPs, it showed a decrease, and under thermal treatments, also lower MDA accumulation was estimated in C-Tol plants suggesting improved redox status of plants by TiO₂ NPs during cold stress what supports potential of TiO₂ NPs to be used for the increase of cold tolerance in crops (Mohammadi et al. 2013). In addition, TiO₂ NPs considerably increased the activity of Rubisco of chickpea plants compared to controls, although it markedly decreased at 4 °C compared to optimum temperature. TiO₂ NPs-treated plants were found to acclimate during cold stress to survival or recovery, which was manifested with decreased H₂O₂ content and higher photosynthetic activity, whereby phosphoenolpyruvate carboxylase activity increased particularly in C-Tol plants compared to C-Sus ones and, in TiO₂ NPs-treated plants compared to controls, which could be connected with an increase in energy efficiency through different mechanisms like malate (Hasanpour et al. 2015).

Haghighi et al. (2014) exposed some tomato (*Lycopersicon esculentum* Mill. cv. 'Halil') plants in hydroponic solution to Se and nano-Se (added to the nutrient solution in the form of Na₂SeO₄) for 3 days to optimal temperature (25/17±2 °C day/night) and then exposed them for 24 h to low temperature stress (10 °C) followed by cultivation (10 days) at optimal temperature. Nano-Se did not affect plant growth; however treatment with 2.5 µmol/L nano-Se caused an increase of the Chl content by 27%, root fresh mass by 11.7%, and root dry mass by 45.4% relative to control, and increased shoot dry mass and relative water content in stressed plants were estimated as well.

Seed prechilling of tall wheatgrass (*Agropyron elongatum* L.), a grass that could be used as a forage and for hay, in combination with SiO₂ NPs largely broke the seed dormancy and notably increased seed germination as well as dry weight of shoots and roots (Azimi et al. 2014). Beneficial effects of CS/SiO₂ NPs on postharvest quality and antioxidant capacity of white-flesh loquat (*Eriobotrya japonica* Lindl.) fruit during cold storage (5 °C for 40 days) resulting in longer storage life with acceptable external and internal quality in the fruit were connected with enhanced activities of antioxidant enzymes; lower levels of O₂[•], H₂O₂, and MDA; and membrane permeability (Song et al. 2016).

11.4.7 UV Light

Reduction of the stratospheric ozone layer due to anthropogenic activities results in increase of UV-B radiation showing adverse effects on plants due to excessive generation of ROS reflected in impaired growth, yield, and photosynthesis; modification of morphology; physiological processes; damage of DNA, lipids, and membranes; and denaturation of proteins. Physiological responses to UV-B stress and subsequent development of defense mechanism by plants to adapt to the changing environment were described by Hollósy (2002), Zlatev et al. (2012), and Sharma et al. (2017).

Chen et al. (2014) tested the impact of CdTe quantum dots (QDs) and UV-B radiation (280–315 nm) as well as their combined application on 5-day-old wheat

seedlings and found that CdTe QDs and UV-B radiation inhibited growth of roots and shoots with additive inhibitory effects at combined treatment group. Moreover, CdTe QDs applied at a dose of 200 mg/mL or UV-B radiation of 10 kJ/m²/day induced the activation of plant antioxidant enzymes and caused programmed cell death due to accumulation of CdTe QDs in root cells. Negative effect of ambient and enhanced UV-B radiation on growth of *Triticum aestivum* seedlings was manifested by declined photosynthetic performance, altered vital leaf structures, enhanced levels of O₂⁻ and H₂O₂, increased lipid peroxidation, and electrolyte leakage, whereby reduction of SOD and APX activities and enhanced activities of guaiacol peroxidase and non-enzymatic antioxidants were observed as well.

