Chapter 2
Terrestrial Nanotoxicology: Evaluating the Nano-Biointeractions in Vascular Plants

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Abstract The effects of engineered nanoparticles (ENPs) in living organisms are described in a myriad of articles. Most of the literature on this topic is devoted to plants of different gender and species. Studies from laboratories and greenhouse facilities highlight effects on chlorophyll production, plant growth, stress enzyme activities, phytotoxicity, cytotoxicity, and genotoxicity. With few exceptions, research reports show that toxic effects of ENPs on plants are associated with particle size, phase, surface properties, exposure concentration, and soil chemistry. ENPs have been found to be taken through roots from soilless/soil media and translocated to the aboveground organs. However, the uptake and translocation can occur in reverse if important amounts of ENPs are exposed to the foliage. This chapter includes an analysis of the most recent and relevant information about the interaction of ENPs with vascular plants. Most of the reviewed literature refers to highly produced and used ENPs. Data about exposure to carbon nanotubes (CNTs), cerium dioxide (nano-CeO_2), titanium dioxide (nano-TiO_2), zinc oxide (nano-ZnO), copper oxide (nano-CuO), gold (nano-Au), iron (nano-Fe_3O_4), silver (nano-Ag), and others ENPs are discussed.

Keywords Engineered nanoparticles · Toxicology · Uptake · Exposure pathways · Risk assessment

2.1 Introduction

Plants have evolved exposed to naturally produced particulate matter (PM). However, exposure to PM has increased since the industrial revolution due to emissions from stationary and mobile sources [1]. In current times, PM at the nanoscale is progressively released from devices, goods, personal care items,

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and agriculture-intended products. Recent reports indicate that industrial facilities [2], cars, trucks, agriculture, and farming equipment [3], agricultural applications of nanotechnology [4], and the constant increase of nanomaterials in biosolids [5], have dramatically increased the risks of plant exposure to PM.

Concerns about the environmental impacts of nanotechnologies are becoming more and more voiced. US federal agencies like the National Science Foundation and the Environmental Protection Agency, governmental agencies of other countries, public and private universities, and other organizations are devoting capitals to investigate possible effects of nanotechnologies in human beings and basic resources like beneficial microorganisms, animals, and plants. So far, thousands of research and review articles (ScienceDirect.com shows more than 1,600 for 2015 and 2016 only) have described a variety of effects of nanomaterials in living organisms. This chapter includes the most recent and relevant information about the interaction of nanomaterials with vascular plants. Most of the reviewed literature refers to highly produced and used engineered nanoparticles (ENPs) including carbon-based, such as carbon nanotubes (CNTs), and metal-based, like cerium dioxide (nano-CeO_2), copper oxide (nano-CuO), titanium dioxide (nano-TiO_2), zinc oxide (nano-ZnO), gold (nano-Au), iron (nano-Fe_3O_4), silver (nano-Ag), and other ENPs. When available, information concerning micrometric particles was included. Emphasis was given to industrially produced or garden grown agricultural plants. Most of the reported studies have been performed under controlled environments (laboratory, growth chamber, and greenhouse), and to the authors' knowledge, there are no reports of field conditions.

2.2 Evidence of Uptake Accumulation and Biotransformation of ENPs and Exposure Pathways

The reported literature highlights effects of ENPs in root and shoot lengths, activity of stress enzymes, carbohydrates, sugars, amino acids, proteins, chlorophyll production, phytotoxicity, cytotoxicity, genotoxicity, and biotransformation. Analytical techniques including electron microscopy (SEM/TEM) [6], synchrotron micro X-ray fluorescence (μ-XRF) and micro X-ray absorption near edge structure (μ-XANES) [7, 8], and confocal microscopy [9], among others, have been used to study the uptake of ENPs and related ions, and to determine their location and oxidation state.

It is believed that the physiological and agronomical impacts of ENPs on plants rely on their uptake, translocation, accumulation, and biotransformation within plant systems. It is also hypothesized that impacts depend on the exposure pathway, concentration, plant species, and environment. There are reports from plants grown in liquid and solid media exposed to different concentrations of ENPs, either through the roots or the foliage. The most abundant reports correspond to root

