

Chapter 8

Early Developmental Responses of Plants Exposed to Metals and Oxides Nanomaterials

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Abstract Over the last decade or so, one question about engineered nanomaterials (ENMs) has been constantly asked: Are nanomaterials inherently toxic? It is because characteristics such as “nano” scale size, surface charge, surface plasmon resonance, greater surface area, and propensity to ligand with (in)organic and/or polymeric molecules set ENMs physicochemically apart from their bulk/parent analogs. Related to unique properties, which enable greater functionality in a wide range of consumer applications, is the uncertainty about whether unique risk is posed to the environment, health, and safety (EHS) as ENMs are anthropogenically released into the environment. Recognized as the major sinks, soil, water, and air contamination of ENMs, including their leachable or modified by-products, is inevitable. Understanding of potential impacts on terrestrial plant species has remained unclear as anomalies in morphological, anatomical, and physiological endpoints, which have potential for impairing later development in life, are not routinely screened for, however. In this chapter, we report valuable information synthesized via thorough literature review of the current understanding of potential implications of ENM release and exposure to plants via soil, water, and atmospheric deposition. In particular, we report potential fate, biouptake, site of translocation/associated mechanisms, in vivo transformation, and toxicity (germination rate, growth and development, anatomical and physiological anomalies, and yield) of metal-based ENMs. Additionally, potential mechanisms and factors influencing ENMs’ toxicity are explained. Such information is critical to direct future research aimed at uncovering better understanding of nanotoxicology in plants, and to determine whether risk to public health exists from exposure to ENMs through the dietary route.

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8.1 Introduction

From doughnuts' icing to world's darkest vantablack (carbon nanotubes-based coating that absorbs 99.96 % of the incident light), from odorless apparels to sunscreen lotion, from energy harvesting devices to environmental remediation (Behar 2013; Owano 2014, www.nanotechproject.org/cpi/): One thing these different products have in common is the applications of engineered nanomaterials (ENMs). ENMs are synthetically engineered materials with size less than 100 nm in one dimension (NNI 2006). When materials exist in near atomic size, they tend to exhibit higher reactivity than their bulk counterparts (Bowker 2002). Due to unique properties, ENMs are touted to bring the next industrial revolution, if not already underway. Realizing ENMs' potential in improving agricultural production, some ENMs may have already made their way into our farms in the form of fertilizer, pesticide, or via contaminated biosolid applications, or remediation technologies (e.g., zero-valent iron to treat subsurface organic plumes) (Pokhrel and Dubey 2013; Gardea-Torresdey et al. 2014). Continual use of ENMs in agriculture, including in various consumer applications, will undoubtedly contaminate the environment (soil, water, and air), potentially impacting the agriculture and food/feed quality, and may pose unknown risk to human health and safety (NNI 2006; Pokhrel et al. 2014a).

Although much research to date focused on animal, mammalian cell lines, microbial, and algal models for understanding nanotoxicology (Navarro et al. 2008; Yu et al. 2009; Pokhrel et al. 2012; Pokhrel and Dubey 2012a, b; Silva et al. 2014), phytotoxicity studies of ENMs are limited for assessing potential risks of this emerging contaminant to human health and the environment (Pokhrel and Dubey 2013). Plants represent basal component (primary producer) in most ecosystems, serve as an important source for trophic transfer of contaminants (heavy metals) including the ENMs, and may represent a pathway for ENM transport in the environment (Gardea-Torresdey et al. 2014). In this review, we assess current understanding of toxicology of ENMs in plants. Specifically, we evaluate the potential fate, biouptake, site of translocation/associated mechanisms, in vivo transformation, and toxicity (germination rate, growth and development, anatomical and physiological anomalies, and yield) of various metal-based (metals and oxides) ENMs. Concurrently, potential factors and mechanisms of ENMs' toxicity are discussed. Figure 8.1 depicts important information as synthesized in this review and also highlights important areas for future research. These information are critical as they direct future research aimed at uncovering better understanding of nanotoxicology in plants, and whether potential risk of ENMs exists in humans through the dietary route.