Pre-additions of SiNPs as well as Si were found to protect *T. aestivum* plants against UV-B-induced oxidative stress by enhancement of antioxidants, and because the greatest increase of nitric oxide (NO) content was observed at combined application of SiNPs with UV-B enhanced treatment, it was supposed that NO-mediated triggering of antioxidant defense system of seedlings by SiNPs counterbalancing the damage of photosynthetic apparatus by ROS resulted in protection of seedlings. Higher bioavailability of SiNPs to plants compared to bulk Si was reflected in more effective reduction of UV-B stress (Tripathi et al. 2017). Hybrid nanofilms fabricated using 3-methacryloxypropyl-, vinyl- and (3-glycidioxypropyl)-polyhedral oligomeric silsesquioxane ([RSiO_{3/2}]_n) modified with titanium tetrabutoxide were found to provide a physical barrier for blocking the UV-B absorbed into greenhouse suggesting that these materials could be used as the sun protection ingredients (Wang et al. 2010). The protective effect of TiO₂ NPs against UV-B radiation (200 μW/cm² for 5 or 10 min) predominantly caused by the blockage of UV-B by TiO₂ NPs adsorption was estimated in a small planktonic crustacean *Daphnia magna* as well (Liu and Wang 2017).

Nano-anatase also decreased the oxidative stress in spinach chloroplasts caused by UV-B radiation what was manifested by notably reduced levels of O₂⁻, H₂O₂, and MDA content and increased activities of SOD, CAT, APX, GPX as well as elevated O₂ evolution suggesting that nano-anatase could absorb UV-B light and convert light energy to stable chemical energy via electron transport in spinach chloroplasts (Lei et al. 2008). Photocatalytic ROS production and phototoxicity of TiO₂ NPs depend on the solar UV radiation spectrum, whereby removing UV-B (280–320 nm) from solar radiation did not affect considerably the photocatalytic ROS production of TiO₂ NPs, while removal of UV-A (320–400 nm) notably reduced ROS production, and removal of radiation with λ <400 nm resulted in negligible ROS production (Ma et al. 2012).

Irradiation with UV-A light (315–400 nm) of suspensions of TiO₂ and SiO₂ NPs agglomerates (300–600 nm) for 24 h showed remarkable adsorption on *Allium cepa* root surface only for TiO₂ NPs, while adsorption of SiO₂ NPs was minute, and no significant biological effects were observed even at high exposure concentrations of both types of NPs (up to 1000 μg/mL) suggesting protection of plants against NPs by the cell wall, which is able to shield the cell membrane from direct contact with the NPs (Koce et al. 2014). On the other hand, UV radiation pronouncedly reduced the photosynthetic capacity of the aquatic macrophyte *Elodea nuttallii*, which was

indeed unaffected by Cu(II) or CuO NPs treatments. However, at combined exposure with UV, metal accumulation in plants increased in both treatments, but it was higher from CuO NPs compared to dissolved Cu(II) (Regier et al. 2015).

11.4.8 Elevated CO₂

Although CO₂ is indispensable for photosynthesis, being one of its most limiting factors, the anthropogenic CO₂ pronouncedly contributes to greenhouse effects and could adversely affect global climate. Rising CO₂ is expected to result in changes in plant traits that will increase plant productivity, primarily in C₃ plants, because CO₂ enrichment could enhance photosynthetic capacity reflected mostly in the vegetative growth of young plants and it can also alter the partitioning of secondary metabolites in plants (Ibrahim and Jaafar 2011).

No visible signs of toxicity in rice plants cultivated at the ambient CO₂ level (370 μmol/mol CO₂) were observed in TiO₂ NPs-treated rice plants, while under 570 μmol/mol CO₂, pronouncedly reduced grain yield was observed. Moreover, at 570 μmol/mol CO₂, a dose of 200 mg/kg TiO₂ NPs increased accumulation of Ca, Mg, Mn, P, Zn, and Ti, but reduced fat and total sugar in grains suggesting effects on the nutritional quality of crops and also modified the functional composition of soil microbial communities (Du et al. 2017). Comparison of TiO₂ NPs-treated wheat plants grown at the normal CO₂ condition (400 mg/L CO₂) showed that treatment of wheat seedlings cultivated under super-elevated CO₂ conditions (5000 mg/L CO₂) with TiO₂ NPs resulted in increased root biomass and large numbers of lateral roots, increased ABA content, and pronounced decrease in indolepropionic acid and jasmonic acid content, and considerably enhanced Ti accumulation and translocation in wheat treated with certain concentrations of TiO₂ NPs was observed as well (Jiang et al. 2017).

Enhanced accumulation of Fe and Zn in hydroponically cultivated rice plants treated with Fe₂O₃ and ZnO NPs at elevated atmospheric CO₂ concentration (610 ± 10 ppm) compared to ambient one (390 ± 10 ppm) was reported by Yadav et al. (2014).