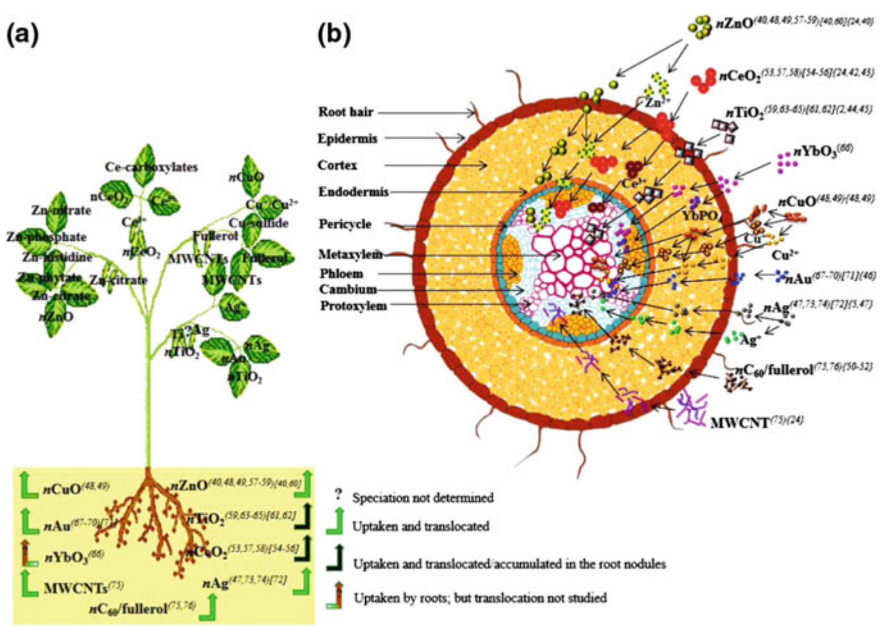

Fig. 2.1 Schematic diagram of uptake and biotransformation of nanomaterials (NMs) in plant systems, including hydroponic and soil culture. **a** Speciation of ENMs in plant tissues (roots, stems, leaves, and fruits/grains); **b** Transverse cross section of root cell illustrating biotransformation of NMs. Reference numbers in the figure correspond to the original review article and *n* stands for nano. (Reprinted with permission from Gardea-Torresdey et al. [10]. Copyright @ 2014 American Chemical Society)

exposure and only a few of them refer to foliar exposure. Figure 2.1 [10] illustrates comprehensive possible uptake routes and mechanisms. As shown in this figure, independent of the substrate, plants take up the ENPs through roots or foliage by active or passive mechanisms. Detailed information is presented in the following sections and in a critical review by Ma et al. [11].

2.2.1 Root Exposure Studies

Applications of nanoscale agricultural products such as fertilizers [4, 12], additives for soil remediation [13], growth regulators [14], and discharges of wastewater and biosolids [5, 15] could be great contributors for the uptake and accumulation of ENPs from root exposure. Studies performed in soilless or soil media have explored effects on seeds [16], seedlings [17], and tubers [18]. One of the first studies about ENPs' uptake and translocation was performed by Zhu et al. [19]. In such study, pumpkin (*Cucurbita maxima*) was exposed to magnetic nano-Fe_3O_4 through roots in an aqueous medium. After 20 days of growth, Zhu et al. measured the concentration of ENPs in stems and leaves by busing a vibrating sample magnetometer (VSM, LakeShore 7400), demonstrating the uptake and translocation of the nano-Fe_3O_4 from roots to the aboveground plant system. Later on, Khodakovskaya et al. [16] reported that carbon nanotubes penetrated the thick seed coat of tomato (*Solanum lycopersicum* L.), affecting seed water transportation, germination, and seedling growth. More recently, Zhao et al. [9, 20] exposed corn (*Zea mays*) seedlings to fluorescein isothiocyanate (FITC)-stained CeO_2 and ZnO ENPs, and found that both penetrated the root tissues, reaching the transport system. Confocal images showed that the Casparian strip retained the stained ENPs; however, they further entered the vasculature at the emission point of lateral roots [21]. This was later confirmed by Majumdar et al. [22] in kidney bean plants (*Phaseolus vulgaris*). The images suggested that the ENPs entered the root endodermis through the apoplast, followed by the symplast [9], ultimately reaching the aboveground plant system (Fig. 2.2) [11].

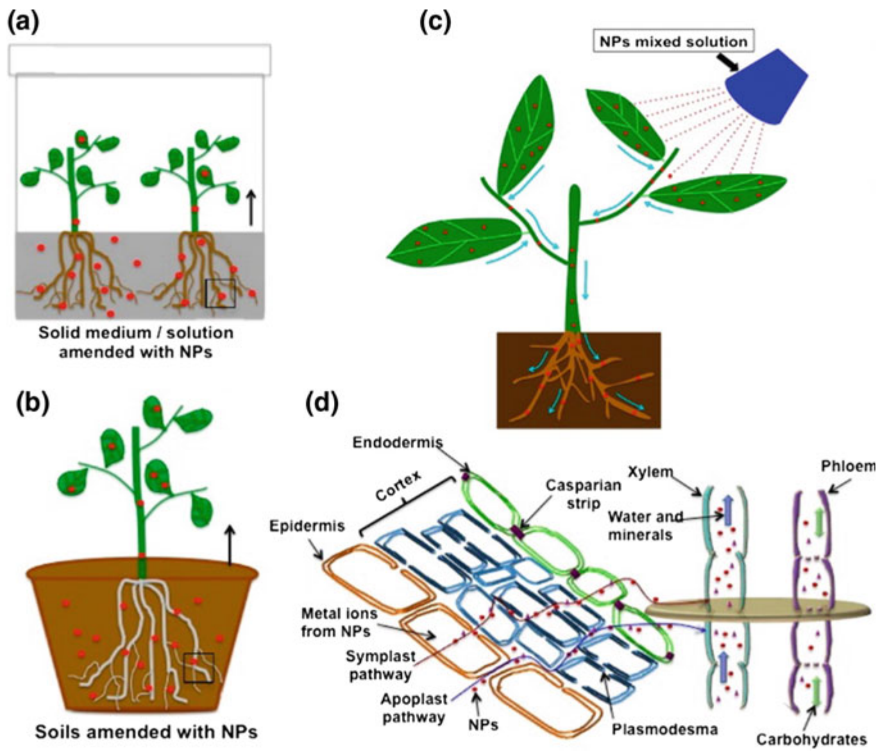

Fig. 2.2 Schematic diagram of possible pathways of ENPs uptake and translocation. **a**, **b** Plants grown in media amended with NPs. **c** ENPs exposed to plants via foliar spray. **d** ENPs entered into plants through symplastic and apoplastic regions. (Reprinted with permission from Ma et al. [11]. Copyright @ 2015 American Chemical Society)

