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Mitigation of Abiotic Stress in Plants

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Preface

The emergence of nanotechnology have opened up exciting opportunities for novel applications in agriculture, food, medicine, and biotechnology industries. Nanotechnology has the potential to modernize agricultural research and practice, although it has gained momentum in the agriculture sector over the last decade. Abiotic stresses are important constraints that adversely affect the production of agricultural crops. Nanobiotechnology may be a boon for the mitigation of plant abiotic stress impact.

This book provides up-to-date knowledge of the promising field of nanobiotechnology with emphasis on the mitigation approaches to combat plant abiotic stress factors including drought, salinity, waterlog, temperature extremes, mineral nutrients, and heavy metals. These factors adversely affect the growth as well as yield of crop plants worldwide especially under the global climate change. The book consists of 24 chapters discussing the status and prospects of this cutting-edge technology in relation to the mitigation of the adverse impact of the abovementioned stress factors. Moreover, it highlights contemporary knowledge of tolerance mechanisms and the role of signaling molecules and enzyme regulation as well as the applications of nanobiotechnology in agriculture.

The book is perceived as an important reference source for plant scientists and breeders interested in understanding the mechanisms of abiotic stress in pursue of developing stress-tolerant crops to support agricultural sustainability and food security. It is valuable for professional researchers as well as advance graduate students interested in nanotechnology fundamentals and utilization.

The chapters are contributed by 61 internationally reputable scientists from 10 countries and subjected to review process to assure quality presentation and scientific accuracy.The chapters start with an introduction covering related backgrounds and provide in-depth discussion of the subject supported with a total 95 of high-quality color illustrations and relevant 31 data tables. The chapters conclude with recommendations for future research directions and a comprehensive list of up-to-date pertinent references to facilitate further reading. The editors convey their appreciation to all the contributors for their delegacy and to Springer for the opportunity to publish this work.

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Chapter 21
Nanonutrients: Plant Nutritive and Possible Antioxidant Regulators

Ayoob O. Alfalahi and Fadwa W. Abdulqahar

Abstract There is a growing use of nanotechnology in agriculture, especially in the densely populated countries looking for unconventional sources for feeding their peoples. One of the main concerns considering nutrients application is very low of applied nutrient succeeded in reaching the targeted site, thus the delivered quantity will be much below the required concentration adequate for specific biological activity. Notably, only 20% of the applied nutrients through soil can be uptaken by the plant, whereas the residue either creating stable complexes with soil components or being washed away with water. In both cases, plants will be capable to get advantage only from the minimum limit of the applied nutrients. The nanoparticle-based nutrients have several key advantages over traditional nutrients. Primarily, nanonutrient does not release as fast as the traditional nutrient, hence it will not significantly affect the soil pH due to gradual release. This, in turn, will guarantee a slow and steady release of a specific nutrient that permits plants to continuously take up the nutrient as they grow. Throughout their development, plants face a vigorously shifting in environment conditions falling within either biotic or abiotic factors. Regarding this, nanofertilizers have proven efficiency in reducing the adverse side effects of unfavorable environmental conditions by activating antioxidant enzymes and decreased oxidative processes outputs, primarily reactive oxygen species (ROS) and/or reactive nitrogen species (RNS). Although, plants needed micronutrients in small quantities, they still playing a vital role in several metabolic pathways. Even as plants are cultivated in a variety of stressful conditions, nanoparticles (NPs) can be an effective tool for endorsing a protective antioxidant system. Considerable investigations/studies have to be done before decisively determining the biosafety of nanomaterials, as long as their toxic effects have already been demonstrated on many occasions.

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21.1 Introduction

Strategy plans must be taken into consideration with the constant increase in the human population. During the last few decades, conventional fertilizers participate significantly in boosting plant productivity to ensure requirements of the global food basket. However, the shift in the lifestyle of societies and human activities on agricultural lands causes them to lose their fertility, thus, it is more likely to search for nanoscale alternatives in an attempt to restore soil nutritive capabilities and secures an acceptable level of production to bridge the food gap (Henchion et al. 2017; Savci 2012). Although the adoption of different fertilizers is laying behind the tremendous augmentation of crop productivity, particularly during the green revolution, chemical fertilizers have their own drawbacks (Lin et al. 2019). Thereby, there is an urgent need for innovative strategies marked with low waste and cost of the supplemented agrochemicals. Nanomaterials (NMs) are not novel as some peoples think, nanoscale particles are naturally occurred via geological or biological processes in the ecosystem, however precipitation and bioreduction are on the top of the list (Kamle et al. 2020). Definitely, the naturally emanated NMs with a relative difference in terms of physical, chemical and optical characteristics. In this context, volcanoes and hydrothermal activities are the most common examples of natural emanated nanoscopic particles (Jacob 2018). Remarkably, the natural biological system that we part of is generating NPs infrequently (Gupta and Xie 2018). In response to this, human beings are exposed daily to different types of nanoparticles with or without their awareness, at the same time they have a limited ability to control either the generation or distribution of natural nanoparticles (Jeevanandam et al. 2018).

The field of engineered nanotechnology has made numerous innovative progress over the last two decades, especially in agricultural and industrial sectors. Nanoparticles (NPs) involved a wide range of particulate substances with at least one dimension less than 100 nm (Khan et al. 2019). Due to their various biological, pharmaceutical, chemical, food and industrial applications, the engineered nanomaterials (ENMs) will be released in a considerable amount to the local environment, consequently their deposition should be considered (Zoufan et al. 2020). Depending on their distinctive characteristics, nanomaterials can interact directly or indirectly with most components of the biological system, nevertheless the arising threat lies behind unsatisfactory knowledge of either the nature or outputs of these interactions (Bundschuh et al. 2018). Alternatively, the production of plant-derived NPs shows substantial benefits over other bio-systems as plants are readily obtainable and the biogenic synthesis process offering value-effective technique (Sharma et al. 2019). Nanofertilizers can be practiced as macro or micro-nutrients per se or as carriers (Kah et al. 2018), and even as coated nutrients (DeRosa 2010). Furthermore, molecular coatings with various biomolecules have a great significance for their use as smart delivery systems to ensure the slow-release of nutrients at the root zone (Usman et al. 2020). Falling within nanotechnology, nanocarriers may be a common concept in pharmaceutical and animal systems, while it is less shared in the botanical system despite its importance.

