

Chapter 13

Toxicity of Nanomaterials in Plants and Environment



Majid Peyravi, Mohsen Jahanshahi, and Ali Bali Eslami

Contents

13.1	Introduction.....	377
13.2	Toxicity Effects of NMs on Plant Growth.....	378
13.2.1	Plant Uptake of ENMs.....	378
13.2.2	Carbon Based Engineered Nanomaterials.....	379
13.2.3	Metal and Metal Oxide Engineered Nanomaterials.....	383
13.3	Effect of ENMs on the Toxicity of Environmental Pollutants.....	394
13.3.1	Carbon Nanomaterials.....	394
13.3.2	Metal and Metal Oxide Nanoparticles.....	397
13.4	Conclusions.....	398
	References.....	399

13.1 Introduction

Nanomaterials are chemical materials or substances that are produced and used at a very small scale. The most important feature of nanomaterials is their small size which ranges between 1 and 100 nm. These intrinsic unique features are the reason for the widespread potential applications of NMs (Ball 2002). Smaller size of NMs helps them to penetrate particular cellular sites and their additional surface area simplifies more adsorption and targeted distribution of substances (Kashyap et al. 2015). The NMs exist in anthropogenic waste materials like coal combustion,

M. Peyravi (✉)

Department of Chemical Engineering, Babol Noshirvani University of Technology,
Babol, Iran

Nanotechnology Research Institute, Babol Noshirvani University of Technology, Babol, Iran
e-mail: majidpeyravi@nit.ac.ir

M. Jahanshahi · A. B. Eslami

Department of Chemical Engineering, Babol Noshirvani University of Technology,
Babol, Iran

welding fumes, diesel exhaust (incidental NMs), as well as in volcanic dust, mineral composites, etc. (natural NMs) (Monica and Cremonini 2009). Moreover, engineered nanomaterials (ENMs) produced with nanoscale dimensions are commonly grouped into four kinds, viz., metal based NMs, carbon based NMs, metal oxides, composites, and dendrimers (Ju-Nam and Lead 2008). Due to their wide range in uses, NMs might easily be intentionally or incidentally released into the environment (Hashimoto et al. 2017).

Nanomaterials have been shown to affect plants at every step of their life cycle (Liu et al. 2016a). NPs play important role in the conservation of plants against diverse abiotic stresses such as cold, drought, and salinity. Tiny size and large active surface area of NPs provide access for toxic metals for binding and thus alleviate accessibility and toxicity of metals (Worms et al. 2012). Apart from their positive effects several NMs illustrate toxicity symptoms. The presence of NMs in the soil and water induces oxidative stress and causes loss of photosynthesis, chlorophyll (Chl), biomass and nutritive value of crop plants (Peralta-Videa et al. 2014), and decrease in germination rate, root, and shoot length (Da Costa and Sharma 2016; Wang et al. 2016c). Also, when released into the environment, ENMs can interact with a wide array of environmental pollutants (e.g., organic pollutants and heavy metals), which may effect on environmental behavior (Deng et al. 2017; Canesi et al. 2015). At the same time, an interaction between ENMs and pollutants may also effect on physicochemical property and bioavailability of ENMs (Cui et al. 2016). Therefore, it is necessary that we understand the destiny and toxicity of NMs, specifically in plants and environment.

In this chapter, toxicity of nanomaterials in plants and environment is investigated. First the toxicity effect of NPs on plant growth and then the effect of ENMs on the toxicity of environmental pollutants are discussed.

13.2 Toxicity Effects of NMs on Plant Growth

13.2.1 Plant Uptake of ENMs

It is not completely clear as to how NMs may penetrate into the plant. However, NMs penetrate into the plant through adsorption on the root surface, incorporation into the cell wall, and uptake into the cell (Nowack and Bucheli 2007). The NMs, larger than the cell wall pore size, stick to the epithelial root cells causing physical injuries to the cells (Miralles et al. 2012), pores fouling, and decrease root hydraulic conductivity leading to changed color of the roots surface (Martínez-Fernández et al. 2016), alleviated water absorption, and nutrient uptake capacity. However, NMs smaller than the pore size of cell could diffuse through lateral root junctions and have been found in the roots, stems (xylem and phloem), and leaves of the plant (Tripathi et al. 2017). It is also noted that NMs can enter the nucleus, mitochondria, and chloroplast of the plant cell as well as directly interact with DNA, RNA, or

proteins (Serag et al. 2010). Direct interaction of NMs to DNA, RNA, or proteins causes mechanical infraction and affects integrity of cell membrane and cell walls (Jang et al. 2003).

13.2.2 Carbon Based Engineered Nanomaterials

A wide use of carbon-based NMs (CNMs) has led to its potential transport to living systems, either intentionally in discharges, or incidentally in spillages, and greater probability of the unfavorable environmental effects (Baughman et al. 2002). Among CNMs, the most studied materials are carbon nanotubes (CNTs) and graphene oxide (GO). As CNMs are considered extremely hydrophobic with the great tendency to aggregate, these could be expected to reside in the living system (De La Torre-Roche et al. 2013). This feature would increase the CNMs capability to interact with various organic substances. So, the low surface friction of CNTs is needed to help the transfer of organic substances into the cytoplasm (Santos et al. 2013).

13.2.2.1 Carbon Nanotubes

Carbon nanotubes (CNTs) may have possibly single or multiple layers of carbons established in a cylinder. CNTs are in the form of fibers, with the properties very diverse from massive graphite or carbon. Thus, CNTs have great tensile strength and are possibly the powerful, smallest fiber recognized. There is proof that CNTs could dislocate to systemic sites, such as roots, leaves, and fruits, which could involve a potent interaction with the cells of the tomato seedling. This resulted in considerable alteration in roots gene expression, leaves, and total fruits. CNTs have phytotoxic effects on plant cells because of accumulation and reason cell death in a dose dependent manner. Cell death is illustrated by electrolyte leakage and the swelling of the cell plant. Also, alterations in the content of plant metabolites after exposure to CNTs have been identified. For example, the tomato treated with CNTs showed an increase in fruit metabolites, such as alkaloid senecionine and terpenoids (McGehee et al. 2017).

13.2.2.2 Graphene and Graphene Oxide

Graphene is a two-dimensional allotropic form of carbon. It can be considered as a one atom layer of graphite. At higher concentrations of graphene (1000 mg L^{-1}), the root growth of red cabbage and spinach alleviated compared to the control plant (Begum et al. 2011; Al-Ghamdi et al. 2014; Ye et al. 2012) (Fig. 13.1). This is because of the accumulation of graphene using H_2O_2 visualization, together with observable

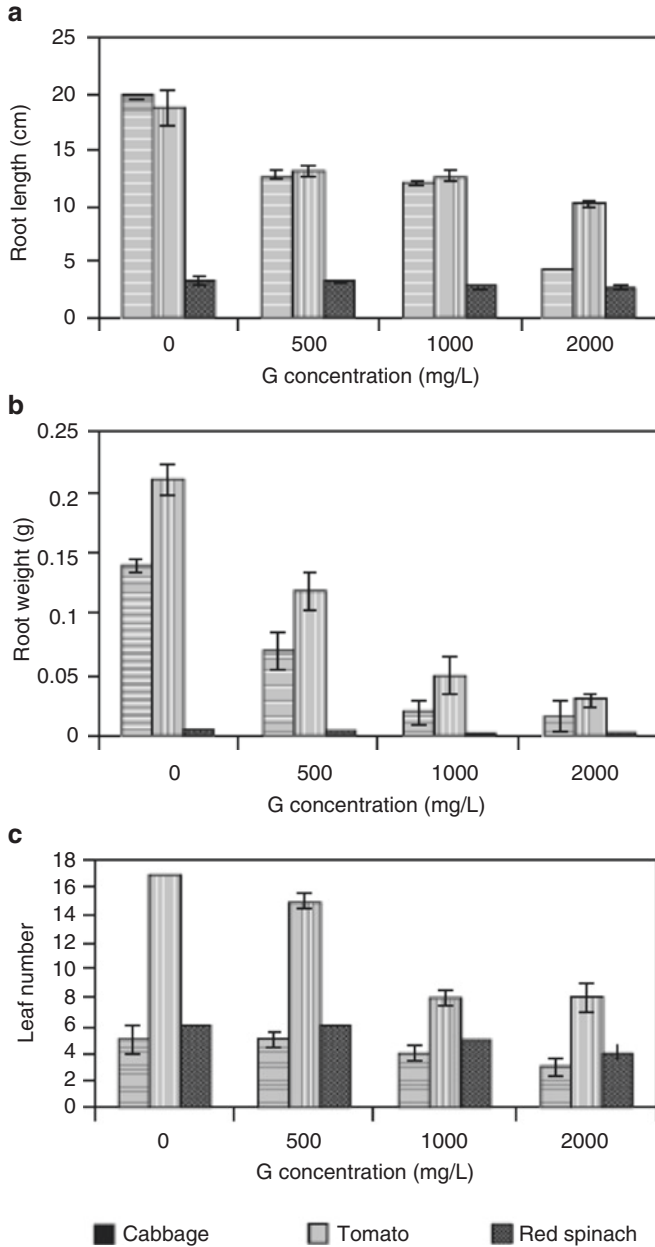


Fig. 13.1 Effect of graphene (G) on red spinach, cabbage, and tomato seedlings. At 21 days seedling growth on Hoagland media with graphene (0, 500, 1000, and 2000 mg L⁻¹) was utilized for all measurements. (a) Root length, (b) shoot length, (c) root weight, (d) shoot weight, (e) leaf number, and (f) leaf area (Begum et al. 2011)

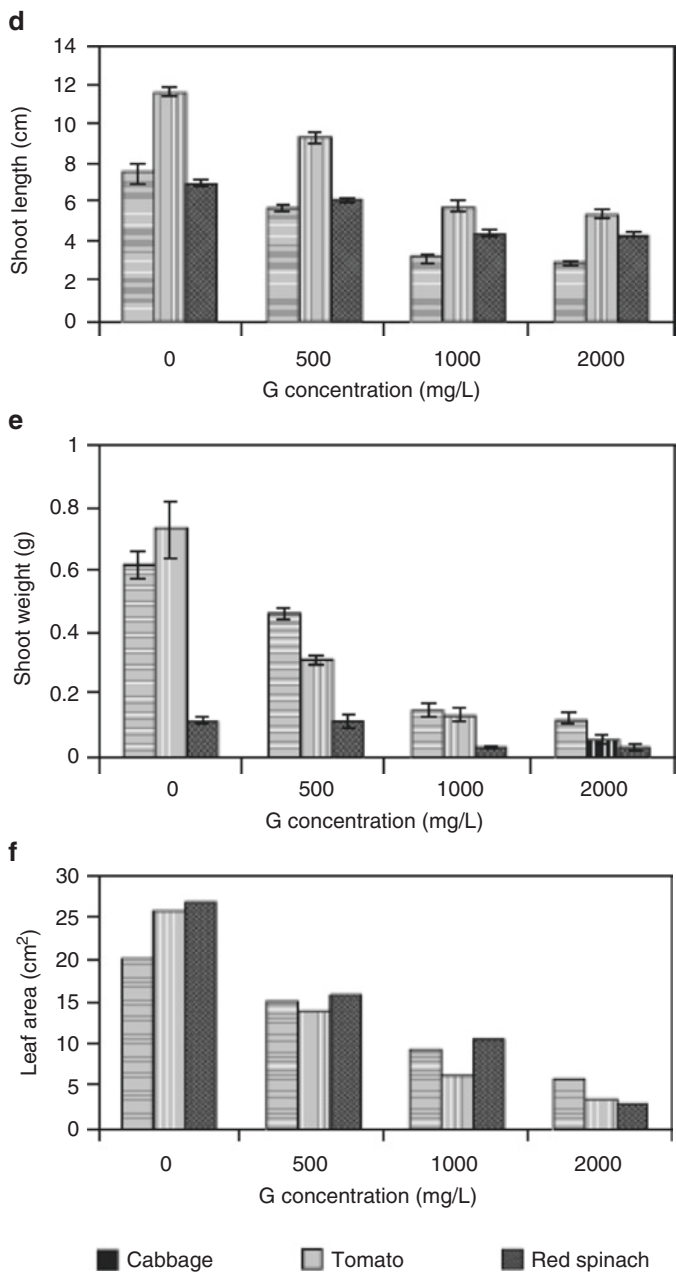


Fig. 13.1 (continued)