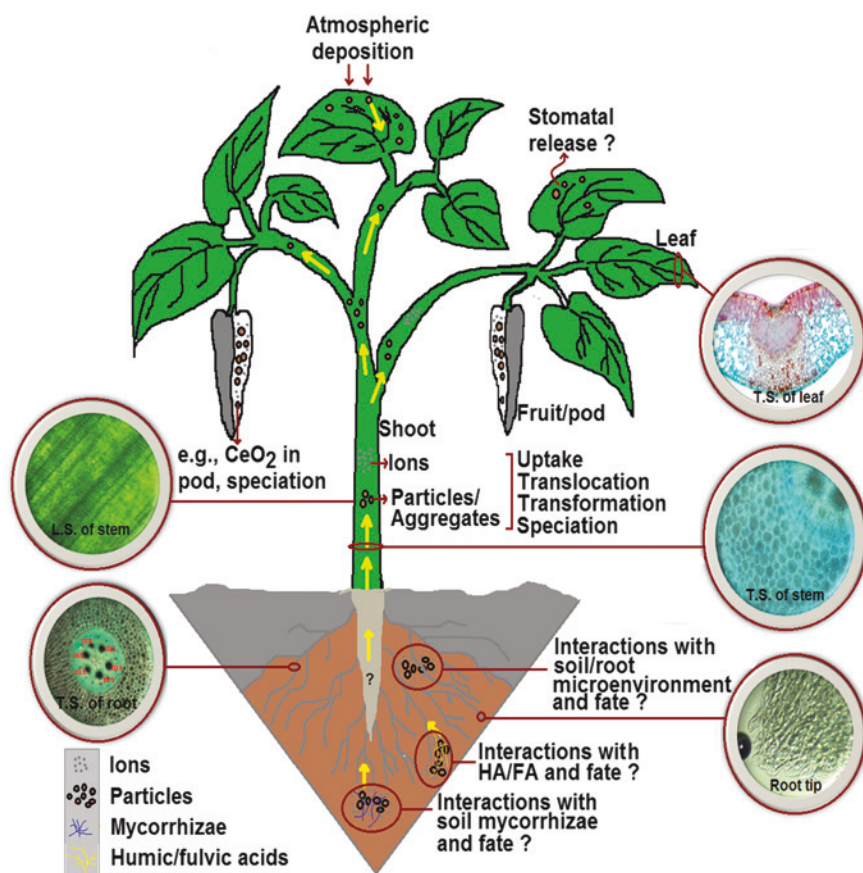


Fig. 8.1 Summary schematic depicting potential for engineered nanomaterial (ENM) interactions with the plant system. Potential fate (e.g., transformation, speciation, etc.) of ENMs within the soil system, uptake by the root system, further translocation, biotransformation, and speciation within the root and shoot systems (stem, leaf, and fruit/pod) are highlighted, with unknowns denoted by "?". Anatomical anomalies upon ENM stress and localization of ENMs can be revealed via microscopic observation (longitudinal [L.S.] or transverse sections [T.S.]) of the respective plant tissues. For additional information, see text. *HA* humic acids; *FA* fulvic acids; *mx* metaxylem; *yellow arrow* showing direction of transport; T.S. of leaf section modified from <https://www.flickr.com/photos/blueridgekitties/6475212645/> (BlueRidgeKitties 2011)

8.2 Toxicity of Nanoparticles to Plants

8.2.1 Effects on Seed Germination Rate

Although ZnONPs led to dose-dependent inhibition of seed germination in cabbage, it did not affect germination in maize, however (Pokhrel and Dubey 2013; El-Temseh and Joner 2012). Zn^{+2} ions exposure, on the other hand,

resulted in significantly greater effects in seed germination in both the species tested (Pokhrel and Dubey 2013). Smaller size (6 nm) and more negative (ζ potential = -49.5 mV) gum Arabic (GA)-coated AgNPs were found to be relatively more inhibitory than larger size (21 nm) and less negative (ζ potential = -22.5 mV) PVP-coated AgNPs, or Ag^+ (used as AgNO_3) on germination in American pokeweed (*Phytolacca americana*), soft rush (*Juncus effuses*), or woolgrass (*Scirpus cyperinus*) (Yin et al. 2012). Overall, the effects were greater when assayed in deionized water medium compared to the soil culture experiments, and that plants susceptibility varied by types of species assayed and forms or types of Ag treatments (Yin et al. 2012). Larue et al. (2012) reported no impact of various sized TiO_2 NPs on seed germination in wheat (*Triticum aestivum*) despite that the NPs were able to internalize through roots and translocate up to the leaves. Overall, these results suggest that ENM toxicity on seed germination may likely depend on the type of ENMs (material, size, and charge) and the plant species tested as the responses are remarkably variable—ranging from noninhibitory (e.g., TiO_2 NP) to inhibitory (e.g., AgNP, ZnONP).