The level at which nanomaterial affects plant performance varies according to general and particular features of these materials (origin, synthesis method, size, charge, surface, concentration and plant species). In this context, some nanomaterials retain a purely nutritional effect reflected on improved growth parameters, meanwhile, it may constitute a catalyst influence by generating Reactive oxygen species (ROS) and/or secondary metabolites (Aslani et al. 2014). Despite the great ability of nanomaterials to trigger disruptive and toxic effects through ROS generation, these substances are holding significant promises in enhancing the nutritional value of agricultural products from a fortification viewpoint (Armstead and Li 2016).

This chapter is focusing on the agricultural applications of nanomaterials in what became known as "Agronanotechnology", in which the most common approaches for synthesizing NPs especially the green biosynthesis will be addressed. As a promising technology, the key advantages of using nanomaterials in developing an effective delivery system via nanocarriers, modulating secondary metabolites and oxidative response as well as the possible eco-toxicological effects of their application will be outlined.

21.2 Biosynthesis of Nanonutrients

Nanomaterials are widely used for agricultural applications due to their small sizes and efficient delivery system for nutritive elements. Likewise, NPs exhibit entirely unique or improved properties, meanwhile retaining some distinctive features such as structure, shape, optical properties and nano-size that falling between 1 and 100 nm (Shang et al. 2019). Moreover, the NPs have a high surface-to-volume ratio that qualifies them to incorporate with numerous moieties and in term of size, NPs has become a bridge link between traditional bulk and molecular systems (Henriksen-Lacey et al. 2017; Sharma et al. 2015). Traditionally, several physical and chemical approaches have been employed for the preparation of NPs (Fig. 22.1). Commonly, all fall in either top-down or bottom-up approaches (Khan et al. 2019). However, most of these methods have some drawbacks, e.g., toxicity, labor, high cost and requirement. Hence, in recent years, researchers focused on developing new simple, cheap and safe protocols that guarantee easy preparation and manipulation (Singh et al. 2018). Generally, NPs can be classified into organic and inorganic, and despite their different physical, optical, chemical, electrical, thermal properties, both NPs categories share the same nano sizes. Inorganic NPs integrate metallic, magnetic and semiconductor NPs. In contrast, organic NPs are mainly integrate carbon NPs, e.g., carbon nanotubes, fullerenes and quantum dots (Khan et al. 2019).

The development of more reliable and eco-friendly approaches to synthesize nanonutrients is a significant step in the field of nanotechnology in general, and

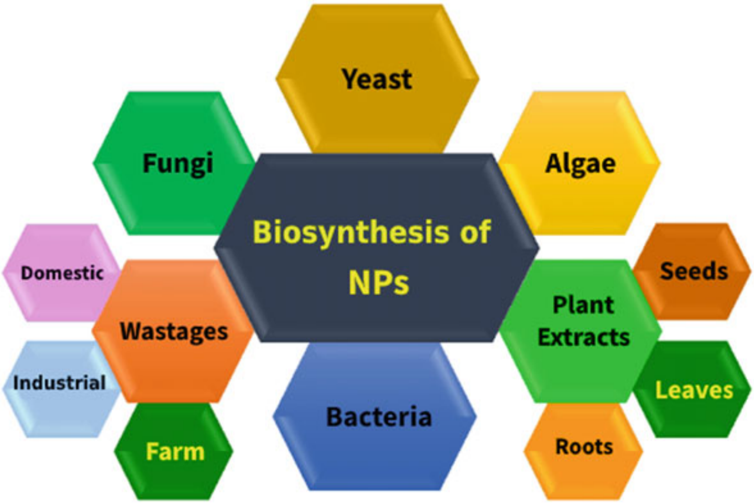

Fig. 22.1 Potential approaches serving biosynthesis of nanoparticles (Figure constructed by Ayoob O. Alfalahi)

agronanotechnology in particular (Prasad et al. 2017). Inorganic metal ions can be transformed into metal nanoparticles through proteins-mediated reductive process by and some other metabolites exist in a wide range of biological systems including eukaryotes such as plants and algae (Makarov et al. 2014), yeasts (Khandel and Shahi 2018), fungi (Chan and Mat Don 2013) and even human cells (Anshup et al. 2005; Khan et al. 2019) and prokaryotes; like bacteria (Das et al. 2017; Shivaji et al. 2011), (Fig. 22.1). However, using microbes to synthesize nanoparticles can be a comparatively challenging technique since maintaining cell cultures will require complicated operations and consecutive purification steps (Kajbafna et al. 2012). Thereby, the using of plant in the production of nanoparticle offer important benefits more than other biological systems where plants are easier to deal with and more available. Furthermore, the procedure of plant-based biogenic synthesis is low-priced and less elaborate as compared to other suggested approaches which are time consuming, elaborate, and require aseptic conditions, such as fungi (Chaudhuri and Malodia 2017).

Interestingly, enzymes and other active components contained by the plant cellular system including alkaloids, flavonoids, glycosides, terpenoids, terpenes, saponins, steroids, tannins and volatiles play an important role as natural capping and reducing agents (Raghunandan et al. 2009). Recently, potassium nano-fertilizer was prepared from banana peels, and the resulted peels-extract was physically and chemically characterized. Although the nanofertilizer was ranged in size between 19 and 55 nm, the majority of the nanoparticles (36%) were in the size of 40 nm. However, only 6% of the synthesized nanoparticles were in a larger size of 55 nm. The prepared nanofertilizer composed of potassium and iron in chelated form, urea, proteins and different amino acids. The results indicated that the increased dosage of banana peels extract improved the germination percentage from 14 to 97%; and from 25 to 93.14% after seven days in tomato and fenugreek crops, respectively (Hussein et al. 2019).

The microwave-assisted hydrothermal technique was successfully adopted by Shebl et al. (2019) to synthesize manganese zinc ferrite nanoparticles using 13 green chemistry techniques. FE-SEM and HR-TEM tests demonstrated the cubic shape of the resulted nanoparticles with 10–12 nm sizes. The efficiency of prepared nanofertilizers was proved in nourishing squash plant (*Cucurbita pepo* L.) and the 23 minerals content. The results showed that lower concentrations had a more positive effect on growth and yield traits, compared to the higher concentrations. Leaf extract of Calotropis (*Calotropis gigantea* L.) was used in green synthesis of zinc oxide nanoparticles in combination with zinc acetate salt mediated by NaOH. An amount of 200 mM zinc acetate found ideal to produce zinc oxide nanoparticles with less than 20 nm size. The prepared crystalline nanoparticles were characterized throughout FTIR (Fourier transform infrared spectroscopy), XRD (X-ray diffraction) and UV–Vis spectroscopy. Biogenic zinc oxide enhances the parameters of seedlings growth and normal development at the nursery stage (Chaudhuri and Malodia 2017).