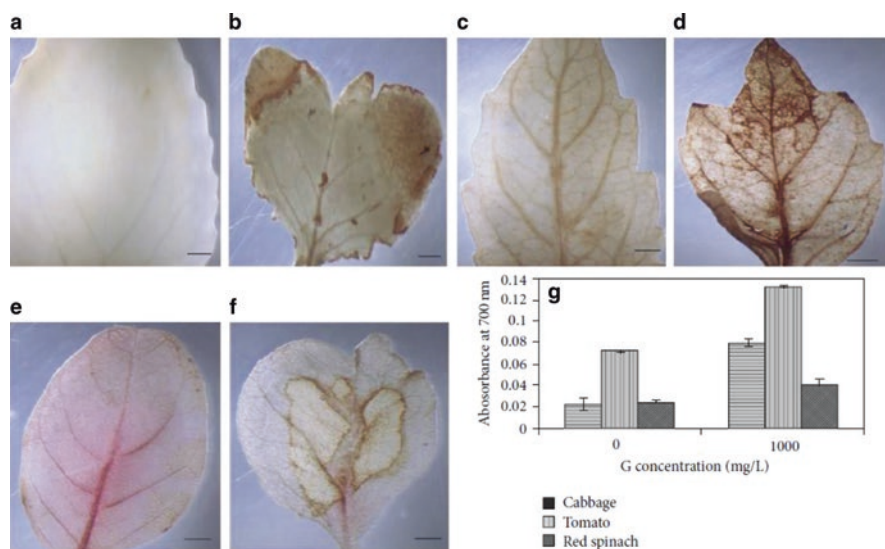


Fig. 13.2 Influence of graphene (G) on accumulation of H₂O₂ in leaves tested by means of the ROS-sensitive dye DAB of tomato, red spinach, and cabbage seedlings. At 21 days leaves treated with or without 1000 mg L⁻¹ graphene were employed for all measurements. (a), (c), and (e) are cabbage, tomato, and red spinach leaves untreated, respectively. (b), (d), and (f) are cabbage, tomato, and red spinach leaves treated, respectively. The brown staining shows the formation of a brown polymerization product when H₂O₂ reacts with DAB. (g) Influence of graphene (1000 mg L⁻¹) on the aggregation of H₂O₂ in treated leaves as measured utilizing DAB (Begum et al. 2011)

signs of necrotic damage lesions and proof of a bulky electrolyte leakage, showing an oxidation stress mechanism (Begum et al. 2011; Mogharabi et al. 2014).

For example, intracellular decrease in oxidation system possibly has a crucial function in the induction of loss of cell life induced by graphene (Fig. 13.2). It explained the aggregation graphene as leading to cell death, demonstrated by electrolyte leakage from cells. The use of extra graphene may cause swelling in *Origanum vulgare* and *Origanum* (Begum et al. 2011). Graphene is known as inducing phytotoxic effects in cells of plants because of the aggregation mechanism. This causes loss of cell life and the aggregation in a dose-dependent manner (Akhavan and Ghaderi 2010; Sasidharan et al. 2011). There is inevitably proof that graphene could translocate to systemic sites, such as roots, leaves, and fruits, which engage in a strong interaction with the tomato seedlings cells, leading to essential modifications in total gene expression in leaves, roots fruits, and applying toxic effects (Anjum et al. 2014; Kim 2013). With that, it is unexpected to detect the graphene toxicity effects on earthy plant species, in cabbage, red spinach, and tomato (Lee and Kim, 2014; Kim, 2013). Past studies observed the similar growth pattern in cabbage, red spinach, and tomato utilizing graphene NMs (Anjum et al. 2013; Lee and Kim 2014). At high concentrations of graphene (1000 mg L⁻¹), the root hair growth of red spinach and cabbage compared to control plants was alleviated (Begum et al. 2011) (Fig. 13.3).

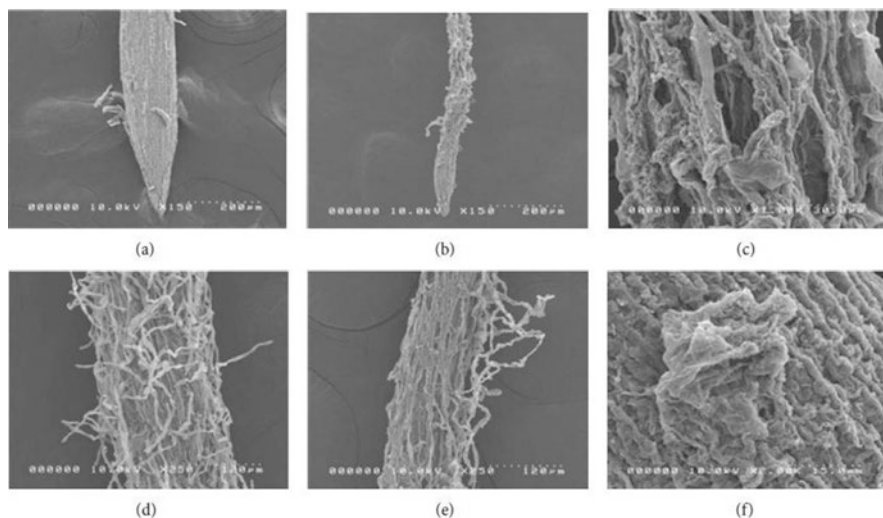


Fig. 13.3 Effect of graphene (1000 mg L^{-1}) on the root surface of tomato seedlings grown in Hoagland medium. **(a, d)** SEM image of the untreated control of tomato root elongation and root hair zone, respectively. **(b)** Root elongation zone of tomato root and **(c, e, and f)** demonstrate surface detachment and aggregates of graphene on the tomato roots surface treated with graphene

Graphene oxide can affect phytohormones of plant. Phytohormones were also affected following exposure of rapeseed to graphene oxide. In a recent research, abscisic acid (ABA) and indole-3-acetic (IAA) levels were changed after exposure to $0\text{--}100 \text{ mg L}^{-1}$ graphene oxide. ABA increased at high concentrations of graphene oxide, showing that the plant may be under stress. IAA reduced with an increase in graphene oxide concentration. The roots of rapeseed were shorter in plants exposed to high concentrations of graphene oxide. IAA is in the auxin class (growth promoters) of phytohormones; therefore, a reduction in IAA can destructively effect on root growth in plants (Cheng et al. 2016).

13.2.3 Metal and Metal Oxide Engineered Nanomaterials

Metal oxide NPs represent a field of materials chemistry which attracts significant interest owing to the potential technological applications of these compounds. Research has shown that the metal/metal oxide NPs production has increased more than three times in the last decade (Niederberger 2007; Stoimenov et al. 2002). Metal/metal oxide NPs exhibit size dependent properties, such as photocatalytic degradation, magnetism, or fluorescence, which has biotechnological applications in sensor development, agrochemicals, and soil remediation (Franke et al. 2006; Kolmakov and Moskovits 2004). In environment, the effect of metal/

metal oxide via plants is expected to depend mostly on the colloidal properties such as organic content, sediments, and soil or sludge, as well as chemical properties. The most studied metal-based NMs are CeO₂, Fe₃O₄, TiO₂, and ZnO NPs (Niederberger et al. 2006; Moisola et al. 2003). Indeed, Fe₃O₄ NPs induce some durability effect on aquatic suspensions of carbon nanotubes and fullerene. It has been proved that the effect of varying pH and humic acids can combine the effects on the destiny of Fe₃O₄ NPs by enhancing pH, resulting in a higher content of accumulation. A same effect was lately shown for CeO₂. Metal NPs, under low concentration conditions, play a vital role at the restriction of plant endurance in the growth of plants (Stoimenov et al. 2002). The absorption of excess amounts of metals by plants causes toxic effects such as reduction of growth and disarrangement in cell division (Niederberger 2007; Kolmakov and Moskovits 2004). In this case, extra metal NPs, acting as cofactor for enzymes, are involved in the development of intermediate metabolites. However, the reaction of plants to metal NPs is affected by the stage of growth, type of plant species, and the nature of the metal.

13.2.3.1 Gold (Au)

Gold (Au) is classified as a noxious substance, and the toxicity of Au in many studies has been reported in ionic or dissolved form (Karamushka and Gadd 1999; Murphy et al. 2008; Goodman et al. 2004; Boisselier and Astruc 2009). Au NPs have been utilized in many applications as antibacterial. In this case, the toxicity of Au has been limited in the form of Au NPs (Goodman et al. 2004; Murphy et al. 2008). The production and the utilization of Au NPs in the environment and its potential transport to the environment might cause intense toxicity problems in the long term (Hauck et al. 2008; Khlebtsov and Dykman 2011; Johnston et al. 2010). For instance, *Medicago sativa* and *Brassica juncea* displayed an enhancement in Au uptake, with a conforming betterment in the layer of Au exposure time and concentration (Saison et al. 2010; Perreault et al. 2012; Zhai et al. 2014).

The Au NPs to be found in the nucleus and the usage of defamation suggested at both types are considered as hyperaccumulators of Au NPs (Arora et al. 2012; Gardea-Torresdey et al. 2000; Green and Renault 2008). Additionally, it is proved that Au NPs are transported inside the cells via plasmodesmata. TEM¹ images of rice roots revealed that various Au particle sizes are stored inside the cells of root in the form of vacuoles. The cell damage happened because of penetrations of large Au NPs entering through small pores (Perreault et al. 2012).

Au NPs are noted to disrupt the onion root tip cells (*Allium cepa*), thus negative effect on the cell division process by causing the formation of cell disintegration, stickiness, and chromatin bridge (Feretti et al. 2007).

¹Transmission electron microscope.

13.2.3.2 Silver (Ag)

Silver (Ag) NPs have played an essential role in the field of biomedicine chemical sensing including imaging utilization. Ag NPs are produced using different methods, electrochemical, chemical, laser ablations photochemical, and others (Rizzello and Pompa 2014). Although bulk Ag is regarded “safe,” Ag NPs need to be tested for biocompatibility and environmental impact if they are to be manufactured for in vivo utilization on a large scale (Wagner et al. 1975; Jasim et al. 2017; Belava et al. 2017). Moreover, exposure data had shown Ag NPs to be widespread in the environment, at low but enhancing concentrations, with estimation of up to 0.1 and 2.9 mg L⁻¹ at the surface water and sludge (Ferguson and Hogstrand 1998; Lee et al. 2005; Wood et al. 1996). Thus, some research demonstrated that the biological effect of dissolved Ag⁺ ions might be seen at concentrations of up to 1000 times higher than that for the Ag NPs (Lee et al. 2005). Also, some results from the research documented that the toxic effect of Ag NPs is minor at exposures as low as 5 mg L⁻¹, with higher inhibitions of growth (Vishwakarma et al. 2017).

It is obvious that Ag NPs within the environment pose a potential hazard to greater plants, and thus, the function of ecosystems (Bianchini and Wood 2003; Lee et al. 2005). Ag NPs illustrate different effects on root, shoot growth, and seed germinations at concentrations of 6000 μg mL⁻¹, 3000 μg mL⁻¹, and 4500 μg mL⁻¹ on species of Mung bean (*Vigna radiata*), Chinese cabbage (*Brassica campestris*), and rice (*Oryza sativa*), respectively (Justin and Armstrong 1991; Nguyen et al. 2003; Mao et al. 2004). Furthermore, Ag NPs with sizes of about 40 nm have the potential to cause toxic effects in *Cucurbita pepo* and *Chlamydomonas reinhardtii* algae. In the case of *Cucurbita pepo*, Ag NPs induced 4.4–10 times more alleviation in transpiration rates and biomass, rather than bulk sizes (Ouda 2014; Cheng et al. 2011). Meanwhile, the limits of uptake and the distribution of Ag NPs have been studied for *Medicago sativa* and *Brassica juncea* species (Ouda 2014; Kumari et al. 2009; Saxena et al. 2010) (Fig. 13.4). Meanwhile, research has been done on the limits of distribution and the uptake of Ag NPs for *Brassica juncea* and *Medicago sativa* species.

Diverse groups have tested the cellular uptake and cytotoxicity of Ag NPs in systems of plant. Research on the root development and the seed germination of zucchini plants in hydroponic solution modified with Ag NPs presented no negative effects, whereas alleviations in plant transpiration and biomass were detected on prolonging the plants' growth in the existence of Ag NPs. The cytotoxic and genotoxic effects of Ag NPs have been reported on the onion root tips. In this case, the results showed that the use of Ag NPs caused cell disintegration and impaired the stages of cell division (Yin et al. 2012; Cheng et al. 2011). There are some notes on greater toxic impacts in the *Chlamydomonas reinhardtii* algae exposed to Ag NPs as AgNO₃, at the particle size of about 40 nm (Cheng et al. 2011).