Lopez-Moreno et al. [23] firstly reported the speciation of ZnO and CeO_2 within plant tissues. These researchers exposed soybean [23] to either ZnO or CeO_2 ENPs and through XANES analyses determined that, within the root, most of the Ce was in the same oxidation state as CeO_2, but ZnO was not present. Lopez-Moreno et al. [24] also exposed CeO_2 to alfalfa (*Medicago sativa*), corn, cucumber (*Cucumis sativus*), and tomato, and corroborated that CeO_2 ENPs were stored within the roots of the four plant species. Additionally, by using XANES and STXM, Zhang et al. [25] reported that in cucumber exposed to CeO_2 ENPs, Ce distributed in the root in nanoparticulate (NP) form and as $CePO_4$, and reached the aerial system as CeO_2 ENPs and carboxylates. Majumdar et al. [22] reported that in kidney bean (*P. vulgaris*) roots, 12% of the CeO_2 ENPs was transformed into Ce(III) and distributed to shoots time dependently. Zhao et al. [26] exposed CeO_2 ENPs to cucumber roots and detected Ce in the leaf veins. Thus, these researchers concluded that once these ENPs penetrated the roots, they were translocated to the leaves with the flow of water during transpiration. A hydroponic study with CeO_2 ENPs of different size showed significant Ce translocation from roots to shoots in plants exposed to particles of 10 nm; however, no significant Ce accumulation was observed in shoots of plants exposed to particles >20 nm [27]. Servin et al. [17] exposed cucumber to a mixture of anatase (82%)-rutile (18%) TiO_2 ENPs and analyzed the tissues with μ-XRF and μ-XANES. They found that cucumber absorbed Ti through the roots and translocated it to the leaves. Moreover, they found Ti in leaf trichomes and suggested these structures might work as sinks or excretory structures for TiO_2 ENPs. Avanasi et al. [28] cultured radish (*Raphanus sativus*) in soil amended with ^{14}C-labled C_{60}, and found that only ~7% of the C_{60} was taken up by plants, of which 40–47% was retained in roots, 22–23%, translocation to tubers, 12–16% to stems, and 18–22% to leaves. Studies with CuO and ZnO ENPs exposed to wheat (*Triticum aestivum*) through roots have shown that Cu accumulated in shoots as CuO and Cu(I)-sulfur complexes, while ZnO dissociated, leaving Zn in the form of Zn-phosphate [29]. The above-mentioned results clearly show that further studies are needed in order to fully understand the fate of ENPs absorbed through the roots. In addition, there is a lack of knowledge concerning the accumulation of ENPs in root nodules, contribution of root exudates in surface modification and uptake, retention in xylem vessels, and accumulation in organelles of the aboveground plant system.

2.2.2 Foliar Exposure

There is a long history in the use of foliar applications of micronutrients or pesticides to improve plant health. Currently, there is an increasing trend in the use of ENPs as pesticides [30], herbicides [31], and fertilizers [14]. In determined environments, plants' foliage is unintentionally exposed to ENPs from industrial fallouts [32]. In general, foliar exposure has been less investigated and remains largely unclear. A few reports have shown physiological effects, accumulation, speciation, and have explored the uptake mechanisms.

One of the first reports about foliar exposure to ENPs was performed by Uzu et al. [33]. These researchers exposed lettuce (*Lactuca sativa*) to lead particles. After 43 days of exposure, they found aggregated Pb nanoparticles (NPs) in necrotic zones and leaf central veins. Additionally, Pb particles were detected in stomatal openings and leaf cuticles. Subsequently, Schreck et al. [34, 35] examined the impact of foliar application of Pb-containing particles in lettuce, parsley (*Petroselinum crispum*) and ryegrass (*Lolium perenne*). These researchers found Pb-rich particles in stomata, $PbCO_3$ or organic Pb crystals on the leaf surface, and $PbSO_4$ underneath leaf membranes. Larue et al. [36, 37] exposed Ag and TiO_2 (pristine and aged paint-containing) ENPs to lettuce leaves and found that some particles were retained by the cuticle and others penetrated through leaf stomata, upon which they were translocated to all plant tissues. Similarly, Hong et al. [6] exposed atmospheric (powder) CeO_2 ENPs to cucumber seedling leaves and, through ICP-OES analyses of mature plants, detected Ce in roots, stems, leaves, and flowers, demonstrating that the powdered CeO_2 reached the transport system through leaves, and remained within the plant until maturity. It seems that entrapment in the cuticle and penetration through stomata are the two main routes of ENPs entry after foliar exposure. However, Birbaum et al. [38] reported no translocation of Ce in corn plants exposed to CeO_2 ENPs, either through foliage or roots, which suggest exclusion mechanisms that deserve more in depth studies.