21.3 Nanofertilizers as a Crop Nutrients

A growing plant needs about eighteen essential elements to grow and develop normally. However, only three of these elements, light, air and water can be obtained naturally from the surrounding environment. Accordingly, the plant depends completely on the soil to ensure the rest of fifteen elements. Nutrients deficiency is a common problem hindering the development of many essential crops (Manwaring et al. 2016). Typically, the use of traditional fertilizers is accompanied by many obstacles, in the forefront of which is the massive additions will lead to; low bioavailability of other microelements, higher accumulation rate of soil and groundwater pollutants, as well as irreversibly impact the soil chemical and/or physical ecology, finally leading to low crops productivity (Meena et al. 2017). To overcome this, nanotechnology has the potential to transfer the agricultural and food industry to a new level, by evolving new insecticide, herbicide and more absorbable nutrients (Duhan et al. 2017).

Nanotechnology started to appeal more attention to develop nanofertilizers with minimum loss to the surrounding environment, slowly and controlled release and improving nutrient use efficiency, thus it became the successful alternative option of improving new forms of fertilizers serving for sustainable agriculture (Zulfiqar et al. 2019). Most of nanonutrients share the same positive effect at relatively low concentrations, meanwhile adverse effects of growth inhibition and deterioration of physiological and morphological indicators are established along with the higher concentrations of NPs (Mahakham et al. 2017; Raliya et al. 2018). For instance, TiO_2 reflected on improved photosynthesis and metabolic activities at very low concentrations (20 mg/L) (Yang et al. 2006). However, higher dosages of TiO_2 adversely affected transcriptomic patterns and root hair development of *Arabidopsis* (García-Sánchez et al. 2015). Nanofertilizers can be categorized into three kinds, nanoscale fertilizers, additive fertilizers, and coated fertilizers (Pandorf et al. 2020). The first category including NPs that contain nutrients. While the second category of nanosize additive fertilizers involved conventional fertilizers combined with nanosize additives. However, loading or coating the conventional fertilizers with NPs represents the nanosize coated fertilizers (Shang et al. 2019).

Commonly, there are two approaches to produce NMs; physical that described as a top-down approach, and chemical that described as a bottom-up approach (Slepička et al. 2019). The desired nutrient can be encapsulated either within nanoporous materials or nanoemulsions. The rapid advancement in the nanotechnology field has shaped alternative classification for nanofertilizers consistent with their actions, control-release or loss fertilizers and nanocomposite fertilizers where nanodevices ensure gradual release of collected micro- and macro-nutrients (Shang et al. 2019). The encapsulated microorganism will be a successful practice to improve the availability of major nutrients around the root area like nitrogen, phosphorus and potassium, thus positively affecting growth and yield attributes (Bargaz et al. 2018). As for the nanoporous, it is an effective option to improve nutrient use efficiency by rationing nutrient supply according to the actual need, furthermore porous nanomaterials can notably increase the solubility of nutritional minerals. For example, ammonium charged zeolites found to be efficient for long-lasting release and diminish leaching losses (Preetha and Balakrishnan 2017). Nevertheless, the synthesized nanofertilizer may be a nano potassium, phosphorus, zinc, silver, silica, iron or titanium dioxide, ZnCdSe/ZnS core shell QDs, Mn/ZnSe QDs, gold nanorods, nanozeolite etc. (Elemike et al. 2019). Particle properties, pH, and kinetics hamper the synthesized fertilizer efficiency. Hence, it is vital to appreciate the nanonutrients mechanism in the plant–soil system (Ruttkay-Nedecky et al. 2017).

Several studies approved the positive significant effect of zinc oxide nanofertilizer ZnO-NPs in improving agronomic, physiologic and yield indices of wheat (Munir et al. 2018) and common bean (Salama et al. 2019). Remarkably, ZnO-NPs found to be more effective in improving germination and growing indicators than ZnSO4, and the latter was more toxic compared to ZnO-NPs, especially in higher dosages (Du et al. 2019). Meanwhile, Khodakovskaya et al. (2013) found that carbon nanoparticles improve growth and yield parameters of tomato. In a pot experiment conducted in growth chamber conditions, Cieschi et al. (2019) applied F, S and M hybrid nanomaterials to synthesize iron-humic nanofertilizers applied in 35, 75 and 150 mmol pot^{-1} on calcareous soils. Treated soybean plants showed a significant increase in iron uptake, reflected on higher shoot fresh weight. The availability of the applied humic nanofertilizers lasted for a long period and was verified in the harvested soybean pods. The applications of nanomaterials are emerging and diversifying rapidly, serving in presenting solutions for the growing challenges (Table 22.1). For example, the development of nanosensors has a promising future in improving plant tolerance to biotic and abiotic stresses known as precision agriculture (Afsharinejad et al. 2016; Kwak et al. 2017). Nanofertilizers can contribute to supporting plant nutritional status in one of two forms. The first is the use of the nanostructured element combined

Table 22.1 The inductive effect of different types and doses of plant nanofertilizers

Nanofertilizer	Applied dose	Targeted plant species	Inductive effect	References
Iron oxide nanoparticles (γ–Fe_2O_3 NPs)	20–100 mg L^{-1}	Pummelo (*Citrus maxima* Burman)	Reduced nutrient loss, inconsequential effect on plant growth	Hu et al. (2017)
Silver nanoparticles (Ag NPs)	10–20 mg L^{-1}	Rice (*Oryza sativa* L.)	Enhanced enzymatic activity, soluble sugar content and seed germination	Mahakham et al. (2017)
Nanozeolite	50 mg L^{-1}	Maize (*Zea mays* L.)	Increased twofold Chlorophyll content, vegetative growth, protein and yield	Khati et al. (2018)
Iron-humic nanofertilizer	35, 75, and 150 mmol pot^{-1}	Soybean (*Glycine max* L.)	Boosted shoot fresh weight	Cieschi et al. (2019)
Zinc oxide nanoparticles (ZnO NPs)	1000 mg L^{-1}	Chili pepper (*Capsicum annuum* L.)	Positively affected Chlorophyll content, vegetative growth, and fruit yield	García-López et al. (2019)
Zinc oxide nanoparticles (ZnO NPs)	50 mg L^{-1}	Common bean (*Phaseolus vulgaris* L.)	Heightened vegetative growth, fresh pod yield, pods physical quality and nutritional value.	Marzouk et al. (2019)