There are some researches concentrated on impact of Ag NPs on aquatic plant (Inokuchi et al. 1997). The studies noted on utilization of *Lemna minor* L. clone *St* to study the phytotoxicity of Ag NPs. The results illustrated that the inhibition of plant growth was apparent after exposure to a wide speared range of Ag NPs (20–

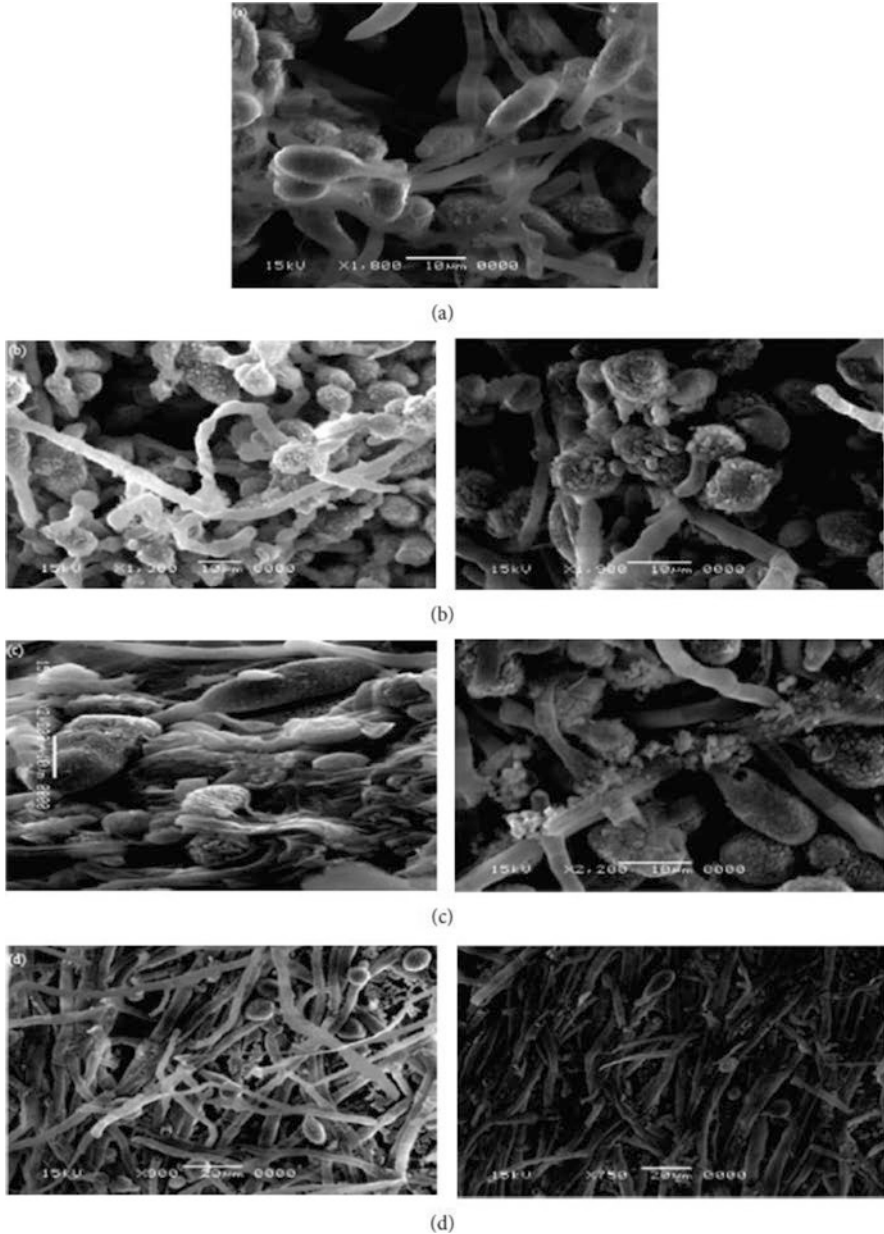


Fig. 13.4 Antifungal impact of Ag NPs on culture filtrate and cell. SEM images of hyphae of *Alternaria alternata* treated with silver, copper, or copper/silver NPs. Fungal hyphae grown on potato dextrose agar plates as (a) control or supplemented with 15 mg L⁻¹, (b) Ag, (c) Cu, or (d) Ag/Cu nanoparticle solution, respectively, images were taken at 7 days after the incubation period (Ouda 2014)

100 nm), even at low concentrations (5 mg L^{-1}) (Unrine et al. 2012). The impacts of Ag NPs have also been assessed in many different studies involving plant mediums (Lee et al. 2012). This research focused on soil nematodes, soil microbial community, and other associated concerns. It has been proved that Ag NPs with sizes of up to 29 nm employed visible alleviation effects on the germination of lettuce seeds and cucumber, but no toxic impact has been detected and noted on the alleviation germination of ryegrass and barley exposed to Ag NPs.

Ag NPs with sizes less than 100 nm have also displayed to alleviate the biomass and transpiration of pumpkin (*Cucurbita pepo*) (Ratte 1999). It noted enhanced Ag NPs content in the common grass *Lolium multiflorum*, with enhancing concentration of Ag NPs. Additionally, the cytological impacts of onion (*Allium cepa*) have been noted to include chromatin bridge, stickiness, disturbed metaphase, and other impacts. The majority of nano-toxicological studies illustrated on plants thus far have used alternative methods rather than soil media. Most of these studies have been conducted in an aqueous media, such as basal medium, distillation water, or Hoagland medium (Slade and Pegg 1993). Few studies proved the toxicity impact of Ag NPs on seed germination, translocation, and plant uptake of NPs in soil (Roh et al. 2009). Furthermore, the toxicity and bioavailability of Ag NPs to species *Polyboroides radiatus* and *Sorghum bicolor* were calculated in both agar and soil medium (Kumari et al. 2009)

Polyboroides radiatus and *Sorghum bicolor* in agar media presented Ag NPs' concentration dependent-growth inhibition and the EC50s values of *Polyboroides radiatus* and *Sorghum bicolor* measured to be 13 and 26 mg L^{-1} , respectively (Dimkpa et al. 2013). *Polyboroides radiatus* were not influenced via the hindrance within the examined concentration in the soil media. *S. bicolor* demonstrated a slightly alleviated growth rate (Lee et al. 2012). Bioavailability and impact of Ag-ions dissolved from Ag NPs are reported to be less in soil than in agar. The results of these studies confirmed that bioaccumulation, phytotoxicity, and dissolution of Ag NPs are obviously affected by the exposure medium (Dimkpa et al. 2013).

All such researches throw light on the need for a more genotoxic and cytotoxic assessment by considering the features of Ag NPs, uptake, distribution, and translocation in diverse plant tissues.

13.2.3.3 Cadmium (Cd)

The short-term impacts of cadmium (Cd) NPs for the root growth of cucumber, tomato, lettuce, and carrot species were tested, using standard toxicity examining (Jiang et al. 2003). The results demonstrated that the growths of seedling were inversely associated to the exposure concentration of Cd, and among the analyzed plants, the sensitive endpoint be visible in order of tomato, carrot, lettuce, and cucumbers (Kashem and Kawai 2007). The growth of root has not been meaningfully inhibited by the existence of Cd NMs, except for tomatoes, but unusually promoted by specific Cd NMs (Clarke and Brennan 1989). Microscopic images

demonstrated the roots of analyzed plants exposed to Cd displaying an alleviation in the root diameter and wilt and the decomposition of the root epidermis; the clutter root surface displayed obvious stress in Cd solution (Groppa et al. 2008). After the adding of Cd NPs, many root hair and a lack of decomposition on the surface soft of the root system were detected, and Cd NPs crystals were also observed on the plants' root surface (Cho and Seo 2005).

13.2.3.4 Titanium Oxide (TiO₂)

Although titanium oxide NPs (TiO₂) are extensively used in daily life products, the study of their uptake and translocation in the plant is limited, especially on food crops (Seeger et al. 2009; Kurepa et al. 2010). Because of small size of TiO₂ NPs (<5 nm), these tend to form a covalent bond with most of the nonconjugate natural organic matter, translocate, and follow the tissue and specific distribution of cell (Song et al. 2013). The general toxic impacts of TiO₂ NPs are found in the algal species, for instance, *Desmodesmus subspicatus* (Hund-Rinke and Simon 2006). Moreover, TiO₂ NPs generate reactive oxygen species on interaction with ultraviolet radiation or organisms (Wang et al. 2011). For instance, with the existence of TiO₂, the root of *A. thaliana* releases *mucilage* and procedures a pectin hydrogel capsule neighboring the root (Elghniji et al. 2012). TiO₂ NPs display that an enhancement in nitrate reeducates in soybean (*Glycine max*), increases the capability to absorb/use water, and stimulates the antioxidant system.

For instance, TiO₂ NPs treated seeds produced plants that had 73% more dry weight, and 45% increase in chlorophyll, a formation compared to the control over the germination period of 30 days (Qi et al. 2013). The development rate of spinach seeds, on the contrary, is proportional to the size of the materials, showing that the smaller the NMs, the better the germination. Some researches show that the TiO₂ NPs might have raised the absorption of inorganic nutrients, enhanced the decomposition of organic substances, and caused quenching by oxygen free radicals formed during the photosynthetic process, consequently improving the photosynthetic rate (Zheng et al. 2005). To enhance seed germination rate, the penetration of NMs into the seed is crucial (Han et al. 2010; Gao et al. 2008) (Fig. 13.5).

Meanwhile, TiO₂, in the anatase phase, rises plant growth in spinach by modifying nitrogen metabolism that promotes the adsorption of nitrate (Wu et al. 2012). The same research illustrated the negative impacts of TiO₂ NPs upon the seed germination percentage and the number of roots for the species *Oryza sativa L.* This, in turn, increases the conversion of inorganic nitrogen into organic nitrogen, so enhancing the fresh and dry weight (Foltête et al. 2011).

Utilizing TiO₂ NPs at 60 mg L⁻¹ increased sage and seed germination percentages (Feizi et al. 2013). Exposure of sage seeds to 60 mg L⁻¹ TiO₂ NPs achieved the lowest mean germination time, but higher concentrations did not enhance the mean germination time (Feizi et al. 2013).

For spinach seeds, TiO₂ NPs helped to water absorption, and thus enhanced seed germination (Zheng et al. 2005). Thus, some studies declared that altered TiO₂ NPs

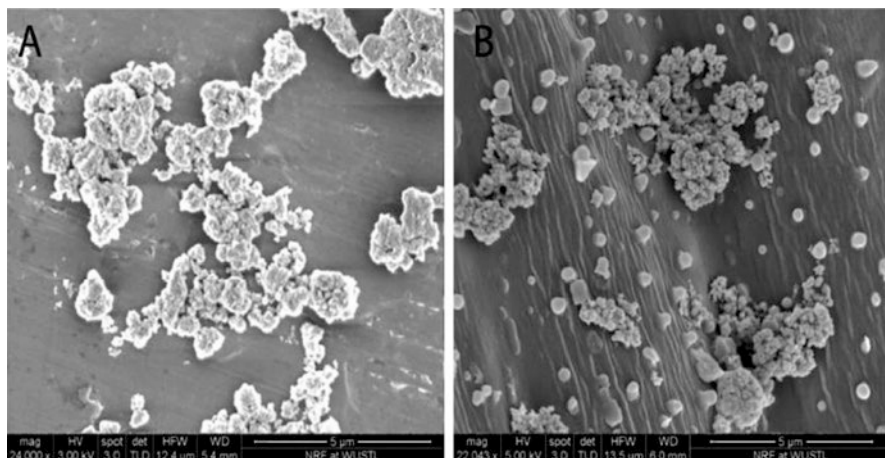


Fig. 13.5 SEM images for NPs/lettuce seeds. In the aqueous phase, the SEM image shows that metal oxide NPs (a) (TiO_2 NPs 1000 mg L^{-1}) and (CuO NPs 1000 mg L^{-1}) were adsorbed on (b) the seed surface (Wu et al. 2012)

were tested in the liquid phase on the plant model *Vicia faba*, which was exposed to three nominal concentrations: 5, 25, and 50 mg commercial sunscreen TiO_2 NPs per liter for 48 h. Plant growth, photosystem II maximum quantum yield, genotoxicity by micronucleus examination, and phytochelatin levels illustrated a lack of change compared to the control samples. TiO_2 NPs seem not to exert deleterious effects on our plant model in 48 h, but detected important clogging onto the roots (Xie et al. 2011).