8.2.2 Effects on Plant Growth and Development

Pokhrel and Dubey (2013) investigated early growth and developmental responses of corn (*Zea mays*) and cabbage (*Brassica oleracea* var. *capitata*) exposed to well-characterized nanoparticles of silver (AgNPs) and zinc oxide (ZnONPs) in a week-long experiment. The authors discovered a deep invagination, dubbed *tunneling-like effect*, in the primary root tip in corn exposed to ZnONPs (1,000 mg/L), likely a result of cell dissolution via structural disintegration upon interaction with the NPs. However, microscopic observation of the root surface revealed root hair density being unaffected by NPs or their ionic salts treatments. With AgNPs or ZnONPs, effects on root elongation were minimal, whereas ionic Ag^+ or Zn^{+2} significantly inhibited root development in a dose-dependent fashion in both species (Pokhrel and Dubey 2013). Assaying noncrop species, Yin et al. (2012) observed enhanced biomass growth in root and leaf with PVP-AgNPs treatments in woolly sedge (*Carex lurida*), including a significant root elongation in American pokeweed and switchgrass (*Panicum virgatum*) with PVP-AgNPs or Ag^+ treatments. Yin et al. (2011) documented complete inhibition of root hair development in seedlings of *Lolium multiflorum* with gum Arabic-coated AgNPs (40 mg/L); however, such effect was not observed with similar dose of AgNO_3 treatment. Moreover, overall growth effects were more pronounced with 6 nm AgNPs than with 25 nm AgNPs (Yin et al. 2011), suggesting particle size-mediated toxicity of AgNPs. Lee et al. (2012) documented significantly higher toxicity of Ag^+ ions in root and shoot growth in two crop species (*Phaseolus radiates* and *Sorghum bicolor*) compared to AgNPs treatments, and with effects rather greater when assayed in agar medium compared to soil experiments. Pradhan et al. (2013) observed significant enhancement in root and shoot growth, including in plant biomass and rootlet density,

in mung bean (*Vigna radiata*) treated with NPs of manganese (MnNPs) compared to the controls or Mn^{+2} ions (used as $MnSO_4$) treatments. Furthermore, MnNPs promoted O_2 evolution through increased photophosphorylation without eliciting oxidative stress (Pradhan et al. 2013).

Likewise, significant enhancement in fruit yield and biomass were documented in cucumber through foliar applications of higher AgNPs concentrations (500–3,000 mg/L; Shams et al. 2013), which, however, reduced fruit yield and chlorophyll with higher superoxide dismutase activity in tomato at as high as 60 mg/L levels (Song et al. 2013). AuNPs significantly increased vegetative growth and seed production in both noncrop (*Arabidopsis thaliana*) (Kumar et al. 2013) and crop (*Brassica juncea*) species (Arora et al. 2012). Interestingly, in lettuce, foliar applications of AgNPs did not affect leaf biomass and other measured physiological endpoints (Larue et al. 2014). Fe_2O_3 NPs enhanced pod and grain biomass by 48 % in soybean (Sheykhabaglou et al. 2010), CeO_2 NPs treatments led to increased fruit yield in tomato (Wang et al. 2012), and ZnONPs improved kernel and pod biomass, including shelling percentage, in peanut (Prasad et al. 2012).

On the other hand, several studies have reported no significant implications of various oxide NPs to plants. For example, TiO_2 NPs had no effect on biomass in beans or wheat (Jacob et al. 2013), and in fruit yield in tomato (Song et al. 2013). CeO_2 NPs did not affect seed production in soybean (Priester et al. 2012) or biomass growth in cilantro (Morales et al. 2013). ZnONPs showed no effect on vegetative growth (Kim et al. 2011; Zhao et al. 2013), photosynthetic pigment content, and gaseous exchange in cucumber (Zhao et al. 2013), except at unusually high concentrations (800 mg/L) of CeO_2 NPs which resulted in reduced fruit yield (Zhao et al. 2013).

8.2.3 Effects on Anatomical Structures

Potential modifications which may occur in plant anatomical structures upon exposure to ENMs have not been fully realized as only a few studies have explored anatomical changes with ENM exposure. However, toxicity literature on heavy metal ions suggest that changes in cellular morphology (shape and size) at earlier life stages can severely alter cellular functions related to solute transport and tissue differentiation in plants (Puertas-Mejia et al. 2010; Delmail et al. 2011). In a seminal study, Pokhrel and Dubey (2013) investigated structural changes in primary root cells at the zone of elongation in maize exposed to AgNPs and ZnONPs and compared to responses from respective ionic salt ($AgNO_3$ and $ZnSO_4$) treatments. The authors found consistently elongated cells with each type of NPs treatments, whereas the responses from Ag^+ or Zn^{2+} ions exposure varied: cells showed thinner and irregular morphology with Ag^+ treatments while Zn^{2+} treatment resulted in a relatively shorter but wider cells compared to controls. These novel findings indicate that the mechanism(s) underlying ENM stress is unrelated to that incurred by specific ions during early growth and development