2.2.3 Accumulation of ENPs in Fruits and Seeds

A few studies have shown that ENPs exposed through root or foliage can be transported and accumulated in fruits and seeds and ingested by human beings. By using μ-XRF and μ-XANES, Hernandez-Viezcas et al. [7] found CeO_2 ENPs in soybean seeds harvested from plants cultivated in soil amended with such ENPs. Using the same techniques, Servin et al. [39] demonstrated that cucumber plants absorbed TiO_2 ENPs from soil and translocated them to fruits. Rico et al. [40] evaluated the Ce accumulation in grains of three rice varieties divergent in amylose content, cultivated in soil amended with CeO_2 ENPs. Results showed that Ce concentrated the most in gains of the varieties with medium and low amylose contents. More recently, Hong et al. [6] exposed CeO_2 ENPs to the foliage of 21-day-old cucumber seedlings and analyzed the fruits for Ce content. They found significantly higher Ce concentration, compared with control and the other treatments, in fruits of plants exposed to 200 mg/L of the CeO_2 ENPs. Although Rico et al. [40] and Hong et al. [6] did not use synchrotron or microscopy techniques to show the presence of CeO_2 ENPs, previous works [7, 12, 41] have demonstrated that these ENPs are very stable and undergo little transformation in soil or within plant tissues. Consequently, it is hypothesized that most of the Ce in cucumber fruits and rice grains was in nanoparticulate form. This suggests that TiO_2 and CeO_2

ENPs can reach the human body through grains and seeds of plants grown in ENPs impacted soils.

In conclusion, the uptake and accumulation of ENPs depend on the species of plant [42], particle size [27], concentration [43], and surface property [44]. The literature indicates that the exposure to ENPs through roots or foliage results in modification of enzyme activities [45], fruit quality [46], and nutrient content [47], among others. This may bring risks to human health, and even disruption of the ecological balance.

2.3 Mechanisms of Interactions Between ENPs and Plants

The literature has shown that ENPs tend to bioaccumulate and persist in plant tissue, influencing cell metabolism and development. They also tend to get deposited in aggregated or unaggregated form on subcellular sites. Figure 2.3

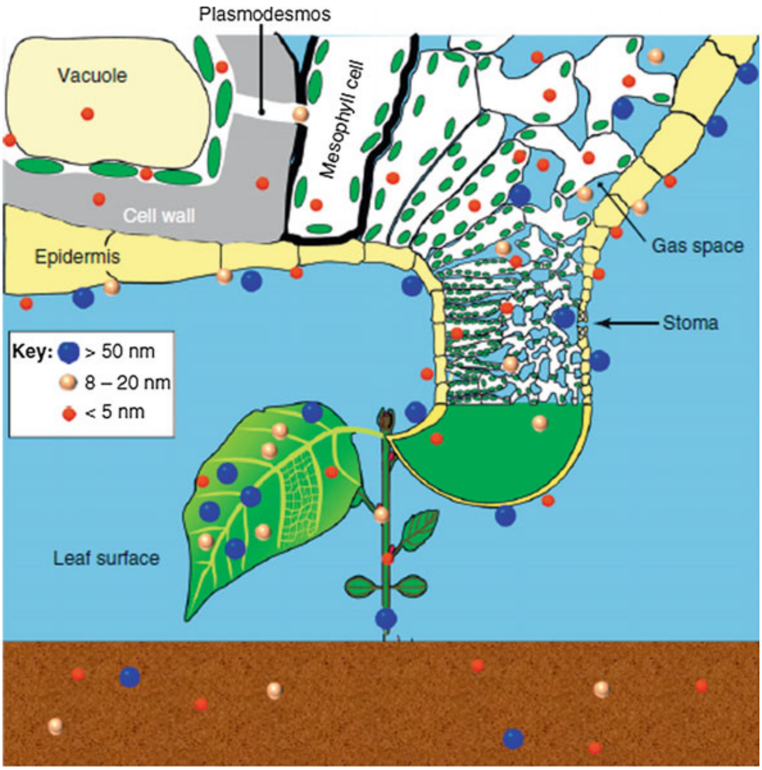

Fig. 2.3 Distribution of NPs of three different sizes in plant shoots at organ, tissue and cell level. (Reprinted with permission from Dietz et al. [48]. Copyrights @ 2011 Elsevier Ltd.)

elaborates the routes that different sized ENPs (>50, 8–20, and <5 nm) can take in the plant [48]. The ENPs translocate from the root, via stem, to the aerial parts of the plant. They enter the intercellular space and traverse to the outer apoplast, whereas only the minute ones are able to diffuse through the plant cell wall and enter the protoplast [48]. ENPs can also be taken up by roots through endocytosis [49].

There are five major mechanisms of action of ENPs on biological systems: (i) metal ions produced from the dissociation of ENPs show chemical effects in solution on dissolution. Essential heavy metals including Cu, Ni, and Zn, and toxic elements like Cd have their ionic form released from the nano forms. They biochemically bind with proteins, carboxyl, sulfhydryl, or imidazole groups hampering their normal functioning. Their meddling with cellular life processes may lead to redox imbalances and, subsequently, induce oxidative stress in plant cells [50, 51]. Metal atoms such as Cu and Fe act as oxidizing agents and give electrons to O_2 to form O_2^- or to H_2O_2 to form the reactive $OH^{\cdot}$ radical. This adds to the oxidative stress in the plant cells. (ii) Mechanical blocking of open pores that then become unavailable for biochemical transport processes. The blocking is size dependent [52]. (iii) Catalytic effect on surfaces due to ions including Ag, Pd, Au, Fe, Pt, and Co that act as catalysts for redox reactions. At very low concentration, the metal ions either bind to organic acids, inducible or constitutive chelators, like phytochelatins, metallothioneins, and ferritin [52], or they participate in transport processes [53]. Such catalytic effect enhances the toxicity of ENPs. (iv) Effects due to proteins bound to the surface of the ENPs, which could be by oxidative effects, ionic, or covalent bonds. Atoms that have an oxidic surface frequently form a layer of hydroxyl groups on the surface [48]. Being negatively charged, the layer bonds with positively charged groups of plant proteins [54]. This deteriorates the work efficiency of the proteins. If the bond between proteins and ENPs is covalent, then the toxic effect is extreme. The bond between cysteine and Au ENPs is one such example of a permanent bond. The most prominent reason for ENPs toxicity is oxidative stress caused by an excess of reactive oxygen species (ROS) [55]. (v) Changes in chemical effects like pH [49]. ENPs present in soil are influenced by variations in surrounding conditions. Factors such as temperature, pH, ionic strength, particle size, and concentration determine their surface properties that further control particle aggregation and deposition [56]. These external factors likely manifest their effect in plant roots at cellular level, via the ENPs that enter the system.