It is shown that a blend of nanosized TiO_2 could improve the nitrate reductase enzyme in soybean (*Glycine max*), enhance its abilities of absorbing and using fertilizer and water, encourage its antioxidant system, and actually hasten its germination and growth (Molina-Barahona et al. 2005). In addition, it is stated that the positive effects of TiO_2 could be due to antimicrobial properties of ENMs, which can improve the stability and strength of plants to stress. Therefore, the acute toxic effects of TiO_2 NPs are considered low, with the effects not following a clear dose impact relationship. This is perhaps due to particle agglomeration and subsequent sedimentation. Genomic DNA quantification was observed in the root tips of cucumber after 7 days and displayed that plants treated with $2000\text{--}4000 \text{ mg L}^{-1}$ of TiO_2 NPs alleviated the genomic DNA compared to the control sample (Elghniji et al. 2012). The toxic effect of TiO_2 NPs is possibly not attributed by the released Ti^{2+} ions from particles that are tentatively proved by the limited dissolution of Ti from a TiO_2 sample (Qiu et al. 2013).

13.2.3.5 Aluminum (Al)

Al is not necessary for crop growth and expansion; but, Al toxicity is primarily caused via Al^{3+} which is a high limiting factor for crop growth in acidic soils (Von Uexküll and Mutert 1995). Al ions are very toxic to plants at elevated level concentrations (Kochian et al. 2004).

Toxic levels of Al prevent the growth and decrease the efficiency of Al-sensitive crops with disrupting different cellular processes and components through binding with phosphate, sulfate, and carbonyl functional groups (Valle et al. 2009).

Physiological studies imply that plants utilize two principal techniques to resist Al toxicity: obstruction of Al^{3+} uptake and detoxifying cellular Al by the formation of inoffensive complexes with organic ligands, which are then separated to particular organelles (Ma and Furukawa 2003). Comparative proteomic analyze and bioinformatic strategies are impressive tools for manifesting the molecular mechanisms underlying replies to abiotic stress (Xu et al. 2010). Soybean is susceptible to Al toxicity (Xu et al. 2006). Comparative proteomic analyze has manifested that Al induces tolerance-related proteins in the tolerant cultivar; while, proteins relevant to stress responses are raised in the susceptible cultivar (Duressa et al. 2011).

In the Al-tolerant soybean cultivar, the raise in ROS scavenging depends on the enhanced plenty of proteins preoccupied in sulfur metabolism. Furthermore, the levels of ABC transporter ATP-binding proteins facilitate in transmitting Al far from the roots. In response to Al toxicity, the cysteine synthase and glutathione reductase played main role in the soybean conformity to heavy metal stress (Duressa et al. 2010). Glutathione-S-transferase was enhanced under the Al stress in soybean (Duressa et al. 2011). The antioxidation and detoxification enzymes played a main role in Al tolerance in rice, soybean, and tomato (Zhen et al. 2007). Rice is the most Al-tolerant species (Foy 1988); but, exposure of rice to Al causes intense efficiency decrements (Fageria and Carvalho 1982). Comparative proteomic studies considering mechanisms of Al tolerance in rice manifested that the relative plenty of vacuolar H^{+} -ATPase was enhanced in Al-tolerant rice cultivars compared to Al-sensitive cultivars, while structural proteins were diminished in both cultivars (Wang et al. 2013).

Furthermore, Al toxicity in rice caused enhancement in antioxidative, carbohydrate, and nucleotide anabolism-related proteins in the resistant cultivar, whereas a number of pathogenesis and carbohydrate catabolism-related proteins were enhanced in redundancy in the sensitive cultivar. Another study indicated that activation of the glycolysis/gluconeogenesis shunt becomes clear to be a quick and impressive way to equilibrium the levels of accessible energy to barricade an intracellular energy deficiency resulting from the increased cellular levels of Al. In wheat, exposure to Al enhanced proteins containing S-adenosylmethionine synthase, oxalate oxidase, malate dehydrogenase, and cysteine synthase (Oh et al. 2014). In barley, a comparative proteomic study manifested that proteins preoccupied in energy, cell growth, protein synthesis, protein destination/storage, transmit, signal transduction, and disease/defense were enhanced in the tolerant cultivar in reply to Al toxicity (Dai et al. 2013). The recognized proteins were related with Al

tolerance and indicated that Tibetan wild barley is a new genetic resource. In *Arabidopsis thaliana*, the proteins depend on the tricarboxylic acid cycle, glycolysis, reactive oxygen quenching, detoxification, and signal transduction pathways that played role in mediating plant response toward Al stress (Karuppanapandian et al. 2012). Comprehending the mechanism of action of Al at the molecular level is significant for the expansion of stress-tolerant crop.

Also, phytotoxicity of uncoated and phenanthrene-coated alumina (Al_2O_3) NPs displayed that uncoated Al_2O_3 NPs at 2 mg L^{-1} concentrations inhibited the root elongation of corn, cabbage, carrot, soybean, and cucumber [224–226] (Kollmeier et al. 2000). It is noted that the toxic effect is possibly not nanospecified but is because of the dissolution of Al_2O_3 NPs. The effects of submicron Al_2O_3 particles were examined to evaluate the chemical material that might be toxic against the growth of seedling roots. Therefore, particle surface features play an acute role in the phytotoxicity of Al_2O_3 NPs (Tian et al. 2007). Research has supported the fact that the existence of Al_2O_3 can stunt root growth in cucumber, corn, carrot, cabbage, and soybean, although preliminary findings suggest that very high concentrations of such particles are essential to induce harm (Kinraide et al. 1992). The existence of Al_2O_3 NPs did not have a harmful effect on the expansion of *Lolium perenne* and *Phaseolus vulgaris* in the tested concentration range (Rangel et al. 2007).

13.2.3.6 Fe_3O_4

The extra amount of iron oxide (Fe_3O_4) as a magnetic NMs resulted in some negative effect against plant growth. For instance, “Chlorophyll a” levels were amplified at low Fe_3O_4 NPs fluid concentrations, while at higher concentrations it inhibited it (Zhu et al. 2008). A small repressing effect was found on the growth of the plantlets that led to brown spots on leaves at higher volume fractions of Fe_3O_4 NPs fluids (Kraemer 2004).

The extra Fe_3O_4 NPs treatment produced some oxidative stress, which in turn affected photosynthesis and resulted in alleviated rates of metabolic process. The oxidative impact was induced by the Fe_3O_4 fluid concentration in the tissues of living plants (Raven 1988).

In order to overcome such limitations, the coating provides Fe_3O_4 NPs with a large adsorption surface and biocompatible characteristics (Chen et al. 1980).

For instance, in the case of pumpkin (*Cucurbita pepo*), the extent of carbon coated- Fe_3O_4 at certain concentrations within some cells and in extracellular space reduces the problems for plant tissues and the amount of chemicals released into the environment (Katsoyiannis and Zouboulis 2002). Moreover, the effect of tetramethylammonium hydroxide coated Fe_3O_4 NPs on the development of corn (maize) found that the chlorophyll level enhanced at low Fe_3O_4 NPs fluid, while at higher concentrations it was inhibited. A slight inhibitory effect was detected in the growth of the plantlets, which in turn resulted in brown spots on leaves at greater volume fractions of the magnetic fluid (Liu et al. 2006). The oxidative effect was induced by the Fe_3O_4 NPs fluid toward the living plant tissue (Ma et al. 2010). The extra Fe_3O_4

NPs generated some oxidative effect, affected photosynthesis, and resulted in the decrease of metabolic process rates.

13.2.3.7 Zinc (Zn)

Zn NPs are a vital micronutrient for various cellular processes and are required for both animal and plant growth (D'Alessandro et al. 2013). In particular, Zn NPs serve as a cofactor for enzyme reactions involved in carbohydrate and energy metabolism, energy transfer, protein synthesis, protein folding, and gene expression regulation (Maret 2013). The significance of Zn NPs in cellular functions is highlighted by the finding that 10% of protein binding sites contain Zn (Andreini et al. 2006). However, at high level concentrations, Zn is toxic for plants. The main response to Zn toxicity is expansion inhibition and is determined by alleviated root growth, impaired cell division/elongation enhanced, and enhanced root thickening (Barceló and Poschenrieder 1990). Comparative researches on Zn-sensitive *A. thaliana* and tolerant *A. halleri* revealed that toxicity leads to the changed expression of genes involved in metal binding and homeostasis. The proteomic analysis of the leaves and roots of *A. thaliana* indicated that protein profiles were significantly changed in response to Zn NPs toxicity. In the leaves, the declined proteins were predominantly associated to one-carbon metabolism, such as glycine decarboxylase P protein, serine hydroxymethyltransferase, and methionine synthase (Weber et al. 2004).

In the roots, Zn toxicity reduced V-ATPase activity results in growth defects (Fukao et al. 2011). In the shoots of *A. thaliana*, Zn mostly affected the levels of proteins associated to ribosomes, photosynthesis, and transporter (Zargar et al. 2015). Enhanced Zn NPs concentrations induce metabolic reprogramming in *Beta vulgaris* (Van Assche and Clijsters 1990). In response to Zn treatment, a shutdown of metabolism because of alleviation aerobic respiration, lipid peroxidation, and cell death was detected in *B. vulgaris* (Gutierrez-Carbonell et al. 2013). In the *Populus × euramericana* roots (clone 10214), Zn NPs modulate the abundance of proteins associated to the antioxidant system, carbohydrate/energy, and amino acid metabolism. In addition, coordination between cell death and proliferation was identified and was speculated to be an attempt by the plant to alleviate the harm caused by Zn stress (Romeo et al. 2014). *Noccaea caerulea* is a part of the Brassica family and a great model system for checking the effects of Zn NPs hyper-aggregation (Milner and Kochian 2008). In *N. caerulea*, several glutathione S-transferases are enhanced in the epidermal cells and function to alleviate oxidative stress caused by extra Zn NPs (Schneider et al. 2013). Furthermore, the concentrations of citrate and malate were also enhanced, demonstrating the important role of these metabolic intermediates in the complexation of epidermal Zn NPs.

13.2.3.8 Copper (Cu)

Cu is a vital micronutrient for plant development and growth, as it is mostly connected with proteins involved in electron transfer and redox reactions, and is also as a cofactor in oxidative stress responses, mitochondrial respiration, ethylene transduction signals, and photosynthesis. Despite its significance for enzymatic function, Cu is toxic to plants at high concentrations because it is able of catalyzing Fenton and Haber–Weiss reactions, leading to the production of ROS that have the potential to harm cellular constituents (Bona et al. 2007).

Recently, Adrees et al. (2015) studied the effects of extra Cu on the growth and physiology of crops. Exposure to high concentrations of Cu caused growth inhibition, oxidative damage, and antioxidant responses in cucumber, sunflower, maize, rice, and wheat. Cu treatment also changes enzyme activities, chlorophyll content, mineral nutrition enzyme activities, and leaf photosynthetic; leading to alleviation growth and yield. In the *Elsholtzia splendens*, a tolerant species, cellular metabolism redox homeostasis, and cellular metabolism pathways are redirected in cells of root as a significant survival response under Cu stress. It has also been illustrated that Cu NPs effect on antioxidant defense/signaling pathways, protein, and energy synthesis in *E. splendens* (Liu et al. 2014). In roots of rice, Cu stress effects on the proteins involved in antioxidant defense, carbohydrate metabolism, nucleic acid metabolism, protein folding/stabilization, protein transport, and cell wall synthesis (Chen et al. 2015a).

A comparative proteomic study between Cu-tolerant and Cu-sensitive rice cultivars was conducted to better understand the molecular mechanisms involved in plants responses to Cu stress (Chen et al. 2015a). The identified Cu-responsive proteins were involved in antioxidant defense, detoxification, pathogenesis, and regulation of gene transcription. Karmous et al. (2014) examined the role of the ubiquitin-proteasome pathway and peptidases in plant responses to Cu stress in bean cotyledons. Cu induced the inactivation of the ubiquitin-proteasome pathway and leucine/proline aminopeptidases, and/or limitation of the role in modulating the removal of regulatory and oxidative damaged proteins. However, the activities of trypsin and chymotrypsin were increased due to Cu stress and the activities of their inhibitor were decreased, indicating that these endoproteases play a role in protecting cells against Cu toxicity.

In *Agrostis capillaris*, exposure to Cu increases the abundance of Cu/Zn superoxide dismutase, leading to the increased detoxification of superoxides, and also associated with changes in the cytoskeleton and ethylene metabolism (Hego et al. 2014). The resulting increase in the levels of L-methionine and S-adenosylmethionine facilitates the production of nicotianamine, which binds to Cu and is required for the synthesis of metallothioneins and glutathione. In rice, Cu exposure regulates the activities of metallothionein-like, membrane-associated, and pathogenesis-related proteins.