11.4.9 Toxic Metal Stress

Toxic metals or metals as bioelements in higher than normal concentrations, are harmful to living organisms including plants and their widespread accumulation in agricultural soils results in elevated uptake by crops causing not only reduced yield and economic losses but significantly affecting both food quality and safety as well. Toxic metals have an adverse impact on uptake and transport of nutrients by crops, and they can seriously damage photosynthetic apparatus. They reduce the levels of photosynthetic pigments, proteins, free amino acids, and soluble sugars; negatively affect the

integrity of the cytoplasmic membrane and water relations; and induce oxidative stress resulting finally in lower yield (e.g., Masarovičová and Kráľová 2012, 2013, 2017; Masarovičová et al. 2010, 2014; Kráľová et al. 2019). One of the ways to counteract the adverse effects of toxic metals on crops is treatment with metal/metalloid NPs (e.g., Liu et al. 2015, 2018; Marchiol et al. 2016; Rizwan et al. 2018).

AgNPs used as a priming agent promoted the germination and growth of wheat plants and stimulated indole-3-butyric acid, 1-naphthalene acetic acid, and 6-benzylaminopurine contents and reduced abscisic acid content, and AgNPs priming at a dose of 1 mg/L considerably improved phytohormone balance, growth parameters, and photosynthetic efficiency of wheat plants also under salinity stress (25 and 100 mM NaCl) (Abou-Zeid and Ismail 2018).

Nanomaterials such as nanoscale hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$; 20 and 40 nm), Fe_3O_4 NPs, and Fe^0 NPs effectively reduced As uptake of hydroponically cultivated rice seedlings at low arsenic concentrations (Huang et al. 2018). Adverse effects of chromium stress on sunflower plants connected with increased Cr uptake resulting in considerable reduction in morphological and physiological parameters could be alleviated by application of Fe^0 NPs or Fe^{2+} ions that are able to reduce Cr concentration in root and shoot; increase root and shoot dry weight, plastid pigments (Ch and carotenoids), and proline contents; and also pronouncedly reduce the levels of MDA and H_2O_2 , whereby Fe^0 NPs positively affected all abovementioned traits longer than Fe^{2+} suggesting that they could effectively prevent Cr uptake by sunflower plants (Mohammadi et al. 2018). Treatment of wheat seedlings grown on quartz sand supplemented with 2.67 mg Cd^{2+} /kg and 5.53 mg Cr^{6+} /kg (causing a 50% decrease of root length) with 1000 mg/kg magnetite (Fe_3O_4) NPs resulted in an increase of root length by 25 and 50%, and Cd and Cr accumulation in vegetable tissues was notably reduced (Lopez-Luna et al. 2016). Carbon-coated semicrystalline Fe_3O_4 NPs were found to enhance bioproductivity, photosynthetic electron transport, antioxidant enzyme activity, and Fe accumulation under Ca stress in rice plants. They reduced Ca accumulation in plants by physical adsorption, and Fe release from the NPs ameliorated Ca-induced Fe deficiency in plants (Sebastian et al. 2017). *Brassica juncea* var. Pusa Jagannath plants exposed to combined treatment with As^{3+} (150 μM) and Fe_3O_4 NPs (500 mg/L) for a period of 96 h showed besides improved plant growth also higher photosynthetic pigment and protein content compared to plants treated with As alone what could be connected with reduced oxidative stress by possible involvement of Fe_3O_4 NPs as nano-adsorbents in reducing As toxicity (Praveen et al. 2018).