2.4 Toxicity Symptoms

Nanotechnology has experienced immense growth; by extension, plant nanotoxicology has become an emerging field of interest. Many studies on the effects of ENPs to terrestrial plants have materialized within the past few years. Table 2.1

includes an extensive list of the most recent studies, while the most notable ones are summarized in the following paragraphs.

Nano-CuO was found to be translocated from roots to shoots when exposed to maize in hydroponic culture [57]. There was no effect on germination, which was in agreement with previous literature stating that germination is an obtuse measure for phytotoxicity of ENPs [57–59]; however, root elongation was reduced by 55 and 84% at 10 and 100 mg/L of CuO ENPs. Plants also developed chlorotic symptoms, and root and shoot biomass decreased at the same CuO ENP concentrations [57]. Overall, roots of maize were found to be more susceptible to CuO ENPs' toxicity than the shoots. When Ag ENPs were exposed to mung bean (*Phaseolus radiatus*) and sorghum (*Sorghum bicolor*) in soil and agar test media, a concentration dependent-growth inhibition was discovered [60]. The bioavailability of Ag ENPs was also found to be reduced in soil, most likely explained either by changes in physiochemical properties when mixed with soil components or by the intensified aggregation that Ag experiences in the presence of clay [61].

In a comprehensive study that evaluated five commercial ENPs (MWCNTs, Al, Al_2O_3, Zn, ZnO) on seed germination and root growth of radish, rape (*Brassica napus*), ryegrass, lettuce, corn, and cucumber, the most toxic effects were produced by Zn and ZnO ENPs, which suppressed ryegrass and corn germination, respectively [59]. Root growth of five of the tested plant species was essentially terminated. When calculating dose–response curves, 50% inhibitory concentrations (IC_{50}) of 50 mg/L Zn was calculated for radish and 20 mg/L ZnO for rape and ryegrass [59]. Details about other ENPs and plant species are shown in Table 2.1.

2.5 Comparison of the Effects of Microparticles (Bulk) Versus Those of Nanoparticles

In a few studies, the effects of ENPs versus microparticles of the same metal element or compound have been compared. Hong et al. [42] exposed various copper compounds including Cu and CuO ENPs, μCu, and μCuO to lettuce and alfalfa in hydroponics. The root length was consistently affected by all the copper treatments. At 20 mg/L, both plant species absorbed more Cu from the Cu ENPs treatments, compared with both the bulk Cu and CuO treatments. Stress enzyme studies showed that the ascorbate peroxidase (APOX) activity increased at all Cu treatments in roots of both plant species, with the exception of bulk Cu in lettuce. A similar study was conducted with nano and bulk ZnO compounds in green peas (*Pisum sativum*) [91]. The ENP exposed plants resulted in significantly longer roots, whereas the bulk ZnO treatments produced significant longer roots and shoots. The chlorophyll content in leaves was diminished under both bulk and nano treatments. At all ZnO NP treatments, the catalase (CAT) activity was significantly decreased in leaves and APOX activity in roots and leaves. The bulk ZnO exposure, on the other hand, caused no changes in the CAT activity, but reduced APOX

Table 2.1 Summary of results from studies on nano-biointeractions in vascular plants

ENPs and concentration	Plant	Determination/method	Findings	Reference
Ag 25, 50, 75, 100 mg/L	Onion	Genotoxicity, cytotoxicity	Decreased mitotic index; chromosomal aberrations	[62]
Ag 100 μg/mL Au 62 μg/mL Fe_3O_4 116 μg/mL	Cucumber Lettuce	Germination	Low or no toxicity	[63]
Ag 100, 500 mg/L Cu 100, 500 mg/L	Yellow squash seeds	Toxicity induced by bulk versus nano Cu and Ag particles	Ag ENPs reduced biomass and transpiration rate by 66–84% compared to bulk Ag. Both bulk and nano Cu were toxic and brought down the two parameters by 60–70%	[64]
Al 10, 100, 1000, 10,000 mg/kg	Red kidney bean Ryegrass	Growth	Low or no toxicity	[65]
Al_2O_3, SiO_2, Fe_3O_4, ZnO 400, 2000, 4000 mg/L	Mouse-ear cress	Germination, elongation, yield	Reduced germination	[66]
Au 3.6, 7.2, 10.6, 14.0, 17.3 μM	Soybean	Chlorophyll fluorescence quenching, fluorescence spectroscopy, spectrofluorimeter	Seeds were treated with the Au ENPs. The NPs were found in plant tissues There was a chlorophyll fluorescence quenching	[67]
Au, Cu, Pd and Si 0.013 and 0.066% w/w	Lettuce seeds	Effect of ENPs exposure on seed germination and shoot to root ratio	All ENPs produced higher shoot to root ratio under the treatments (0.013% or 0.066% (w/w)), compared to controls	[68]
SWCNT 50 μg/mL QD 0.5 μg/mL SWCNT-QD 50 μg/mL	Tomato	Fluorescent and Raman-scattering 2D mapping analysis	Curtailing root development, reduced leaf life span. Decrease chlorophyll in leaves; fourfold reduction in root weight for 50 μg/mL SWCNT-QD exposure	[69]
MWCNT 50 μg/mL	Tomato	Nano-bubble amplified photothermal/photoacoustic imaging, spectroscopy, and burning method	Novel changes observed in gene expression for leaves and roots. Upregulation of genes related to stress MWCNTs observed in leaves, fruits, and root	[70]
CeO_2 100, 200, 400 mg/L	Moon trefoil	Nano vs bulk CeO_2 effects on plants, uptake of nanoceria and effect on in vitro plantlets	At low nano concentration, the root length and trifoliate leaf count increased, but the root biomass decreased. Both nano	[71]