(continued)

Table 22.1 (continued)

Nanofertilizer	Applied dose	Targeted plant species	Inductive effect	References
Nanophosphorus (P NPs)	0.0781 g L^{-1} –0.1563 g L^{-1}	Rice (*Oryza sativa* L.)	Induced higher biomass accumulation and photosynthetic rate	Miranda-Villagómez et al. (2019)
2-D graphite carbon nanoparticles (CNPs)	3000 mg CNP per kg Conventional fertilizer	Lettuce (*Lactuca sativa* L.)	Decreased nitrate leaching, no growth inhibition	Pandorf et al. (2020)
Iron phosphate nanoparticles ($FePO_4$ NPs)	100 µM	Maize (*Zea mays* L.), Cucumber (*Cucumis sativus* L.)	Improved Chlorophyll content and fresh biomass	Sega et al. (2019)
Zinc, iron, and manganese oxide nanoparticles	20 mg L^{-1}	Pumpkin (*Cucurbita pepo* L.)	Enhanced vegetative growth, fruits, yield, and Chlorophyll content	Shebl et al. (2019)

with a carrier that may or may not be in nano scale, like, clay, chitosan, or zeolite (Mohammad et al. 2016). The second is to directly use nutritional elements per se in nanoform supplying through the irrigation system, incorporate with soil or foliar feeding (Fedorenko et al. 2015).

21.4 Nanocarriers Delivering Plant Nutrients

Nanomaterials may be found more frequently in the agricultural and food sectors. Therefore, it can be mentioned that nanotechnology is a rapidly expanding field that provides opportunities for developing nanoscale materials with unique properties as well as creating a wide range of applications (Zoufan et al. 2020). Solutions that secure the nutrients needed for normal plant growth have attracted great attention in the view of industrial and academic prospects in an attempt to guarantee protected and sustainable release of the required nutrients, while minimizing the production cost (Shang et al. 2019). NPs have many unique characteristics that distinguish them from their larger counterparts micro- and macro-scale nutrients, making them more suitable for designing bio-based delivery systems (Jeevanandam et al. 2018). More recently, the application of nanomaterials for the purpose of delivering nutrients and active compounds that promote plant growth has become more popular progressively. The use of nanonutrients in the proper place, time, quantity and composition will determine the efficacy of supplied nutrients (Duhan et al. 2017). In this context, many researchers investigating more effective ways to manufacture and use nanotechnologies to design mechanisms through which an efficient delivery system for agrochemicals can be secured in a streamlined manner (Gunasekaran et al. 2014; Mura et al. 2013). Therefore, to design an efficient nano-transport system for the required nutrient, significant familiarity with the bioavailability of relevant active compounds and their metabolism should be addressed.

Nanoscale delivery systems provide improved nutritional exactness by overwhelming biological obstacles and enhancing nutrient targeting active sites (Vega-Vásquez et al. 2020). Regarding this, it has been confirmed that the plant-derived NPs penetrate the leaf and transmit active components in a two directions, up towards plant leaves and down towards root system (Banerjee et al. 2019). In addition to other features, NPs have an improved penetration property that outperforms their traditional counterparts, thus nearly 33% of the sprayed nanoparticles penetrated into plant leaves, against less than one percent of the ordinary nutrients applied in the identical way (Ruttkay-Nedecky et al. 2017). Treating tomato plants with lipo-nanoparticles loaded with micronutrients (Mg and Fe) were able to bypass acute nutrient deficiency that was not treatable with conventional agricultural nutrients. These applications support the expanded use of nanotechnology to deliver nutrients and increasing crops productivity (Karny et al. 2019).

In the agriculture field, numerous nanostructures have been adopted to deliver macronutrients like N, P, K, and base minerals that stimulate plant growth as well as mono and multilayer carbon nanotubes and non-metallic minerals that positively enhancing plant growth and can be broadly applied in the agriculture sector (Yatim et al. 2018). Clay minerals are natural soil components with modified charge and surface properties capabilities enable them to be a decent option for delivering nutrients and ensuring gradual release at the targeted zones (Jampílek and Kráľová 2017). Alternatively, silica nanoparticles have emerged as potential delivery vehicles for plant nutrients due to its structural resilience in creating nanoparticles of different sizes and shapes, as well as its unique capability to form pores for packing a wide range of biomolecules (Shi et al. 2010). Moreover, silica is a vital micronutrient that significantly supports plant growth and modulates stress response (Campbell et al. 2011; Jang et al. 2013). For example, the absorption and distribution of mesoporous silica nanoparticles (MSNs) have been examined during seeds germination in each of *Arabidopsis*, lupine and wheat grew in a hydroponic system. The nanoparticles were detected in the leaves and roots of plants, however, they did not affect seed germination and had no toxic effects. Nanoparticles are localized within cells and cell walls of the developed root as well as in vascular transport elements, as well as other associated cells. Accordingly, it has been suggested that MSNs can be hired for delivering nanoparticles into plant biosystems (Hussain et al. 2013).

21.5 Nanofortifiers

Agricultural products are vital components in the food basket, especially for rural society and, hence decreasing crop productivity will pose a serious threat to the nutritional security of these societies and may result in starvation (Vijaya Bhaskar et al. 2017). Always, there is a need for concerting efforts to develop plants towards magnifying production and to diminish the adverse effects on plant production that can lead to malnutrition and starvation. Nevertheless, key micronutrient deficiencies has become a persistent issue in resource-poor communities. Meanwhile, many major crops are limited suppliers for essential nutrients necessary for normal human growth and development (Garg et al. 2018).