Also CuO NPs applied at concentrations 50 and 100 mg/L, respectively, mitigated the negative effect of As (10 mg/kg) on the number of root branches of *Oryza sativa* Japonica seedlings (Liu et al. 2018). At studying the impact of binary combinations of metal-based nanomaterials on zucchini (*Cucurbita pepo* L.), it was found that co-exposure of plants grown on vermiculite to CeO_2 NPs and La_2O_3 NPs applied at doses 100 g/L for 21 days notably reduced La uptake, while 100 mg/L La_2O_3 NPs completely deregulated Cu uptake (two- to fivefold higher) upon CuO NPs (100 mg/L) co-exposure (Pagano et al. 2017). CeO_2 NPs were reported to reduce both the boron nutritional status of *Helianthus annuus* L. plants cultivated in original

soil and the boron phytotoxicity in boron-spiked soil (Tassi et al. 2017). At co-exposure of hydroponically cultivated *Glycine max* (L.) Merr. seedlings to CeO₂ NPs and Cd, the CeO₂ NPs were found to reduce the translocation of Cd from roots to shoots by 70%; however they did not influence the total Cd associated with soybean roots, while Ce levels in soybean roots were reduced by 45% and showed notable increase (by 60%) in soybean shoots. It could be mentioned that at co-exposure of Cd and CeO₂ NPs, higher excretion of plant root exudates was observed, which could affect the chemical environment in the plant rhizosphere (Rossi et al. 2018).

After priming of wheat seeds with ZnO NPs (25, 50, 75, and 100 mg/L) and Fe NPs (5, 10, 15, and 20 mg/L) and sowing the seeds in Cd-contaminated soil, the investigation of mature plants showed beneficial effects of NPs on photosynthesis and biomass, and the metal NPs also reduced the electrolyte leakage and SOD and POD activities in leaves compared to control plants. Moreover, Cd levels in roots, shoots, and grains were considerably lower, while the concentrations of essential metals, Zn and Fe, in plant organs and grains increased with NPs application (Rizwan et al. 2018). Positive impact of foliarly applied ZnO NPs on wheat plants grown in Cd-contaminated soil was observed also by Hussain et al. (2018). The researchers estimated that foliar and soil application of ZnO NPs resulted in decreased Cd concentrations in grains by 30–77%, and 16–78%, respectively, reduced electrolyte leakage, and increased SOD and POD activities in leaves. ZnO NPs were reported to alleviate Cd- and Pb-induced toxicity in *Leucaena leucocephala* seedlings resulting in an increase in photosynthetic pigment and total soluble protein contents, considerable decrease of lipid peroxidation in leaves, and elevated level of antioxidative enzyme activities (Venkatchalam et al. 2017).

TiO₂ NPs stimulated growth of barley plants and were able to compensate the adverse effects of CeO₂ NPs in plants grown in soil enriched with both TiO₂ NPs and CeO₂ NPs (500 or 1000 mg/kg), whereby the growth cycle of plants treated with both CeO₂ NPs and TiO₂ NPs was approximately 10 days longer than that of control plants (Marchiol et al. 2016). TiO₂ NPs reduced the bioaccumulation of Pb in rice and at high TiO₂ NPs exposure levels (1000 mg/L) reduced the Pb concentration in rice roots by >80% and by 77–97% in shoots, if nanoscale pristine anatase and rutile particles as well as nanosized rutile particles with hydrophilic surface were used, while at application of bulk TiO₂ or nanoscale rutile particles with hydrophobic surface, Pb reduction in roots and shoots was only 45–61% and 11–38%, respectively (Cai et al. 2017). At co-exposure to Cd and TiO₂ NPs, the TiO₂ NPs considerably alleviated also Cd stress in rice plants, which was reflected in improved plant growth and significant increase of the net photosynthetic rate and Chl content, and they reduced the Cd uptake and distribution in rice roots and leaves (Ji et al. 2017). Positive impact of TiO₂ NPs on the reduction of Cd toxicity resulting in increased photosynthetic rate and growth parameters was observed also in soybean plants; however treatment with TiO₂ NPs notably enhanced Cd uptake by plants (Singh and Lee 2016). At application of TiO₂ NPs, higher levels of ¹³³Cs were estimated in soybean shoots (731.7 µg/g d.w.) than in the roots (597.8 µg/g d.w.) suggesting that TiO₂ NPs could be used for phytoremediation of ¹³³Cs-contaminated soils (Singh and Lee 2018). On the other hand, co-exposure to TiO₂ NPs did not affect Cd (100

and 250 mg/L) toxicity in *Raphanus sativus* seeds, and morphological alterations in nuclei, vacuoles, and shape of radish root cells, which were observed upon single Cd exposure, were not abolished in the presence of TiO₂ NPs (Manesh et al. 2018).