(continued)

Table 2.1 (continued)

ENPs and concentration	Plant	Determination/method	Findings	Reference
			and bulk reduced maximum photochemical efficiency. Roots were more responsive than shoots to nanoceria	
CeO_2 100, 200, 400, 800 mg/kg	Corn (maize)	Change in CeO_2 ENPs uptake due to surface coating and the presence of organic matter, Fluorescein isothiocyanate (FITC)-stained CeO_2, confocal microscope, μ-XRF	More root Ce in organic soil, compared to low organic matter soil. Reversed results in shoots. Confocal microscopy images showed CeO_2 ENPs aggregates in cortex and epidermal cells, suggesting apoplastic route	[20]
CeO_2 100, 400 mg/kg	Wheat	Wheat lifecycle study (7 months), field lysimeter, low dose (100 mg/kg), high dose (400 mg/kg)	The chlorophyll content was lowered at the high dose along with an increase in the catalase and superoxide dismutase activities. Flowering was delayed by a week in both treatments	[72]
CeO_2 62.5, 125, 250, 500 mg/L	Red kidney bean	Biochemical assay	Reduced enzymes in roots. Enhanced enzymes in leaves	[22]
CeO_2 500, 1000, 2000, 4000 mg/L	Alfalfa Corn Tomato Onion	Germination, elongation	Reduced germination. Increased and reduced root growth. Increased root elongation	[24]
CeO_2, CuO 50, 100, 200 mg/L	Cucumber	Fruit quality	Reduced firmness	[47]
CeO_2, ZnO 400, 800 mg/kg	Cucumber	Chlorophyll, gas exchange, physiological characteristics, ICP-MS, μ-XRF	Ce and Zn bioaccumulation in fruit. μ-XRF showed Ce in the leaf vein system, hinting that Ce moved with water during transpiration	[25]
CeO_2, ZnO 500, 1000, 2000, 4000 mg/L	Soybean	Synchrotron X-ray absorption spectroscopy, random amplified polymorphic DNA assay	CeO_2 ENPs were found in the roots, but not ZnO. Both ENPs produced appearance and disappearance DNA bands, suggesting genotoxic effects	[23]
Cu 200, 400, 600, 800 mg/L	Mung bean, Wheat	Toxic effect of Cu ENPs and their bioavailability to plants, plant agar test, TEM-EDS	Mung bean was much more receptive and responsive to the toxic effect of Cu ENPs than wheat. Bioaccumulation was proportional to Cu ENPs concentration. TEM-EDS was used to visualize the ENPs agglomeration in cells	[73]

(continued)

Table 2.1 (continued)

ENPs and concentration	Plant	Determination/method	Findings	Reference
Cu, CuO 20, 80 mg/kg	Cilantro	Germination, elongation, biochemical assay, nutrient uptake	Decreased germination, impaired nutrient accumulation	[74]
Fe/Fe_3O_4, Cu/CuO 10, 20 mg/L	Lettuce	Plant health, chlorophyll content, CAT and APOX enzyme responses to ENPs exposure	No effects of Fe ENPs. Cu ENPs/ions reduced water content, dry biomass, and root length, compared with control. Cu ENPs increased Cu, Al, and S, but reduced Ca, Mg, Mn, and P	[75]
CuO 2, 5, 10, 20, 30, 40, 50, 100 mg/L	Corn	Split-root experiments, TEM-EDS, HRTEM	TEM-EDS demonstrated that CuO ENPs were translocated from roots to shoots through the xylem. HRTEM showed that the ENPs could translocate from shoots back to roots via phloem. Experiments indicate bioaccumulation and biotransformation of CuO ENPs in maize	[58]
CuO 100, 200, 400, 500 mg/L	Soybean	Root and shoot development, lignification of root cells, total chlorophyll content, H_2O_2 generation, POD enzyme activity	Root length reduced; increased ROS, lignin content, and POD activity. Total chlorophyll content, shoot growth, and weight reduction. Up regulation of POD2, POD4 and POD7 genes	[76]
CuO 0.1,1.0, 10 mg/L	Duckweed	Comparison of the inhibitory effects of CuO ENPs and bulk copper in solution	pH influenced solubility of CuO ENPs The concentration of Cu was found to be four times higher in plants exposed to CuO ENPs, compared to bulk Cu. CuO EPNs affected more morphology than growth	[77]
CuO 1.0 mg/L	Duckweed	Chlorophyll content, cell morphology, plant growth rate, electronic, scanning and light microscopic analysis	Growth inhibition at 0.6 mg/L Cu ion or 1 mg/L. CuO NPs reduced chlorophyll and growth at 1 mg/L	[78]
CuO 20, 50, 100, 200 500 mg/L	Mung bean	Effects of ENPs at physiological and molecular level	Increase H_2O_2 and lipid peroxidation in roots, deceleration of primary and lateral root growth, hampered root length and biomass. Significant curtailment of shoot length and biomass at 200 and 500 mg/L. Lignification of root cells	[79]
CuO 10, 100, 500, 1000 mg/L	Radish, perennial Ryegrass, annual Ryegrass	DNA damage in three different model plants	Marked collection of mutagenic DNA lesions due to reactive oxygen imbalances. Deterioration of plant growth in radish, annual ryegrass, and perennial ryegrass	[80]