13.2.3.9 Other Metal

In addition to the above-described heavy metals, the effects of several other trace metals on plants have been tested in diverse species. In a recent proteomic research of rice seedlings, the effects of Cr toxicity were examined (Zeng et al. 2014). The duration of Cr exposure affects the antioxidant enzymes, such as ferredoxin-NADP reductase, glyoxalase I, NADP-isocitrate dehydrogenase, and glutamine synthetase. Furthermore, the Cr NPs were found to be immobilized into cell walls and have alleviated translocation, and also activated the antioxidant defense system. In maize, Fe exposure adjusts the proteins involved in oxidative stress, development regulation, and cell wall stability and synthesis (Hopff et al. 2013). Hg is also of excellent concern because of its deleterious impacts on the human health and environment. In *Suaeda salsa*, Hg exposure controls proteins associated to immunosuppression, signaling pathways, stress responses, photosynthesis, energy metabolism, metabolic processes, and protein fate (Liu et al. 2013). In roots of rice, Hg controlled numerous proteins are involved in stress responses, metabolism, signal transduction, redox homeostasis, and regulation (Wang et al. 2012). Between the enhanced proteins, translationally adjusted tumor protein was assessed for its important role in Hg tolerance of rice, providing evidence for its role in decreasing Hg harm. The findings from these researches suggest that many processes in plants are affected by metal toxicity; studying that the effects of metal toxicity in combination may be helpful for understanding the molecular mechanisms underlying plant responses to metal toxicity.

13.3 Effect of ENMs on the Toxicity of Environmental Pollutants

Joint toxicities of pollutants and ENMs can be classified as synergistic, antagonistic, multiple effects. Inferior plant, aquatic life, and mammalian cells are mostly used as model organisms for studies on the joint toxicity. Generic research on the influence of ENMs on the toxicity of pollutants is summarized briefly and organized by NMs classification (Tables 13.1 and 13.2).

13.3.1 Carbon Nanomaterials

CNTs have an extremely high affinity for environmental pollutants (Yang and Xing 2010). Four different kinds of CNTs have been shown to considerably increase the critical toxicity of Cd to *Daphnia magna* (*D. magna*), this enrichment of Cd toxicity was observed to enhance in the following order: single-walled CNTs (SWCNTs) > multiwalled CNTs (MWCNTs) > hydroxylated MWCNTs

Table 13.1 Carbon nanomaterials affecting the toxicity of environmental pollutants

Carbon nanomaterials/ concentrations	Pollutants/ concentrations	Organisms/cells	Exposure time	Joint toxicity	Reference
<i>Synergistic effects</i> HNO ₃ -MWCNT1, 2 µg mL ⁻¹	Pb 0.1, 0.5, 2 µg mL ⁻¹	Nile tilapia (<i>Oreochromis niloticus</i>)	96 h	HNO ₃ -MWCNTs increased the histopathological alterations elicited by Pb	Barbieri et al. (2016)
HNO ₃ -MWCNTs 0.1–3 µg mL ⁻¹	Pb 0–2.12 µg mL ⁻¹	Nile tilapia (<i>Oreochromis niloticus</i>)	24, 48, 72, 96 h	HNO ₃ -MWCNTs increased the lethality of Pb	Martinez et al. (2013)
OH-MWCNTs 0.1–5 µg mL ⁻¹	As 0–2.12 µg mL ⁻¹ 0.6– 16.7 µg mL ⁻¹	<i>D. magna</i>	48 h	OH-MWCNTs increased the lethality of As	Wang et al. (2016a)
GO 5 µg mL ⁻¹	As (2.5 µM) and paraquat (100 µM)	Human hepatoma cell line HepG	24 h	GO inhibited the function of efflux transporter	Liu et al. (2016b)
<i>Antagonistic effects</i> SWNTs 0.3, 3 mg g ⁻¹	Pyrene 37.5 µg g ⁻¹	Earthworms (<i>Eisenia foetida</i>)	0–28 d	SWCNTs alleviated the bioaccumulation of pyrene	Petersen et al. (2009)
GO 2–20 µg mL ⁻¹	PCB 5275 µM	Human–hamster hybrid (AL) cells	24 h	GO alleviated the cytotoxicity and mutagenicity of PCB	Liu et al. (2016c)
<i>Multiple effects</i> SWNTs 0.5–6.1 µg mL ⁻¹	Phe 3.1–800 µg L ⁻¹	Algae <i>Pseudokirchneriella subcapitata</i>	0–72	SWCNTs had different effects on the lethality of Phe	Glomstad et al. (2016)

Table 13.2 Metal and metal oxide NPs affecting the toxicity of environmental pollutants

Metal nanomaterials/ concentrations	Pollutants/ concentrations	Organisms/cells	Exposure time	Joint toxicity	Reference
<i>Synergistic effects</i> <i>nTiO</i> 2 $\mu\text{g mL}^{-1}$	Cd 66–200 $\mu\text{g L}^{-1}$	<i>D. magna</i>	24 h, 48 h	<i>nTiO</i> ₂ increased the lethality of Cd	Li et al. (2017)
<i>nTiO</i> ₂ 0.1 $\mu\text{g mL}^{-1}$	PCP 0–30 $\mu\text{g L}^{-1}$	Zebrafish (<i>Danio rerio</i>) embryos or larvae	6 d postfertilization	<i>nTiO</i> ₂ increased the oxidative stress of PCP	Fang et al. (2015)
<i>nTiO</i> ₂ 10 $\mu\text{g mL}^{-1}$	As (III) 0.5, 1, 2 $\mu\text{g mL}^{-1}$	Human-hamster hybrid (AL) cells	24 h	<i>nTiO</i> ₂ elevated the genotoxicity of As (III)	Wang et al. (2017)
<i>Antagonistic effects</i> <i>nTiO</i> 5 $\mu\text{g mL}^{-1}$	Cu 0.06, 0.07 $\mu\text{g mL}^{-1}$	<i>Microcystis aeruginosa</i>	0–72 h	<i>nTiO</i> ₂ reduced Cu-induced oxidative stress to cellular membrane	Chen et al. (2015b)
<i>nTiO</i> 1–1000 $\mu\text{g mL}^{-1}$	As(V) 0–120 $\mu\text{g mL}^{-1}$	Nauplii (<i>Artemia salina</i>)	48 h	<i>nTiO</i> ₂ decreased the lethality of As(V)	Yan et al. (2017)
<i>Multiple effects</i> <i>nTiO</i> ₂ 0–30 $\mu\text{g mL}^{-1}$	Atrazine 0–0.4 $\mu\text{g mL}^{-1}$ PCB 77 0–0.01 $\mu\text{g mL}^{-1}$	Algae (<i>Chlorella pyrenoidosa</i>)	96 h	<i>nTiO</i> ₂ exhibit distinct effects on the toxicity of organic pollutants	Zhang et al. (2017)
	PeCB 0–0.66 $\mu\text{g mL}^{-1}$				

(OH-MWCNTs) > carboxylated MWCNTs (COOH-MWCNTs) (Wang et al. 2016b).

For instance, OH-MWCNTs were noted to enhance the toxicity of *D. magna*, with LC50² values alleviating by 14.1% for As (III) and 14.9% for As(V) in the existence of OH-MWCNTs after 48 h of exposure (Wang et al. 2016a). Also, nitric acid treated MWCNTs (HNO₃-MWCNTs) increased the toxicity of Pb to Nile tilapia: after 24, 48, 72, and 96 h of incubation, the respective LC50 values alleviated from 1.65, 1.32, 1.10, and 0.99 mg L⁻¹ for Pb only to 0.32, 0.25, 0.20, and 0.18 mg L⁻¹ for Pb-CNTs mixtures (Martinez et al. 2013). The excess of HNO₃-MWCNTs also enhanced the pathological changes regarding epithelial structure, displacement of epithelial cells, hyperplasia, and the structure in the secondary lamella in the Nile tilapia (Barbieri et al. 2016). Apart from synergistic effects, carbon NMs may also alleviate the toxicity of environmental pollutants. SWCNTs have been displayed to increase the removal rate of pyrene, and thereby, alleviate its bioaggregation in earthworms (Petersen et al. 2009). Pretreatment of 20 µg mL⁻¹ GO has been noted to enhance the livability of cells exposed to PCB³ 52 from 67.7% to 86.3% (Liu et al. 2016c). Multiple effects of joint toxicity occur when ENMs interact with various pollutants, when diverse ENMs with different physicochemical properties interact with similar pollutant, or when exposure conditions change (e.g., time and concentration).

The existence of SWCNTs reduced the toxicity of Phe with values of 50% development inhibition extremely enhanced from 438.3 for Phe only to 528.4 for a mix of Phe and SWCNTs; however, negligible diversity exists between MWCNTs and Phe (Glomstad et al. 2016). BC⁴ alleviated the toxicity of TBT⁵ to *D. magna* at pH 6 and 8, while the toxicity of DBT was only negligibly affected via the addition of BC (Fang et al. 2011).

13.3.2 Metal and Metal Oxide Nanoparticles

Examples of metal and metal oxide NPs, such as ZnO, AgNPs, and TiO₂, have been thoroughly studied and intensively utilized mainly in personal care and medical products, which naturally enhanced the possibility for them to release into environment and further interact with pollutants.

TiO₂ enhanced the toxicity of Cd to *D. magna*, with the EC50 of Cd reducing by 48% after a 48 h exposure with *n*TiO₂ (Li et al. 2017).

TiO₂ increased the concentration of ROS⁶ induced by As(III) and alleviated the disturbed metabolism and total antioxidant capacity of As (III) in the estuarine polychaete *Laeonereis acuta* (Nunes et al. 2017).

²Median lethal concentration.

³Polychlorinated biphenyls 52.

⁴Black carbon.

⁵Tributyltin.

⁶Reactive oxygen species.

Moreover, TiO₂ enhanced the negative effects of PCP⁷ by increasing the oxidative stress such as DNA damage and lipid peroxidation in zebrafish larvae (Fang et al. 2015). Also, TiO₂ was illustrated to enhance the genotoxicity of As(III) in human–hamster hybrid (AL) cells (Wang et al. 2017).

AuNPs⁸ were noted to enhance the bioaggregation and toxicity of As₂O₃ by facilitating its uptake as well as inhibiting its removal (Guo et al. 2009). In addition to synergistic effects, TiO₂ was illustrated to relieve the lethality of Cu in *D. magna* (Rosenfeldt et al. 2015) and *Microcystis aeruginosa* (Chen et al. 2015b), decrease Cd-induced toxicity in green algae (Yang et al. 2012) and *D. magna* (Tan et al. 2016). Multiple effects exist between metal/metal oxide NPs and pollutants. TiO₂ performed absolutely distinct joint toxicity with four kinds of organochlorine contaminants toward algae (*chlorella pyrenoidosa*). A synergistic toxicity was found for *n*TiO₂ and atrazine, antagonistic interactions happened between TiO₂ in combination with HCB,⁹ or PCB 77,¹⁰ whereas additive responses were reported for the combination of *n*TiO₂ and PeCB¹¹ (Zhang et al. 2017). As a generally utilized sort of metal NPs, AgNPs were proved to facilitate the bioaccumulation of As(V), Cu, and Cd but only increase the acute toxicity of Cd to *D. magna* (Kim et al. 2016).

In general, due to the diverse properties of ENMs, receptor species, pollutants, and environmental conditions in the exposure scenarios, intricate interactions happen between ENMs and environmental pollutants, thus leading to opposite results when studying the joint toxicity of ENMs and environmental pollutant. Thus, in depth exploration on the biological and physicochemical mechanisms involved in the joint toxicity is necessary.

13.4 Conclusions

In summary, the presence of nanomaterial in environment such as (soil and water) can have significant toxicity effects on plants and the environment. Since the utilization of NMs is predicted to enhance, it is important that we continue to study the fate and toxicity of these NMs to plants and environments.

⁷ Pentachlorophenol.

⁸ Gold nanoparticles.

⁹ Hexachlorobenzene.

¹⁰ 3,3',4,4'-tetrachlorobiphenyl.

¹¹ Pentachlorobenzene.