Fertilizers are enriched with minerals necessary for normal plant growth and development. Thereby, macro and/or micro-nutrients deficiency will be manifested in abnormal organs development, as well as edible parts with low essential nutrients (Etienne et al. 2018). Notably, nutrients shortage is not always related to soil deficiency of such nutrients, rather some roots are with small pores that limit their ability to absorb and transport the needed nutrients (Elemike et al. 2019). Although chemical fertilizers is an old common practice and it has enormously improved the agricultural outputs in terms of quality and quantity, they negatively contribute to soil, fertility, structure, nutrient balance, in addition to its side effects on the local ecosystem that representing a significant threat for the long term (Lin et al. 2019). On the other hand, conventional fertilizers have active particles with higher than 100 nm in size, make them vulnerable to leach (Giroto et al. 2017). Furthermore, nutrients can be depleted from the soil due to continuous farming, therefore there is an urgent need for frequent recovery of agricultural lands using various synthesized chemical and green or bio-fertilizers (Khan et al. 2019). Principally, not all peoples are able to change their lifestyle and diversify their food to ensure as many as it possible of necessary nutrients. Alternatively, biofortification is an emerging feasible solution focusing on enhancement of the nutritional value of plant-derived food via crop breeding and cultivation practices (Jha and Warkentin 2020), in addition to modern technologies.

Due to unique properties, NPs have promising applications in the near future of agricultural systems. The application of nutrients in nanoscale will minimize the wasted costly active substances and allow sustainable release at the targeted area. Thereby, effective uptake of the required nutrients can be achieved (Khan et al. 2019; Sekhon 2014). In this contest, achieving healthy nutrition requires the development of novel varieties forfeited with essential minerals (e.g. iron, zinc, manganese, copper, selenium, and iodine), amino acids (tryptophan and lysine) and vitamins. Affordability and availability are the two keys that confer the nanofortification an advantage over other interventions serving in battle against malnutrition particularly in low-income countries (Jha and Warkentin 2020). Fortified crops are extensively cultivated and consumed by the people globally. Staple food crops like cereals (e.g. wheat, rice, maize and sorghum), pulses (soybean, common bean), vegetables and fruits have been fortified for various nutritional aspects using different agronomical and/or biotechnological approaches (Garg et al. 2018).

The successful application of nanofortifiers is mainly depended on the plant type, physical and chemical properties of the prepared NPs. Therefore, nanotechnology will serve efficiently in fortifying plant with the desired nutrients (Patra and Baek 2014; Patra et al. 2018). Nanofortification will use the nanoporous present on the plant part surfaces, therefore, this technology will be a unique platform serving in modulating sustainable nutrient delivery systems (Elemike et al. 2019). The efficacy of applied nanonutrients, and zeolites can be enhanced through the encapsulated NPs. Ultimately, this in turn will quickly restore soil fertility and minimizing environmental pollution (Mout et al. 2017).

21.6 Nanonutrients Mediating Oxidative Response

During their life cycle, plants may expose to a wide range of inappropriate environmental conditions, typically termed stresses. Under this, stresses are divided into two categories; abiotic stress including salinity, drought, pollutants, toxic metals, extreme temperature, radiations and pesticides; and biotic stress comprising high density, pathogens and insects for instance (Waqas et al. 2019). Throughout their adaptive response, plants develop multiple physiological and molecular techniques mainly excessive ROS that in turn will affect the plant cellular processes and shape the total response (Huang et al. 2019). The balance between generated ROS and scavenging them by antioxidant defense system will determine the negative effect of stress condition, and, thereby the sustained productivity of plants (Xie et al. 2019). Stress-induced free radicals (e.g. hydrogen peroxide, peroxy radical, superoxide radical, perhydroxy radical, hydroxyl radical and singlet oxygen) are capable of damaging the plant cellular components involving proteins, lipids, and nucleic acids, thus triggering programmed cell death (PCD) which ultimately results in plant death (Elsahookie et al. 2009). Consequently, the improvement of plant tolerance to harsh environmental conditions begins with maintaining the antioxidants level in order to enhance the machinery defense and minimize the oxidative damage to the lower limit (Khan et al. 2019).

Several enzymes are involving in the machinery defense system combating oxidative stress in a wide range of plant types including superoxide dismutase (SOD), catalase, peroxidase and the ascorbate glutathione enzymes (Sarker and Oba 2018). Biological systems witness a rapid growing of nanotechnology applications. Under this, there is a strong belief that nanoparticles can improve the plants tolerance to oxidative stress by enhancing the ability of their antioxidant system (Zoufan et al. 2020). Via biochemical investigations, a strong believe have emerged that NPs playing a crucial role in regulating key biological processes in plants such as photosynthesis, antioxidant enzymes, oxidative stress and gene expression (Tan et al. 2018). Like other substances, nanoparticles show different norms of action according to the origin, preparation method, size and applied concentration. Regarding this, nanoparticles found to be highly concentration-dependent materials, in which low concentration resulted in low oxidative stress, and finally reduce the antioxidant activity (Sharma et al. 2019).

The adoption of nanocolloidal solutions as micronutrients is an effective approach to improve plant tolerance to unfavorable environmental conditions and ensures high quantity and quality yields of food crops. The recent reports showed that nanomolybdenum was efficiently reduced the oxidation level by activating antioxidant enzymes including superoxide dismutase in about 15%, thereby enhancing plants' adaptation to stress conditions (Taran et al. 2016). The activity of ROS scavenging enzymatic system including superoxide dismutase, catalase and ascorbate peroxidase was investigated in *Brassica juncea* nourished by two types of nanoparticles micronutrients, titanium dioxide (TiO_2) and copper oxide (CuO) (Sunita and Shekhawat 2016). The increased level of TiO_2 NPs had a positive effect on plant growth, whereas the opposite effect was noticed for CuO NPs. Interestingly, the less bioaccumulated NPs improved the defense mechanism against stress conditions via antioxidative enzymes.

Similar findings were stated by Homaee and Ehsanpour (2016) as they compared two sources of silver (Ag NPs and Ag ions) in terms of oxidative response development in potato plant (*Solanum tuberosum* L.) under in vitro conditions. Although both Ag forms, NPs and ions had elevated the activity of the antioxidant enzymes compared to the control, the higher concentration of NPs and ions significantly diminished the oxidative enzymatic activity. Recently, Zoufan et al. (2020) reported a substantial induction in the oxidative stress in response to the subjected concentrations of Zn oxide nanoparticles applied on *Chenopodium murale* using a hydroponic system. The different treatments of ZnO NPs magnified the activity of superoxide dismutase (SOD), catalase (CAT) and guaiacol peroxidase (GPX) along with a significant reduction in growth indices.