(continued)

Table 2.1 (continued)

ENPs and concentration	Plant	Determination/method	Findings	Reference
CuO, ZnO 50, 500, 2000, 4000 mg/L	Buckwheat	Phytotoxic and genotoxic effects RAPS assays, genomic DNA isolation	Internalization of ENPs in root epidermis at high doses. Root growth hampered at 2000 mg/L ZnO and 4000 mg/L CuO ENPs. Different DNA polymorphism	[81]
CuO 625 mg/kg ZnO 640 mg/kg	Wheat	Phytotoxicity, metal speciation, oxidative stress/DLS, AFM	ENPs more toxic, compared to bulk forms. ENPs bioaccumulation in shoots, higher peroxidase and catalase activity, accelerated lipid peroxidation and oxidized glutathione in roots, reduced chlorophyll in shoots	[82]
Graphene 500, 1000, 2000 mg/L	Cabbage, Tomato, red Spinach, and Lettuce	Phytotoxicity in seedlings, morphological and physiological analysis	20 day graphene exposure significantly reduced plant growth and biomass. The leaf growth and number of leaves were reduced. There was marked increase in ROS and cell death. Little or no effects in lettuce	[83]
Pd 1–50 μmol/L	Barley	Growth	Pd uptake affected by particle size. At lower concentration reduced leaf length	[84]
Superparamagnetic iron oxide ENPs (SPIONs) 0.2, 0.4, 1, 2, mg/mL	Soybean	Soybean chlorophyll content, iron deficiency chlorosis, depletion ability in a hydroponic system	SPIONs raised the chlorophyll, levels but did not induce toxicity. Surface chemistry had different effects on chlorophyll	[85]
TiO_2 0.1, 0.2, 0.4%	long raceme Elm	Impact on the photosynthetic properties	0.1, 0.2, and 0.4% of nano-anatase TiO_2 sprayed on the leaves reduced the net rate of photosynthesis in seedlings	[86]
TiO_2 5, 25, 50 mg/L	Bell bean	Ecotoxic and genotoxic effects of TiO_2, ICP-MS, μ-XRF	ICP-MS results showed Ti in roots. μ-XRF showed Ti internalization	[87]
TiO_2 0.3, 1 g/L	Corn	Root hydraulics, growth	Physical effects: reduced hydraulic conductivity, inhibited leaf growth and transpiration. Low or no toxicity observed in long-term experiments	[52]
ZnO 10, 20, 50, 100, 200, 1000 mg/L	Ryegrass	Biomass production, plant growth	Reduced shoot and root length. Decreased biomass. Cellular vacuolation and collapse	[88]

(continued)

Table 2.1 (continued)

ENPs and concentration	Plant	Determination/method	Findings	Reference
ZnO 25, 50, 75, 100 µg/mL	Onion bulb	Genetic toxicity, mitotic index (MI), micronuclei index (MN), chromosomal aberration index, TBARS concentration, TEM, SEM	MI decreased with increasing concentration of ZnO ENPs, MN and chromosomal aberration index increased simultaneously. TEM and SEM images confirmed internalization and aggregation of the ENPs. Marked influence of ZnO ENPs on lipid peroxidation found via TBARs	[89]
ZnO 100, 200, 400, 800 mg/kg	Corn	Release of zinc ions from ZnO ENPs, uptake, translocation, TEM, confocal microscopy	Confocal microscopic images showed aggregates of ZnO ENPs diffused through root epidermis and cortex via the apoplastic route. Few ENPs aggregates were found in the xylem, indicating their passage to the endodermis via the symplastic pathway	[9]
ZnO 250, 1000 mg/k	Green pea	Protein and carbohydrate profile, plant biomass, chlorophyll levels	Plants exposed to alumina doped ZnO at 1000 mg/kg had elevated Zn concentration in roots and seeds, without influencing Si and Al uptake	[90]