References

- Adrees M, Ali S, Rizwan M, Ibrahim M, Abbas F, Farid M, Zia-Ur-Rehman M, Irshad MK, Bharwana SA (2015) The effect of excess copper on growth and physiology of important food crops: a review. *Environ Sci Pollut Res* 22:8148–8162
- Akhavan O, Ghaderi E (2010) Toxicity of graphene and graphene oxide nanowalls against bacteria. *ACS Nano* 4:5731–5736
- Al-Ghamdi AA, Gupta R, Kahol P, Wageh S, Al-Turki Y, El Shirbeeney W, Yakuphanoglu F (2014) Improved solar efficiency by introducing graphene oxide in purple cabbage dye sensitized TiO₂ based solar cell. *Solid State Commun* 183:56–59
- Andreini C, Banci L, Bertini I, Rosato A (2006) Zinc through the three domains of life. *J Proteome Res* 5:3173–3178
- Anjum NA, Singh N, Singh MK, Shah ZA, Duarte AC, Pereira E, Ahmad I (2013) Single-bilayer graphene oxide sheet tolerance and glutathione redox system significance assessment in faba bean (*Vicia faba* L.). *J Nanopart Res* 15:1770
- Anjum NA, Singh N, Singh MK, Sayeed I, Duarte AC, Pereira E, Ahmad I (2014) Single-bilayer graphene oxide sheet impacts and underlying potential mechanism assessment in germinating faba bean (*Vicia faba* L.). *Sci Total Environ* 472:834–841
- Arora S, Sharma P, Kumar S, Nayan R, Khanna P, Zaidi M (2012) Gold-nanoparticle induced enhancement in growth and seed yield of *Brassica juncea*. *Plant Growth Regul* 66:303–310
- Ball P (2002) Natural strategies for the molecular engineer. *Nanotechnology* 13:R15
- Barbieri E, Campos-Garcia J, Martinez DS, Da Silva JRM, Alves OL, Rezende KF (2016) Histopathological effects on gills of Nile Tilapia (*Oreochromis niloticus*, Linnaeus, 1758) exposed to Pb and carbon nanotubes. *Microsc Microanal* 22:1162–1169
- Barceló J, Poschenrieder C (1990) Plant water relations as affected by heavy metal stress: a review. *J Plant Nutr* 13:1–37
- Baughman RH, Zakhidov AA, De Heer WA (2002) Carbon nanotubes—the route toward applications. *Science* 297:787–792
- Begum P, Ikhtiar R, Fugetsu B (2011) Graphene phytotoxicity in the seedling stage of cabbage, tomato, red spinach, and lettuce. *Carbon* 49:3907–3919
- Belava V, Panyuta O, Yakovleva G, Pysmenna Y, Volkogon M (2017) The effect of silver and copper nanoparticles on the wheat—*Pseudocercospora herpotrichoides* Pathosystem. *Nanoscale Res Lett* 12:250
- Bianchini A, Wood CM (2003) Mechanism of acute silver toxicity in *Daphnia magna*. *Environ Toxicol Chem* 22:1361–1367
- Boisselier E, Astruc D (2009) Gold nanoparticles in nanomedicine: preparations, imaging, diagnostics, therapies and toxicity. *Chem Soc Rev* 38:1759–1782
- Bona E, Marsano F, Cavaletto M, Berta G (2007) Proteomic characterization of copper stress response in *Cannabis sativa* roots. *Proteomics* 7:1121–1130
- Canesi L, Ciacci C, Balbi T (2015) Interactive effects of nanoparticles with other contaminants in aquatic organisms: friend or foe? *Mar Environ Res* 111:128–134
- Chen C, Dixon J, Turner F (1980) Iron coatings on Rice roots: morphology and models of development I. *Soil Sci Soc Am J* 44:1113–1119
- Chen C, Song Y, Zhuang K, Li L, Xia Y, Shen Z (2015a) Proteomic analysis of copper-binding proteins in excess copper-stressed roots of two rice (*Oryza sativa* L.) varieties with different Cu tolerances. *PLoS One* 10:e0125367
- Chen J, Qian Y, Li H, Cheng Y, Zhao M (2015b) The reduced bioavailability of copper by nano-TiO₂ attenuates the toxicity to *Microcystis aeruginosa*. *Environ Sci Pollut Res* 22:12407–12414
- Cheng Y, Yin L, Lin S, Wiesner M, Bernhardt E, Liu J (2011) Toxicity reduction of polymer-stabilized silver nanoparticles by sunlight. *J Phys Chem C* 115:4425–4432
- Cheng F, Liu Y-F, Lu G-Y, Zhang X-K, Xie L-L, Yuan C-F, Xu B-B (2016) Graphene oxide modulates root growth of *Brassica napus* L. and regulates ABA and IAA concentration. *J Plant Physiol* 193:57–63

- Cho U-H, Seo N-H (2005) Oxidative stress in *Arabidopsis thaliana* exposed to cadmium is due to hydrogen peroxide accumulation. *Plant Sci* 168:113–120
- Clarke B, Brennan E (1989) Differential cadmium accumulation and phytotoxicity in sixteen tobacco cultivars. *JAPCA* 39:1319–1322
- Cui X, Wan B, Guo L-H, Yang Y, Ren X (2016) Insight into the mechanisms of combined toxicity of single-walled carbon nanotubes and nickel ions in macrophages: role of P2X7 receptor. *Environ Sci Technol* 50:12473–12483
- D'alessandro A, Taamalli M, Gevi F, Timperio AM, Zolla L, Ghnaya T (2013) Cadmium stress responses in *Brassica juncea*: hints from proteomics and metabolomics. *J Proteome Res* 12:4979–4997
- Da Costa M, Sharma P (2016) Effect of copper oxide nanoparticles on growth, morphology, photosynthesis, and antioxidant response in *Oryza sativa*. *Photosynthetica* 54:110–119
- Dai H, Cao F, Chen X, Zhang M, Ahmed IM, Chen Z-H, Li C, Zhang G, Wu F (2013) Comparative proteomic analysis of aluminum tolerance in Tibetan wild and cultivated barleys. *PLoS One* 8:e63428
- De La Torre-Roche R, Hawthorne J, Deng Y, Xing B, Cai W, Newman LA, Wang Q, Ma X, Hamdi H, White JC (2013) Multiwalled carbon nanotubes and C60 fullerenes differentially impact the accumulation of weathered pesticides in four agricultural plants. *Environ Sci Technol* 47:12539–12547
- Deng R, Lin D, Zhu L, Majumdar S, White JC, Gardea-Torresdey JL, Xing B (2017) Nanoparticle interactions with co-existing contaminants: joint toxicity, bioaccumulation and risk. *Nanotoxicology* 11:591–612
- Dimkpa CO, Mclean JE, Martineau N, Britt DW, Haverkamp R, Anderson AJ (2013) Silver nanoparticles disrupt wheat (*Triticum aestivum* L.) growth in a sand matrix. *Environ Sci Technol* 47:1082–1090
- Duessa D, Soliman K, Chen D (2010) Identification of aluminum responsive genes in Al-tolerant soybean line PI 416937. *Int J Plant Genomics* 2010:164862
- Duessa D, Soliman K, Taylor R, Senwo Z (2011) Proteomic analysis of soybean roots under aluminum stress. *Int J Plant Genomics* 2011:282531
- Elghniji K, Hentati O, Mlaik N, Mahfoudh A, Ksibi M (2012) Photocatalytic degradation of 4-chlorophenol under P-modified TiO₂/UV system: kinetics, intermediates, phytotoxicity and acute toxicity. *J Environ Sci* 24:479–487
- Fageria N, Carvalho J (1982) Influence of aluminum in nutrient solutions on chemical composition in upland rice cultivars. *Plant Soil* 69:31–44
- Fang L, Borggaard OK, Holm PE, Hansen HCB, Cedergreen N (2011) Toxicity and uptake of TRI-and dibutyltin in *Daphnia magna* in the absence and presence of nano-charcoal. *Environ Toxicol Chem* 30:2553–2561
- Fang Q, Shi X, Zhang L, Wang Q, Wang X, Guo Y, Zhou B (2015) Effect of titanium dioxide nanoparticles on the bioavailability, metabolism, and toxicity of pentachlorophenol in zebrafish larvae. *J Hazard Mater* 283:897–904
- Feizi H, Amirmoradi S, Abdollahi F, Pour SJ (2013) Comparative effects of nanosized and bulk titanium dioxide concentrations on medicinal plant *Salvia officinalis* L. *Ann Rev Res Biol* 3:814–824
- Feretti D, Zerbini I, Zani C, Ceretti E, Moretti M, Monarca S (2007) Allium cepa chromosome aberration and micronucleus tests applied to study genotoxicity of extracts from pesticide-treated vegetables and grapes. *Food Addit Contam* 24:561–572
- Ferguson EA, Hogstrand C (1998) Acute silver toxicity to seawater-acclimated rainbow trout: influence of salinity on toxicity and silver speciation. *Environ Toxicol Chem* 17:589–593
- Foltete A-S, Masfaraud J-F, Bigorgne E, Nahmani J, Chaurand P, Botta C, Labille J, Rose J, Ferard J-F, Cotelle S (2011) Environmental impact of sunscreen nanomaterials: ecotoxicity and genotoxicity of altered TiO₂ nanocomposites on *Vicia faba*. *Environ Pollut* 159:2515–2522
- Foy CD (1988) Plant adaptation to acid, aluminum-toxic soils. *Commun Soil Sci Plant Anal* 19:959–987

- Franke ME, Koplin TJ, Simon U (2006) Metal and metal oxide nanoparticles in chemiresistors: does the nanoscale matter? *Small* 2:36–50
- Fukao Y, Ferjani A, Tomioka R, Nagasaki N, Kurata R, Nishimori Y, Fujiwara M, Maeshima M (2011) iTRAQ analysis reveals mechanisms of growth defects due to excess zinc in *Arabidopsis*. *Plant Physiol* 155:1893. <https://doi.org/10.1104/pp.110.169730>
- Gao F, Liu C, Qu C, Zheng L, Yang F, Su M, Hong F (2008) Was improvement of spinach growth by nano-TiO₂ treatment related to the changes of Rubisco activase? *Biometals* 21:211–217
- Gardea-Torresdey J, Tiemann K, Gamez G, Dokken K, Cano-Aguilera I, Furenlid LR, Renner MW (2000) Reduction and accumulation of gold (III) by *Medicago sativa* alfalfa biomass: X-ray absorption spectroscopy, pH, and temperature dependence. *Environ Sci Technol* 34:4392–4396
- Glomstad B, Altin D, Sørensen L, Liu J, Jenssen BM, Booth AM (2016) Carbon nanotube properties influence adsorption of phenanthrene and subsequent bioavailability and toxicity to *Pseudokirchneriella subcapitata*. *Environ Sci Technol* 50:2660–2668
- Goodman CM, Mccusker CD, Yilmaz T, Rotello VM (2004) Toxicity of gold nanoparticles functionalized with cationic and anionic side chains. *Bioconjug Chem* 15:897–900
- Green S, Renault S (2008) Influence of papermill sludge on growth of *Medicago sativa*, *Festuca rubra* and *Agropyron trachycaulum* in gold mine tailings: a greenhouse study. *Environ Pollut* 151:524–531
- Groppa M, Rosales E, Iannone M, Benavides M (2008) Nitric oxide, polyamines and Cd-induced phytotoxicity in wheat roots. *Phytochemistry* 69:2609–2615
- Guo D, Wu C, Song W, Jiang H, Wang X, Chen B (2009) Effect of colloidal gold nanoparticles on cell interface and their enhanced intracellular uptake of arsenic trioxide in leukemia cancer cells. *J Nanosci Nanotechnol* 9:4611–4617
- Gutierrez-Carbonell E, Lattanzio G, Sagardoy R, Rodríguez-Celma J, Ruiz JJR, Matros A, Abadía A, Abadía J, López-Millán A-F (2013) Changes induced by zinc toxicity in the 2-DE protein profile of sugar beet roots. *J Proteome* 94:149–161
- Han T, Fan T, Chow S-K, Zhang D (2010) Biogenic N–P-codoped TiO₂: synthesis, characterization and photocatalytic properties. *Bioresour Technol* 101:6829–6835
- Hashimoto Y, Takeuchi S, Mitsunobu S, Ok Y-S (2017) Chemical speciation of silver (Ag) in soils under aerobic and anaerobic conditions: Ag nanoparticles vs. ionic Ag. *J Hazard Mater* 322:318–324
- Hauck TS, Ghazani AA, Chan WC (2008) Assessing the effect of surface chemistry on gold nanorod uptake, toxicity, and gene expression in mammalian cells. *Small* 4:153–159
- Hego E, Bes CM, Bedon F, Palagi PM, Chaumeil P, Barre A, Claverol S, Dupuy JW, Bonneau M, Lalanne C (2014) Differential accumulation of soluble proteins in roots of metallicolous and nonmetallicolous populations of *Agrostis capillaris* L. exposed to Cu. *Proteomics* 14:1746–1758
- Hopff D, Wienkoop S, Luthje S (2013) The plasma membrane proteome of maize roots grown under low and high iron conditions. *J Proteome* 91:605–618
- Hund-Rinke K, Simon M (2006) Ecotoxic effect of photocatalytic active nanoparticles (TiO₂) on algae and daphnids (8 pp). *Environ Sci Pollut Res* 13:225–232
- Inokuchi R, Itagaki T, Wiskich JT, Nakayama K, Okada M (1997) An NADP-glutamate dehydrogenase from the green alga *Bryopsis maxima*. Purification and properties. *Plant Cell Physiol* 38:327–335
- Jang H, Pell LE, Korgel BA, English DS (2003) Photoluminescence quenching of silicon nanoparticles in phospholipid vesicle bilayers. *J Photochem Photobiol A Chem* 158:111–117
- Jasim B, Thomas R, Mathew J, Radhakrishnan EK (2017) Plant growth and diosgenin enhancement effect of silver nanoparticles in Fenugreek (*Trigonella foenum-graecum* L.). *Saudi Pharm J* 25:443–447
- Jiang X, Luo Y, Zhao Q, Baker A, Christie P, Wong M (2003) Soil Cd availability to Indian mustard and environmental risk following EDTA addition to Cd-contaminated soil. *Chemosphere* 50:813–818