21.7 Nanonutrients Modulating Plant Secondary Metabolites

The possible effects of NPs have been investigated consistently across plant species on different morphological and physiological attributes. Unfortunately, the modulatory effect of NPs is still poorly understood, where NPs can improve the secondary metabolite processes, hence active natural compounds (Ebadollahi et al. 2019). The induction of ROS found to be strongly addicted to the applied NPs through the plant kingdom (Marslin et al. 2017). The importance of ROS cannot be summarized in reflecting the cell fatigue, as it has an important role in several developmental processes. Additionally, many literatures have provided strong evidences of ROS-related signal molecules that mediating plant secondary metabolisms (Singh et al. 2016). In fact, some of these literatures referred to ROS themselves as signaling molecules and can be inductive to secondary metabolism pathways (Jacobo-Velazquez et al. 2015; Simon et al. 2010).

Although several reports established the important role of NPs in physiological, growth and developmental plant aspects (Gohari et al. 2020), the influence of NPs on plant secondary metabolites is not fully discovered, however, numerous studies assured the modulation of NPs towards plant secondary metabolism (Ghorbanpour and Hadian 2015). Plant secondary metabolites are commonly regulated by transcriptional process guided by secondary signaling messengers, and the later has a prevailing link with ROS (Meraj et al. 2020). In this perspective, it have been suggested that NPs may regulate the production of secondary metabolites since ROS burst is a common indication of NPs application (Egea et al. 2017) (Table 22.2). More recently, an alternative scenario has been proposed to explain the relationship between nanoparticles and the overproduction of secondary metabolites, in which it is believed that the latter plays a protection role against oxidative response developed after NPs exposure (Ebadollahi et al. 2019). Regardless of the mechanism by which nanomaterials can regulate the cellular production and accumulation of secondary metabolites, a number of investigations have indicated that the plant shows a pattern of response to nanomaterials largely simulating the response to biotic and abiotic stresses (Khodakovskaya et al. 2011b; Kohan-Baghkheirati and Geisler-Lee 2015). The catalytic effect of nanomaterials in increasing the production of secondary metabolites may include a number of cellular signal transduction pathways, primarily via MAPK cascade (mitogen-activated protein kinase), cytosolic Ca^{2+} and ROS burst (Sosan et al. 2016). Zhang et al. (2013) reported enhanced production of secondary metabolites (artemisinin) in hairy roots of *Artemisia annua* in response to silver nanoparticles (AgNPs), along with an elevated level of oxidative stress and antioxidant enzymatic activity. The biosynthesized silver nanoparticles (AgNPs) had the same positive effect on the synthesis of phytochemical diosgenin in fenugreek seedlings. The inducibility of Ag NPs leads to a profound increase in the produced secondary metabolites that open up new techniques by which natural and medicinal plant products can be magnified (Jasim et al. 2017). Garcia-Sanchez et al. (2015) noticed that AgNPs, TiO_2NPs and carbon nanotubes (CNTs) lead to a

Table 22.2 The modulation of plant secondary metabolites in response to different types and doses of nanoparticles (NPs)

Nanoparticles	Applied dose	Plant species	Modulated secondary metabolites	Reference
Aluminum oxide nanoparticles (Al_2O_3 NPs)	100 μg ml^{-1}	Tobacco (*Nicotiana tabacum* L.)	Accumulated phenolics compounds	Poborilova et al. (2013)
Ag-SiO_2 core-shell nanoparticles	900 mg L^{-1}	Sweet wormwood (*Artemisia annua* L.)	Increased artemisinin about four folds	Zhang et al. (2013)
Titanium dioxide nanoparticles (TiO_2 NPs)	100 mg L^{-1}	Spirulina (*Arthrospira platensis*)	Magnifying the secreted phenolic compounds	Comotto et al. (2014)
TiO_2 NPs, Ag NPs and multi-walled carbon nanotubes (MWCNTs)	0.2–25 μg mL^{-1}	*Arabidopsis* (*Arabidopsis thaliana* L.)	Upregulated anthocyanin and flavonoid gene expression	Garcia-Sanchez et al. (2015)
Multi-walled carbon nanotubes (MWCNTs)	100 μg ml^{-1}	*Satureja khuzestanica*	Maximize flavonoid and phenolics content	Ghorbanpour and Hadian (2015)
Cerium (IV) oxide and Indium(III) oxide nanoparticles (CeO_2 and In_2O_3 NPs)	1000 mg L^{-1}	*Arabidopsis* (*Arabidopsis thaliana* L.)	Provoked synthesis of phenylalanine ammonia lyase (PAL)	Ma et al. (2016)
Cadmium oxide nanoparticles (CdO NPs)	2.03 ± 0.45 105 particles cm^3	*Barley* (*Hordeum vulgar* L.)	Increased ferulic acid and isovitexin	Večeřová et al. (2016)

(continued)

Table 22.2 (continued)

Nanoparticles	Applied dose	Plant species	Modulated secondary metabolites	Reference
Silver nanoparticles (Ag NPs)	200 µL of 1 µg mL^{-1} (w/v)	Fenugreek (*Trigonella foenum-graecum* L.)	Enhanced diosgenin synthesis	Jasim et al. (2017)
Titanium dioxide and Cerium (IV) oxide nanoparticles TiO_2 and CeO_2 NPs	500 mg L^{-1}	*Arabidopsis* (*Arabidopsis thaliana* L.)	Upregulated photosynthesis and ethylene	Tumburu et al. (2017)
Titanium dioxide TiO_2-Perlite nanocomposites (NCs)	200 mg L^{-1}	St. John's wort (*Hypericum perforatum* L.)	Elicited the production of volatile compounds, hypericin and pseudohypericin	Ebadollahi et al. (2019)
Titanium dioxide nanoparticles TiO_2 NPs	100 mg L^{-1}	Moldavian dragonhead (*Dracocephalum moldavica* L.)	Improved geranial, geraniol and z-citral content	Gohari et al. (2020)

marked impact on genes coding anthocyanin and flavonoid in *A. thaliana*. Also, the increased concentration of carbon nanotubes in culture medium improved phenolics and flavonoids content, thereby growth parameters of *Satureja khuzestanica* (Ghorbanpour and Hadian 2015).