Species name in order of appearance in the table: onion, *Allium cepa;* cucumber, *Cucumis sativus*; lettuce, *Lactuca sativa*; yellow squash, *Cucurbita pepo*; red kidney bean, *Phaseolus vulgaris*; perennial ryegrass, *Lolium perenne*; mouse-ear cress, *Arabidopsis thaliana*; soybean, *Glycine max*; tomato, *Solanum lycopersicum*; moon trefoil, *Medicago arborea*; corn, *Zea mays*; wheat, *Triticum aestivum*; alfalfa, *Medicago sativa*; mung bean, *Phaseolus radiatus*; cilantro, *Coriandrum sativum*; duckweed, *Landoltia punctata*; radish, *Raphanus sativus*; annual ryegrass, *Lolium rigidum*; buckwheat, *Fagopyrum esculentum*; cabbage, *Brassica oleracea*; red spinach, *Amaranthus dubius*; barley, *Hordeum vulgare*; long raceme elm, *Ulmus elongata*; bell bean, *Vicia faba*; green pea, *Pisum sativum* activity in leaves and roots. Barrios et al. [44] performed a study with coated and uncoated CeO_2 ENPs and bulk CeO_2 in tomato plants. At the highest exposure concentration (500 mg/kg), coated and uncoated CeO_2 ENPs resulted in longer stems, while exposure to bulk reduced the shoot length. Chlorophylls *a* and *b* were markedly increased under coated ENPs' exposure, but reduced under bulk CeO_2 exposure at a lower concentration (62.5 mg/kg). In addition, bulk CeO_2 at 125 mg/kg resulted in a higher percentage of Zn and lower P in stems. Majumdar et al. [92] exposed red kidney bean plants to 1000 mg/kg of either CeO_2 ENPs or bulk CeO_2. After 36 days of exposure, they recorded 26 µg/g Ce in nano-treated roots and 19 µg/g Ce in bulk-treated roots. The translocation from roots to shoots was of 1.02 µg/g Ce in nano exposed plants and of 1.3 µg/g in bulk exposed plants. Other studies have been listed in Table 3.1.

2.6 Risk Assessment Framework for ENPs

The risk assessment of ENPs is a challenge because of the diversity of materials and the ever increasing potential industrial use [45]. It encompasses detailed characterization of the particles and their aggregates before the conventional risk assessment [46]. The risk assessment framework includes hazard identification, dose response assessment, exposure assessment, and risk characterization.

2.6.1 Hazard Identification

Hazard identification is a qualitative examination to determine the ENPs presence, or the degree of hazard that a receptor (plant) is susceptible to because of ENPs exposure. It takes note of the exposure conditions, the detrimental health effect on the plant species, and collection and analysis of the data on the types of health effects due to the exposure [87, 93–95]. It may go further into the detailed characterization of the ENP interactions with plant organs, tissues, and cells; in other words, the toxicodynamics of the ENPs [10, 96, 97].

2.6.2 Dose–Response Assessment

Dose–response assessment implies bringing forth the quantitative relationship between the exposure to the increasing amount of the xenobiotic (ENPs) and the corresponding response from the plant [98, 99]. Also known as the effect assessment, it takes into account the different kinds of hazards and the corresponding kinds of detrimental effects due to ENPs exposure, the relationship between dose, and the resultant response along with the related uncertainties [100].

2.6.3 Exposure Assessment

The exposure assessment step is used to determine the rates at which ENPs are taken up by plant tissues. It estimates the magnitude of the actual and/or any potential plant exposures to the ENPs present in the surrounding environment. The process also considers the routes of exposure to plants, the time interval and frequency of exposure, and the size of the plant population under study. Exposure assessment is performed at laboratory [25, 59] or greenhouse conditions [46, 101]. The ENP characterization prior to the risk assessment gives vital information about the chemical, physical, and other kinds of properties of ENPs. This information gives in turn, hints about the exposure characteristics of the respective ENP.

2.6.4 Risk Characterization

The risk characterization is the process of assessing the probability of a harmful effect to the plants under certain known exposure conditions. It usually puts together the outcomes from hazard identification, toxicity, and exposure assessment in order to qualitatively and/or quantitatively define the risk. It also includes a description of the uncertainties associated with the risk assessment. Another important aspect that is taken into account is the additive or synergistic effect due to exposure to mixtures of ENPs. Sufficient characterization of risk from the hazards of ENPs exposure makes way for efficient risk management and requisite corrective actions for redressal [102]. Currently, there is a lack of information concerning the risk characterization of ENPs in plants. There are no studies incorporating all exposure conditions including dissolution percentage and transformations, among others [103].

2.7 Research Needs

Most of the studies on the effects of ENPs on terrestrial plants have covered the germination and seedling stages [48]. This has limited the analysis to the juvenile phase, when organs are still in development. Very few long-term studies have shown the potential toxicity of ENPs over the complete life cycle of the plant; thus, deeper evaluation is needed. Studies at the reproductive stage offer perspective into transgenerational effects, and this knowledge is in its infancy [44, 104, 105]. A few observations on the trophic transfer of ENPs within terrestrial food chains have shown the potential for great variations [92, 106, 107]. So far, only a few, and very short, food chains have been evaluated [10, 108, 109]. Moreover, the bulk of reports corresponds to studies performed in hydroponic systems. This experimental design allows for increased aggregation of particles, which may play an important role in their interactions with plants [110]. There is a strong tendency to use ENPs as herbicides, pesticides, and fertilizers, among other applications, within the agricultural industry; hence, soil represents a major pathway for exposure [4]. This suggests that future studies might be focused on determining the chemical, physical, and biological interactions of soil and ENPs and their effects on plants [20, 111, 112]. These studies will give a more realistic idea about the behavior of ENPs in the environment. In summary, there is much to do in order to better understand the nano-biointeractions with terrestrial plants.

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