- Johnston HJ, Hutchison G, Christensen FM, Peters S, Hankin S, Stone V (2010) A review of the in vivo and in vitro toxicity of silver and gold particulates: particle attributes and biological mechanisms responsible for the observed toxicity. *Crit Rev Toxicol* 40:328–346
- Ju-Nam Y, Lead JR (2008) Manufactured nanoparticles: an overview of their chemistry, interactions and potential environmental implications. *Sci Total Environ* 400:396–414
- Justin S, Armstrong W (1991) Evidence for the involvement of ethene in aerenchyma formation in adventitious roots of rice (*Oryza sativa* L.). *New Phytol* 118:49–62
- Karamushka VI, Gadd GM (1999) Interaction of *Saccharomyces cerevisiae* with gold: toxicity and accumulation. *Biometals* 12:289–294
- Karmous I, Chaoui A, Jaouani K, Sheehan D, El Ferjani E, Scoccianti V, Crinelli R (2014) Role of the ubiquitin-proteasome pathway and some peptidases during seed germination and copper stress in bean cotyledons. *Plant Physiol Biochem* 76:77–85
- Karuppanapandian T, Rhee S, Kim E, Han B, Hoekenga O, Lee G (2012) Proteomic analysis of differentially expressed proteins in the roots of Columbia-0 and Landsberg erecta ecotypes of *Arabidopsis thaliana* in response to aluminum toxicity. *Can J Plant Sci* 92:1267–1282
- Kashem MA, Kawai S (2007) Alleviation of cadmium phytotoxicity by magnesium in Japanese mustard spinach. *Soil Sci Plant Nutr* 53:246–251
- Kashyap PL, Xiang X, Heiden P (2015) Chitosan nanoparticle based delivery systems for sustainable agriculture. *Int J Biol Macromol* 77:36–51
- Katsoyiannis IA, Zouboulis AI (2002) Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials. *Water Res* 36:5141–5155
- Khlebtsov N, Dykman L (2011) Biodistribution and toxicity of engineered gold nanoparticles: a review of in vitro and in vivo studies. *Chem Soc Rev* 40:1647–1671
- Kim BS (2013) Biological synthesis of nanomaterials using plant leaf extracts. *Nanotechnology (IEEE-NANO)*, 2013 13th IEEE Conference on, 2013. IEEE, pp 1204–1207
- Kim I, Lee B-T, Kim H-A, Kim K-W, Kim SD, Hwang Y-S (2016) Citrate coated silver nanoparticles change heavy metal toxicities and bioaccumulation of *Daphnia magna*. *Chemosphere* 143:99–105
- Kinraide TB, Ryan PR, Kochian LV (1992) Interactive effects of Al³⁺, H⁺, and other cations on root elongation considered in terms of cell-surface electrical potential. *Plant Physiol* 99:1461–1468
- Kochian LV, Hoekenga OA, Pineros MA (2004) How do crop plants tolerate acid soils? Mechanisms of aluminum tolerance and phosphorous efficiency. *Annu Rev Plant Biol* 55:459–493
- Kollmeier M, Felle HH, Horst WJ (2000) Genotypical differences in aluminum resistance of maize are expressed in the distal part of the transition zone. Is reduced basipetal auxin flow involved in inhibition of root elongation by aluminum? *Plant Physiol* 122:945–956
- Kolmakov A, Moskovits M (2004) Chemical sensing and catalysis by one-dimensional metal-oxide nanostructures. *Annu Rev Mater Res* 34:151–180
- Kraemer SM (2004) Iron oxide dissolution and solubility in the presence of siderophores. *Aquat Sci* 66:3–18
- Kumari M, Mukherjee A, Chandrasekaran N (2009) Genotoxicity of silver nanoparticles in *Allium cepa*. *Sci Total Environ* 407:5243–5246
- Kurepa J, Paunesku T, Vogt S, Arora H, Rabatic BM, Lu J, Wanzer MB, Woloschak GE, Smalle JA (2010) Uptake and distribution of ultrasmall anatase TiO₂ Alizarin red S nanoconjugates in *Arabidopsis thaliana*. *Nano Lett* 10:2296–2302
- Lee G, Kim BS (2014) Biological reduction of graphene oxide using plant leaf extracts. *Biotechnol Prog* 30:463–469
- Lee D-Y, Fortin C, Campbell PG (2005) Contrasting effects of chloride on the toxicity of silver to two green algae, *Pseudokirchneriella subcapitata* and *Chlamydomonas reinhardtii*. *Aquat Toxicol* 75:127–135
- Lee W-M, Kwak JI, An Y-J (2012) Effect of silver nanoparticles in crop plants *Phaseolus radiatus* and *Sorghum bicolor*: media effect on phytotoxicity. *Chemosphere* 86:491–499
- Li L, Sillanpää M, Schultz E (2017) Influence of titanium dioxide nanoparticles on cadmium and lead bioaccumulations and toxicities to *Daphnia magna*. *J Nanopart Res* 19:223

- Liu W, Zhu Y, Hu Y, Williams P, Gault A, Meharg AA, Charnock J, Smith F (2006) Arsenic sequestration in iron plaque, its accumulation and speciation in mature rice plants (*Oryza sativa* L.). *Environ Sci Technol* 40:5730–5736
- Liu X, Wu H, Ji C, Wei L, Zhao J, Yu J (2013) An integrated proteomic and metabolomic study on the chronic effects of mercury in Suaeda salsa under an environmentally relevant salinity. *PLoS One* 8:e64041
- Liu T, Shen C, Wang Y, Huang C, Shi J (2014) New insights into regulation of proteome and polysaccharide in cell wall of *Elsholtzia splendens* in response to copper stress. *PLoS One* 9:e109573
- Liu R, Zhang H, Lal R (2016a) Effects of stabilized nanoparticles of copper, zinc, manganese, and iron oxides in low concentrations on lettuce (*Lactuca sativa*) seed germination: nanotoxicants or nanonutrients? *Water Air Soil Pollut* 227:42
- Liu S, Jiang W, Wu B, Yu J, Yu H, Zhang X-X, Torres-Duarte C, Cherr GN (2016b) Low levels of graphene and graphene oxide inhibit cellular xenobiotic defense system mediated by efflux transporters. *Nanotoxicology* 10:597–606
- Liu Y, Wang X, Wang J, Nie Y, Du H, Dai H, Wang J, Wang M, Chen S, Hei TK (2016c) Graphene oxide attenuates the cytotoxicity and mutagenicity of PCB 52 via activation of genuine autophagy. *Environ Sci Technol* 50:3154–3164
- Ma JF, Furukawa J (2003) Recent progress in the research of external Al detoxification in higher plants: a minireview. *J Inorg Biochem* 97:46–51
- Ma Y, Kuang L, He X, Bai W, Ding Y, Zhang Z, Zhao Y, Chai Z (2010) Effects of rare earth oxide nanoparticles on root elongation of plants. *Chemosphere* 78:273–279
- Mao C, Yi K, Yang L, Zheng B, Wu Y, Liu F, Wu P (2004) Identification of aluminium-regulated genes by cDNA-AFLP in rice (*Oryza sativa* L.): aluminium-regulated genes for the metabolism of cell wall components. *J Exp Bot* 55:137–143
- Maret W (2013) Zinc biochemistry: from a single zinc enzyme to a key element of life. *Adv Nutr* 4:82–91
- Martínez D, Alves O, Barbieri E (2013) Carbon nanotubes enhanced the lead toxicity on the freshwater fish. *J Phys Conf Ser. IOP Publishing*, 012043
- Martínez-Fernández D, Barroso D, Komárek M (2016) Root water transport of *Helianthus annuus* L. under iron oxide nanoparticle exposure. *Environ Sci Pollut Res* 23:1732–1741
- McGehee DL, Lahiani MH, Irin F, Green MJ, Khodakovskaya MV (2017) Multiwalled carbon nanotubes dramatically affect the fruit metabolome of exposed tomato plants. *ACS Appl Mater Interfaces* 9:32430–32435
- Milner MJ, Kochian LV (2008) Investigating heavy-metal hyperaccumulation using *Thlaspi caerulescens* as a model system. *Ann Bot* 102:3–13
- Miralles P, Church TL, Harris AT (2012) Toxicity, uptake, and translocation of engineered nanomaterials in vascular plants. *Environ Sci Technol* 46:9224–9239
- Mogharabi M, Abdollahi M, Faramarzi MA (2014) Safety concerns to application of graphene compounds in pharmacy and medicine. *Bio Med Central* 22:23–30
- Moisala A, Nasibulin AG, Kauppinen EI (2003) The role of metal nanoparticles in the catalytic production of single-walled carbon nanotubes—a review. *J Phys Condens Matter* 15:S3011
- Molina-Barahona L, Vega-Loyo L, Guerrero M, Ramirez S, Romero I, Vega-Jarquín C, Albore A (2005) Ecotoxicological evaluation of diesel-contaminated soil before and after a bioremediation process. *Environ Toxicol Int J* 20:100–109
- Monica RC, Cremonini R (2009) Nanoparticles and higher plants. *Caryologia* 62:161–165
- Murphy CJ, Gole AM, Stone JW, Sisco PN, Alkiliary AM, Goldsmith EC, Baxter SC (2008) Gold nanoparticles in biology: beyond toxicity to cellular imaging. *Acc Chem Res* 41:1721–1730
- Nguyen BD, Brar DS, Bui BC, Nguyen TV, Pham LN, Nguyen HT (2003) Identification and mapping of the QTL for aluminum tolerance introgressed from the new source, *Oryza rufipogon* Griff., into indica rice (*Oryza sativa* L.). *Theor Appl Genet* 106:583–593
- Niederberger M (2007) Nonaqueous sol–gel routes to metal oxide nanoparticles. *Acc Chem Res* 40:793–800