21.8 Biosafety of Nanomaterials

Nanomaterials are gaining increased attention for boosting plants' nutrient and agricultural productivity, but then again the safety of these materials should be considered because only a thin line separating shortage and toxicity of nanomaterials (Shafiq et al. 2020). There is no doubt that nano techniques have witnessed a great expansion during the past two decades, and it has imposed itself as one of the fastest growing applications in the pharmaceutical, physical, chemical and agricultural fields (Usman et al. 2020). Accordingly, this huge growth of use has greatly contributed to the increased leakage and accumulation of NMs in the ecosystem (Shang et al. 2019). Soil, water and air are the three major gears of earth ecosystem where plants are growing. Statistics showed that nanomaterials have different accumulation rates in each component, nevertheless, soil has shown the highest rate of accumulated nanomaterials compared to water and air (Yang et al. 2017). Consequently, due to their limited choices in selecting the growing environment, plants are more vulnerable than other organisms to the less apposite component in the ecosystem.

The most important character of nanostructures (NPs) is the low of at least one dimension (1–100 nm), which be responsible for their distinctive properties and biological activity (Ndolomingo et al. 2020). On the other hand, this tiny size offers NPs their destructive ability to the cell components and limits their uses. For that reason, it looks more rational not to exaggerate these materials (Jeevanandam et al. 2018). Subsequently, and for real assessment, it became necessary to study both kinetics and biotoxicity of nanomaterials in the short and long term of use (Ripp and Henry 2011). The time factor is crucial in determining the toxicity level of a specific nanomaterial, as many NPs revealed different toxicity behavior over time. The net effect of nanomaterials is interestingly driven by many variables, such as type of nanomaterial, origin (organic or inorganic), preparation procedure (biosynthesis, physical or chemical), form (ionic or non-ionic), magnetism properties, nano-size and the targeted plant species, however, the applied dose seems the most critical factor in determining NPs toxicity (Jeevanandam et al. 2018). In light of the large number of variables that each nanomaterial holds, it seems difficult to accurately predict its fate in the added environment (Bundschuh et al. 2018) (Fig. 22.2).

Soil represents the largest repository of nanoparticles, that's why biotic (bacteria, mycorrhiza, fungi) and abiotic factors (heat, pH, moisture) have an essential role in the accumulation and release rates of such materials in the soil, which finally determine NPs toxicity (Simonin et al. 2015). Given the concentration, size, solubility, shape, surface and aggregation state that each nanoparticle retains, it seems difficult to accurately predict the biological and chemical and/or physical behavior of those materials in the surrounding environment (Morales-Díaz et al. 2017).

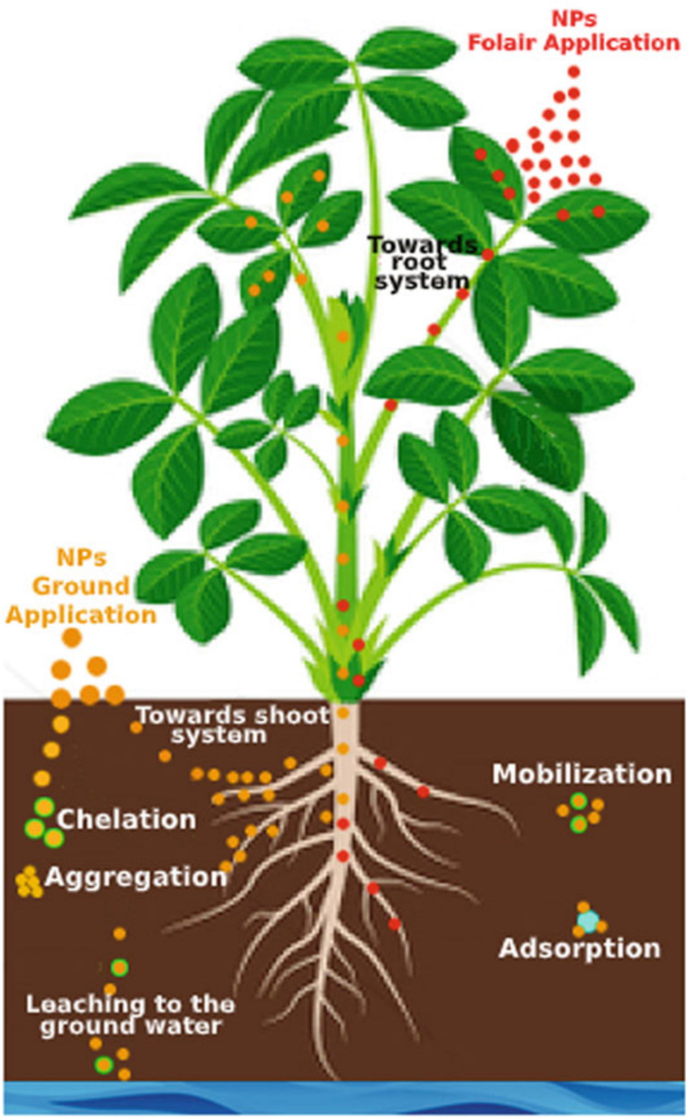

Fig. 22.2 Suggested scenario of the foliar- and soil-applied nanoparticles fate in the ecosystem (Figure constructed by Ayoob O. Alfalahi)

The toxicity of nanomaterials remarkably depends on their surface-to-mass ratio, that gives NPs the higher affinity to adsorb pollutants of the niche, particularly heavy metals like cadmium, cobalt, lead, nickel (Yaqoob et al. 2020).

Several studies have investigated the biotoxicity of nanoparticles using different types, forms and concentrations of NPs (Kalpana and Rajeswari 2018; Zhu et al. 2008). Vicario-Pares et al. (2014) confirmed that the three used metal oxides (TiO_2, CuO and ZnO NPs) were more toxic to zebrafish embryo in the ionic form compared to the NPs. In a part of their biological effects, nano-sized materials have a distinct ability to alter the enzymatic soil content, thereby disrupting their efficacy, and lead to toxic effects (Elemike et al. 2019). It is interesting to note that the nano-scale materials possess features fundamentally different from their larger counterparts (micro- and macro-scale) of the same material (Urban et al. 2016). The sensitivity that revealed by the different organisms is another key factor that may indirectly controls the toxicity effect caused by nanoparticles (Table 22.3). Regarding this, the effect of some nanoparticles may be restricted to the exposed plant, while in other cases the destructive effect can encompass the plant-mycorrhiza and/or rhizobia symbiotic relationships (Tian et al. 2019). In addition, the encapsulation of nanomaterials can significantly alter their properties and solubility, and its effect extends to influence the ecosystem components and toxic level. Yin et al. (2012) stated that the suspension of Ag NPs had a positive effect on the seed germination of several plant species, however the coated Ag NPs showed a higher toxic level and less favorable effect upon seed germination. Physiological and growth parameters of *Eichhornia crassipes* were investigated in response to different concentrations of two Ag nanoforms, biological and synthesized. Although the higher applied concentration of Ag exhibited a higher accumulation rate in different plant parts after 5 days, the synthesized form was more able to inhibit the plant growth (Rani et al. 2016).