SiNPs showed also beneficial effects on growth of rice plants exposed to Pb, prevented Pb transfer from roots to shoots, and blocked Pb accumulation in rice grains, especially in high-Pb-accumulating rice cultivars and in heavily Pb-polluted soils (Liu et al. 2015). Also SiNPs protected *Pisum sativum* L. seedlings against adverse effect of Cr by reducing Cr accumulation and oxidative stress and upregulating antioxidant defense system and nutrient elements, which was reflected in improved plant growth (Tripathi et al. 2015b). Foliar application of SiNPs to *Oryza sativa* L. cv. Xiangzaoxian 45 plants grown in Cd-contaminated soil reduced Cd accumulation in grains by inhibiting translocation of Cd, while it enhanced translocation factors of K, Mg, and Fe from the uppermost nodes to rachises in rice plants, a dose of 25 mM SiNPs being the most effective in reducing translocation factors of Cd from roots to the uppermost nodes and from the uppermost nodes to rachises (Chen et al. 2018). Foliar application of SiNPs (2.5 mM) alleviated Cd stress in rice seedlings (*Oryza sativa* L. cv Youyou 128) hydroponically cultivated in the presence of 20 μM CdCl₂, which was reflected in improved plant growth, Mg, Fe, and Zn nutrition, and Chl contents of Cd-stressed plants as well as in lower oxidative stress reflected in higher glutathione content, and reduced MDA content and reduced Cd translocation from roots to shoots and reduced Cd accumulation in grains (Wang et al. 2015). Using cells cultured in suspension, investigation of beneficial effects of SiNPs on Cd-induced toxicity in rice showed that addition of SiNPs significantly enhanced the proportion of live cells and pronouncedly reduced severe structural changes in the organelle integrity of cells caused by Cd (at treatment with SiNPs, cells remained nearly intact even in the presence of high Cd concentrations). Moreover, Cd²⁺ influx at treatment with SiNPs (19 nm, 48 nm, and 202 nm) decreased by 15.7-, 11.1-, and 4.6-fold, and the gene expression of Cd uptake and transport (OsLCT1 and OsNramp5) was inhibited, while those of Cd transport into vacuole (OsHMA3) and Si uptake (OsLsi1) were enhanced, resulting in at least 1.87-fold increase in the Si uptake capacity. Thus, reduced Cd uptake capacity at co-exposure to Cd and SiNPs resulted in the alleviation of Cd toxicity (Cui et al. 2017).

Comparison of barley plants grown for 14 days under NiO NPs (120 mg/kg) single and co-exposure with SiO₂ NPs (3 mg/kg) showed that co-application of SiO₂ NPs reduced adverse impact of NiO NPs on fresh and dry biomass and photosynthesis-related parameters, lowered or maintained the levels of lipid peroxidation, and stimulated the redox pathway of thiols, and also the response of the antioxidant system was found to be more prominent at co-exposure of NiO NPs with SiO₂ NPs (Soares et al. 2018).

11.5 Conclusions

The crucial role of agriculture is to provide sufficient quality and healthy food for continuously growing population. However, the increasing anthropogenic pollution of the environment and current climate change significantly contribute to a decrease of crop production. Therefore, it is essential to develop and use effective environment-friendly agricultural preparations that will not only be able to secure higher yield of crops and prevent the entry of compounds damaging human health into the food chain but to be economically reasonable as well. In spite of the fact that NPs and nanomaterials could be considered controversial by the world public, they have an irreplaceable place in agriculture and food industry; one of their advantages is lower doses of active compounds needed to achieve the desired effect compared to the application of bulk preparations. Many of metal- and metalloid-based NPs have found their applications as fertilizers, plant growth-promoting compounds, and systems for delivery of nutrients and could be applied to increase the tolerance of crops against the harmful impact of abiotic stresses, including drought and salinity, representing a very serious global problem. However, it is necessary to estimate exactly concentration ranges for individual crop species, in which particular metal-/metalloid-based NPs exhibit growth stimulation but higher concentrations are phytotoxic, verify them in field conditions, and investigate their possible transgenerational impact on seed quality and the development of second-generation seedlings.

Acknowledgment This study was supported by the Ministry of Education of the Czech Republic (LO1305), by the Slovak Research and Development Agency (APVV-17-0373 and APVV-17-0318).

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