- Niederberger M, Garnweitner G, Buha J, Polleux J, Ba J, Pinna N (2006) Nonaqueous synthesis of metal oxide nanoparticles: review and indium oxide as case study for the dependence of particle morphology on precursors and solvents. *J Sol-Gel Sci Technol* 40:259–266
- Nowack B, Bucheli TD (2007) Occurrence, behavior and effects of nanoparticles in the environment. *Environ Pollut* 150:5–22
- Nunes SM, Josende ME, Ruas CP, Gelesky MA, Da Silva Júnior FMR, Fattorini D, Regoli F, Monserrat JM, Ventura-Lima J (2017) Biochemical responses induced by co-exposition to arsenic and titanium dioxide nanoparticles in the estuarine polychaete *Laeonereis acuta*. *Toxicology* 376:51–58
- Oh MW, Roy SK, Kamal AHM, Cho K, Cho S-W, Park C-S, Choi J-S, Komatsu S, Woo S-H (2014) Proteome analysis of roots of wheat seedlings under aluminum stress. *Mol Biol Rep* 41:671–681
- Ouda SM (2014) Antifungal activity of silver and copper nanoparticles on two plant pathogens, *Alternaria alternata* and *Botrytis cinerea*. *Res J Microbiol* 9:34–42
- Peralta-Videa JR, Hernandez-Viezas JA, Zhao L, Diaz BC, Ge Y, Priester JH, Holden PA, Gardea-Torresdey JL (2014) Cerium dioxide and zinc oxide nanoparticles alter the nutritional value of soil cultivated soybean plants. *Plant Physiol Biochem* 80:128–135
- Perreault F, Bogdan N, Morin M, Claverie J, Popovic R (2012) Interaction of gold nanoglycodendrimers with algal cells (*Chlamydomonas reinhardtii*) and their effect on physiological processes. *Nanotoxicology* 6:109–120
- Petersen EJ, Pinto RA, Landrum PF, Weber J, Walter J (2009) Influence of carbon nanotubes on pyrene bioaccumulation from contaminated soils by earthworms. *Environ Sci Technol* 43:4181–4187
- Qi M, Liu Y, Li T (2013) Nano-TiO₂ improve the photosynthesis of tomato leaves under mild heat stress. *Biol Trace Elem Res* 156:323–328
- Qiu Z, Yang Q, Liu W (2013) Photocatalytic degradation of phytotoxic substances in waste nutrient solution by various immobilized levels of nano-TiO₂. *Water Air Soil Pollut* 224:1461
- Rangel AF, Rao IM, Horst WJ (2007) Spatial aluminium sensitivity of root apices of two common bean (*Phaseolus vulgaris* L.) genotypes with contrasting aluminium resistance. *J Exp Bot* 58:3895–3904
- Ratte HT (1999) Bioaccumulation and toxicity of silver compounds: a review. *Environ Toxicol Chem* 18:89–108
- Raven JA (1988) The iron and molybdenum use efficiencies of plant growth with different energy, carbon and nitrogen sources. *New Phytol* 109:279–287
- Rizzello L, Pompa PP (2014) Nanosilver-based antibacterial drugs and devices: mechanisms, methodological drawbacks, and guidelines. *Chem Soc Rev* 43:1501–1518
- Roh J-Y, Sim SJ, Yi J, Park K, Chung KH, Ryu D-Y, Choi J (2009) Ecotoxicity of silver nanoparticles on the soil nematode *Caenorhabditis elegans* using functional ecotoxicogenomics. *Environ Sci Technol* 43:3933–3940
- Romeo S, Trupiano D, Ariani A, Renzone G, Scippa GS, Scaloni A, Sebastiani L (2014) Proteomic analysis of *Populus× euramericana* (clone I-214) roots to identify key factors involved in zinc stress response. *J Plant Physiol* 171:1054–1063
- Rosenfeldt RR, Seitz F, Senn L, Schilde C, Schulz R, Bundschuh M (2015) Nanosized titanium dioxide reduces copper toxicity – the role of organic material and the crystalline phase. *Environ Sci Technol* 49:1815–1822
- Saison C, Perreault F, Daigle J-C, Fortin C, Claverie J, Morin M, Popovic R (2010) Effect of core-shell copper oxide nanoparticles on cell culture morphology and photosynthesis (photosystem II energy distribution) in the green alga, *Chlamydomonas reinhardtii*. *Aquat Toxicol* 96:109–114
- Santos SM, Dinis AM, Rodrigues DM, Peixoto F, Videira RA, Jurado AS (2013) Studies on the toxicity of an aqueous suspension of C60 nanoparticles using a bacterium (gen. *Bacillus*) and an aquatic plant (*Lemna gibba*) as in vitro model systems. *Aquat Toxicol* 142:347–354

- Sasidharan A, Panchakarla L, Chandran P, Menon D, Nair S, Rao C, Koyakutty M (2011) Differential nano-bio interactions and toxicity effects of pristine versus functionalized graphene. *Nanoscale* 3:2461–2464
- Saxena A, Tripathi R, Singh R (2010) Biological synthesis of silver nanoparticles by using onion (*Allium cepa*) extract and their antibacterial activity. *Dig J Nanomater Biostruct* 5:427–432
- Schneider T, Persson DP, Husted S, Schellenberg M, Gehrig P, Lee Y, Martinoia E, Schjoerring JK, Meyer S (2013) A proteomics approach to investigate the process of Zn hyperaccumulation in *Nocca caerulea* (J & C. Presl) FKMeyer. *Plant J* 73:131–142
- Seeger EM, Baun A, Kästner M, Trapp S (2009) Insignificant acute toxicity of TiO₂ nanoparticles to willow trees. *J Soils Sediments* 9:46–53
- Serag MF, Kaji N, Gaillard C, Okamoto Y, Terasaka K, Jabasini M, Tokeshi M, Mizukami H, Bianco A, Baba Y (2010) Trafficking and subcellular localization of multiwalled carbon nanotubes in plant cells. *ACS Nano* 5:493–499
- Slade S, Pegg G (1993) The effect of silver and other metal ions on the in vitro growth of root-rotting *Phytophthora* and other fungal species. *Ann Appl Biol* 122:233–251
- Song U, Shin M, Lee G, Roh J, Kim Y, Lee EJ (2013) Functional analysis of TiO₂ nanoparticle toxicity in three plant species. *Biol Trace Elem Res* 155:93–103
- Stoimenov PK, Klinger RL, Marchin GL, Klabunde KJ (2002) Metal oxide nanoparticles as bactericidal agents. *Langmuir* 18:6679–6686
- Tan L-Y, Huang B, Xu S, Wei Z-B, Yang L-Y, Miao A-J (2016) Aggregation reverses the carrier effects of TiO₂ nanoparticles on cadmium accumulation in the waterflea *Daphnia magna*. *Environ Sci Technol* 51:932–939
- Tian QY, Sun DH, Zhao MG, Zhang WH (2007) Inhibition of nitric oxide synthase (NOS) underlies aluminum-induced inhibition of root elongation in *Hibiscus moscheutos*. *New Phytol* 174:322–331
- Tripathi DK, Singh S, Singh S, Pandey R, Singh VP, Sharma NC, Prasad SM, Dubey NK, Chauhan DK (2017) An overview on manufactured nanoparticles in plants: uptake, translocation, accumulation and phytotoxicity. *Plant Physiol Biochem* 110:2–12
- Unrine JM, Colman BP, Bone AJ, Gondikas AP, Matson CW (2012) Biotic and abiotic interactions in aquatic microcosms determine fate and toxicity of Ag nanoparticles. Part 1. Aggregation and dissolution. *Environ Sci Technol* 46:6915–6924
- Valle SR, Carrasco J, Pinochet D, Calderini DF (2009) Grain yield, above-ground and root biomass of Al-tolerant and Al-sensitive wheat cultivars under different soil aluminum concentrations at field conditions. *Plant Soil* 318:299–310
- Van Assche F, Clijsters H (1990) Effects of metals on enzyme activity in plants. *Plant Cell Environ* 13:195–206
- Vishwakarma K, Upadhyay N, Singh J, Liu S, Singh VP, Prasad SM, Chauhan DK, Tripathi DK, Sharma S (2017) Differential phytotoxic impact of plant mediated silver nanoparticles (AgNPs) and silver nitrate (AgNO₃) on *Brassica* sp. *Front Plant Sci* 8:1501
- Von Uexkull H, Mutert E (1995) Global extent, development and economic impact of acid soils. *Plant Soil* 171:1–15
- Wagner PA, Hoekstra WG, Ganther HE (1975) Alleviation of silver toxicity by selenite in the rat in relation to tissue glutathione peroxidase. *Proc Soc Exp Biol Med* 148:1106–1110
- Wang S, Kurepa J, Smalle JA (2011) Ultra-small TiO₂ nanoparticles disrupt microtubular networks in *Arabidopsis thaliana*. *Plant Cell Environ* 34:811–820
- Wang F, Shang Y, Yang L, Zhu C (2012) Comparative proteomic study and functional analysis of translationally controlled tumor protein in rice roots under Hg²⁺ stress. *J Environ Sci* 24:2149–2158
- Wang CY, Shen RF, Wang C, Wang W (2013) Root protein profile changes induced by Al exposure in two rice cultivars differing in Al tolerance. *J Proteome* 78:281–293
- Wang X, Qu R, Allam AA, Ajarem J, Wei Z, Wang Z (2016a) Impact of carbon nanotubes on the toxicity of inorganic arsenic [As (III) and As (V)] to *Daphnia magna*: the role of certain arsenic species. *Environ Toxicol Chem* 35:1852–1859

- Wang X, Qu R, Liu J, Wei Z, Wang L, Yang S, Huang Q, Wang Z (2016b) Effect of different carbon nanotubes on cadmium toxicity to *Daphnia magna*: the role of catalyst impurities and adsorption capacity. *Environ Pollut* 208:732–738
- Wang X, Yang X, Chen S, Li Q, Wang W, Hou C, Gao X, Wang L, Wang S (2016c) Corrigendum: zinc oxide nanoparticles affect biomass accumulation and photosynthesis in *Arabidopsis*. *Front Plant Sci* 7:559
- Wang X, Liu Y, Wang J, Nie Y, Chen S, Hei TK, Deng Z, Wu L, Zhao G, Xu A (2017) Amplification of arsenic genotoxicity by TiO₂ nanoparticles in mammalian cells: new insights from physico-chemical interactions and mitochondria. *Nanotoxicology* 11:978–995
- Weber M, Harada E, Vess C, Roepenack-Lahaye EV, Clemens S (2004) Comparative microarray analysis of *Arabidopsis thaliana* and *Arabidopsis halleri* roots identifies nicotianamine synthase, a ZIP transporter and other genes as potential metal hyperaccumulation factors. *Plant J* 37:269–281
- Wood CM, Hogstrand C, Galvez F, Munger R (1996) The physiology of waterborne silver toxicity in freshwater rainbow trout (*Oncorhynchus mykiss*) 1. The effects of ionic Ag⁺. *Aquat Toxicol* 35:93–109
- Worms IA, Boltzman J, Garcia M, Slaveykova VI (2012) Cell-wall-dependent effect of carboxyl-CdSe/ZnS quantum dots on lead and copper availability to green microalgae. *Environ Pollut* 167:27–33
- Wu S, Huang L, Head J, Chen D, Kong I-C, Tang Y (2012) Phytotoxicity of metal oxide nanoparticles is related to both dissolved metals ions and adsorption of particles on seed surfaces. *J Pet Environ Biotechnol* 3:126
- Xie W, Wang H, Li H (2011) Silica-supported tin oxides as heterogeneous acid catalysts for transesterification of soybean oil with methanol. *Ind Eng Chem Res* 51:225–231
- Xu C, Garrett WM, Sullivan J, Caperna TJ, Natarajan S (2006) Separation and identification of soybean leaf proteins by two-dimensional gel electrophoresis and mass spectrometry. *Phytochemistry* 67:2431–2440
- Xu C, Sibicky T, Huang B (2010) Protein profile analysis of salt-responsive proteins in leaves and roots in two cultivars of creeping bentgrass differing in salinity tolerance. *Plant Cell Rep* 29:595–615
- Yan C, Yang F, Wang Z, Wang Q, Seitz F, Luo Z (2017) Changes in arsenate bioaccumulation, subcellular distribution, depuration, and toxicity in *Artemia salina* nauplii in the presence of titanium dioxide nanoparticles. *Environ Sci Nano* 4:1365–1376
- Yang K, Xing B (2010) Adsorption of organic compounds by carbon nanomaterials in aqueous phase: Polanyi theory and its application. *Chem Rev* 110:5989–6008
- Yang W-W, Li Y, Miao A-J, Yang L-Y (2012) Cd²⁺ toxicity as affected by bare TiO₂ nanoparticles and their bulk counterpart. *Ecotoxicol Environ Saf* 85:44–51
- Ye X, Gu Y, Wang C (2012) Fabrication of the Cu₂O/polyvinyl pyrrolidone-graphene modified glassy carbon-rotating disk electrode and its application for sensitive detection of herbicide paraquat. *Sensors Actuators B Chem* 173:530–539
- Yin L, Colman BP, McGill BM, Wright JP, Bernhardt ES (2012) Effects of silver nanoparticle exposure on germination and early growth of eleven wetland plants. *PLoS One* 7:e47674
- Zargar SM, Kurata R, Inaba S, Oikawa A, Fukui R, Ogata Y, Agrawal GK, Rakwal R, Fukao Y (2015) Quantitative proteomics of *Arabidopsis* shoot microsomal proteins reveals a cross-talk between excess zinc and iron deficiency. *Proteomics* 15:1196–1201
- Zeng F, Wu X, Qiu B, Wu F, Jiang L, Zhang G (2014) Physiological and proteomic alterations in rice (*Oryza sativa* L.) seedlings under hexavalent chromium stress. *Planta* 240:291–308
- Zhai G, Walters KS, Peate DW, Alvarez PJ, Schnoor JL (2014) Transport of gold nanoparticles through plasmodesmata and precipitation of gold ions in woody poplar. *Environ Sci Technol Lett* 1:146–151
- Zhang S, Deng R, Lin D, Wu F (2017) Distinct toxic interactions of TiO₂ nanoparticles with four coexisting organochlorine contaminants on algae. *Nanotoxicology* 11:1115–1126

- Zhen Y, Qi JL, Wang SS, Su J, Xu GH, Zhang MS, Miao L, Peng XX, Tian D, Yang YH (2007) Comparative proteome analysis of differentially expressed proteins induced by Al toxicity in soybean. *Physiol Plant* 131:542–554
- Zheng L, Hong F, Lu S, Liu C (2005) Effect of nano-TiO₂ on strength of naturally aged seeds and growth of spinach. *Biol Trace Elem Res* 104:83–91
- Zhu H, Han J, Xiao JQ, Jin Y (2008) Uptake, translocation, and accumulation of manufactured iron oxide nanoparticles by pumpkin plants. *J Environ Monit* 10:713–717