21.9 Conclusions and Prospects

The versatility of nanomaterials has become a reality we live in today, yet their use appears to be growing steadily, mainly in areas that do not require a high level of caution. In the agricultural field, nanomaterials have relatively greater flexibility to be used for designing novel fertilizers with enhanced features that enable them to effectively provoke secondary metabolites and plant growth. Although nanomaterials can be disruptive and nanotoxic, in addition to its association with the ROS generation, however, from a fortification viewpoint, it may also be creative in designing agents impacting through a combination of chemical and physical approaches of action. Due to vagueness of nanomaterials biosafety and their complicated environmental interactions, there is a need for extensive investigations before releasing them for prevalent use. It must be said that almost all bulk materials have a corresponding nanoscale, thus the nanomaterials were and still are an integral part of earth biological system. However, nanomaterials are strong candidates for dominating different agricultural sectors, basically for rationalizing the use of expensive agricultural inputs and chemicals whose use in high concentrations pose a real threat to the ecosystem.

Table 22.3 The toxic effect of different nanoparticles against several plant species

Applied nanoparticles	Plant species	Toxic effect	Reference
Zinc oxide nanoparticles (ZnO NPs)	Perennial ryegrass (*Lolium perenne* L.)	Reduced the plant biomass	Lin and Xing (2008)
Carbon nanotubes	Tobacco (*Nicotiana tabacum* L.)	Upregulation of genes responsible for water transport and plant growth	Khodakovskaya et al. (2011a)
Silver nanoparticles (Ag NPs)	*Microstegium vimeneum*	Growth inhibition	Colman et al. (2013)
Silver nanoparticles (Ag NPs)	Wheat (*Triticum aestivum* L.)	Increased oxidative stress	Dimkpa et al. (2013)
Zinc oxide nanoparticles (ZnO NPs)	Onion (*Allium cepa* L.)	Increased chromosomal abnormalities	Raskar and Laware (2014)
Gold nanoparticles (Au NPs)	Arabidopsis (*Arabidopsis thaliana* L.)	Upregulation of genes responsible for oxidative response, glutathione, water transport and plant hormones	Shukla et al. (2014)
Silicon dioxide nanoparticle (SiO_2 NPs)	Cotton (*Gossypium hirsutum* L.)	Reduced plant biomass, SOD activity and IAA concentration	Le et al. (2014)
Iron oxide nanoparticles (Fe_3O_4 NPs)	Duckweed (*Lemna gibba* L.)	Reduced Chlorophyll content, Increased reactive oxygen species (ROS) and growth inhibition	Barhoumi et al. (2015)
TiO_2 nanoparticles, Ag nanoparticles, Multi-walled carbon nanotubes	Arabidopsis (*Arabidopsis thaliana* L.)	Negatively affected transcriptomic patterns and root hair development	García-Sánchez et al. (2015)
Silver nanoparticles (Ag NPs)	Stevia (*Stevia rebaudiana* Bert.)	Inhibits normal development and reduced Chlorophyll content	Castro-González et al. (2019)
Silver nanoparticles (Ag NPs)	Chlamydomonas (*Chlamydomonas reinhardtii* P.A. Dangeard)	Reduced Chlorophyll content and electron transport activity	Dewez and Oukarroum (2012)

(continued)

Table 22.3 (continued)

Applied nanoparticles	Plant species	Toxic effect	Reference
Thin-walled carbon nanotubes (CNTs)	Rice (*Oryza sativa* L.)	Decreasing the concentrations of endogenous plant hormones and inhibited plant growth	Hao et al. (2016)
Iron oxide nanoparticles	Sunflower (*Helianthus annuus* L.)	Reduced the nutrients uptake and root hydraulic conductivity	Martínez-Fernández et al. (2016)
Copper oxide nanoparticles (CuO NPs)	Arabidopsis (*Arabidopsis thaliana* L.)	Increased ROS accumulation, adversely affected chlorophyll contents, stomatal aperture and reduced biomass	Azhar et al. (2020)
Titanium Dioxide Nanoparticles (TiO_2 NPs)	Moldavian dragonhead (*Dracocephalum moldavica* L.)	Increased antioxidant enzyme activity and improved all agronomic traits	Gohari et al. (2020)
Iron oxide nanoparticles (Fe_3O_4)	Yellow alfalfa (*Medicago sativa ssp. falcate* L.)	Increased chlorophyll a fluorescence, miRNA expression, genotoxicity and reduced genome stability	Kokina et al. (2020)
Carbon nanotubes, Carbon nanofibers, Silicon nanotubes	Heterosigma (*Heterosigma akashiwo* Y. Hada)	Inhibited growth	Pikula et al. (2020)
Iron Oxide Nanoparticles (Fe_3O_4)	Rocket (*Eruca sativa* L.)	Induced genotoxicity	Plaksenkova et al. (2019)
Cerium oxide nanoparticles (CeO_2)	Peas (*Pisum sativum* L.)	Reduced Chlorophyll content and plant growth	Skiba and Wolf (2019)
Zinc oxide nanoparticles (ZnO NPs)	Arabidopsis (*Arabidopsis thaliana* L.)	Reduced Chlorophyll content, Growth inhibition	Wang et al. (2016)
Silver nanoparticles (Ag NPs)	Lettuce (*Lactuca sativa* L.)	Blocking nutrient transport, Induce the enzymatic antioxidants activity, Biomass reduction	Wu et al. (2020)

(continued)

Table 22.3 (continued)

Applied nanoparticles	Plant species	Toxic effect	Reference
Zinc oxide nanoparticles (ZnO NPs)	Black mustard (*Brassica nigra* L.)	Adversely affects seed germination and seedling growth, increasing the antioxidative activities and non-enzymatic antioxidants	Zafar et al. (2020)
Zinc oxide nanoparticles (ZnO NPs)	*Nettle-leaved goosefoot* (Chenopodium murale L.)	Reduced Chlorophyll content and Soluble proteins, Increased oxidative stress, SOD and CAT activity, Inhibited growth	Zoufan et al. (2020)

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