in corn. This is consistent with the results of another study, which independently documented collapsed and highly vacuolated root cortical cells, including disrupted root cap and epidermal cells in *L. multiflorum* when exposed to AgNPs (40 mg/L), whereas AgNO₃ exposure did not lead to such anomalies in root cells (Yin et al. 2011). In *Lolium perenne*, considerable effects of ZnONPs in the root epidermis and cortex were observed (Lin and Xing 2008). The evidence suggests that cell structural integrity would likely be compromised when plants are exposed to ENMs of different types, which might have implications on ENM uptake by plants during their early growth and development.

8.3 Biouptake, Localization, and Transformation of Nanoparticles Within Plants

Analysis of biouptake of ENMs are intended to inform about potential risk from consumption of food crops by humans or other organisms higher up in the food chain. Studying multiple types of TiO₂NPs of varied sizes (range: 14–655 nm), Larue et al. (2012) documented low levels of Ti uptake (109.3 µg/g dw.) within wheat root. In another study, Pokhrel and Dubey (2013) reported sevenfold higher Ag uptake with AgNO₃ treatment (22 ng Ag/mg dw.) than with Citrate–AgNPs treatment (1.8 ng Ag/mg dw.) in a week old corn seedlings. Geisler-Lee et al. (2013), however, observed higher Ag uptake with AgNPs treatment than AgNO₃ treatment. Consistent with the previous study, Yin et al. (2011) reported higher toxicity of gum Arabic-coated AgNPs than the same concentration of Ag⁺, with uptake higher with AgNPs compared to Ag⁺ treatments, in *L. multiflorum*.

Translocation of AgNPs and CuONPs were reported in sand-grown wheat seedlings (Dimpaka et al. 2013a, b); while Ag speciation occurred in the form of ionic Ag⁺ and Ag-GSH, including as NPs themselves, within lettuce leaves with AgNPs treatments (Larue et al. 2014). Transformation of YbO₃NPs into Yb phosphates was recently documented within the root cells in cucumber (Zhang et al. 2012). Mesquite (*Prosopis juliflora* var. *velutina*) did not show characteristic signature of ZnONPs, which the plants were exposed to, within the types of tissues analyzed (e.g., root, stem, and leaf), and that the internalized Zn was identified to be in Zn(II) form, likely bound to unknown organics within the tissues (Hernandez-Viezcas et al. 2011). Likewise, Hernandez-Viezcas et al. (2013) found an absence of ZnONPs in soybean tissues when the plants were treated with high ZnONPs concentration (500 mg/Kg) through soil, and reported that Zn detected in grains, pods, and phloem (see Fig. 5 in Hernandez-Viezcas et al. 2013) resembled to model Zn citrate µ-XANES spectrum, indicating Zn–O bonding. In the same study, the authors located Ce within root nodule including in the root epidermis and pods in soybean. µ-XRF analysis revealed the presence of Ce in CeO₂ form, matching the µ-XRF signature of the applied CeO₂NPs to the plants (see Fig. 2 in Hernandez-Viezcas

et al. 2013). Zhang et al. (2012) found that CeO₂NPs were biotransformed to CePO₄, CeO₂ and Ce carboxylates within cucumber root and shoot tissues, and that the transformed NPs demonstrated needle-like, aggregated morphology.

Recently, Wang et al. (2012) reported translocation of CuONPs from root to shoot via xylem vessels and then back from shoot to root via phloem in corn. The authors suggested potential reduction of Cu²⁺ to Cu¹⁺ during translocation, and that the NPs were observed in the form of larger aggregates within corn plant. Lin and Xing (2008) reported ZnONPs internalization in endodermal and vascular tissues in *L. perenne*. Wang et al. (2012) observed CuONPs being transported from root to various tissues/organs (xylem, leaf, root) and that root Cu concentration was twofold higher with CuONPs (100 mg Cu/L) than with Cu²⁺ ions treatments in corn. Zhai et al. (2014) observed modulation of particle size distribution as 15 nm or 25 nm AuNPs were taken up and transported to the shoot in poplar, whereas larger particles (50 nm) could retain their size in vivo. The authors could locate AuNPs within the roots in abundance than in leaves. However, plant uptake of Au(III) ions were significantly higher compared to AuNPs treatments. Within the plants, AuNPs were detected in various tissues including in phloem complex, xylem, cell wall, plastids, mitochondria, and more abundantly in plasmodesmata region (Zhai et al. 2014). Observation of TEM images provided an insight into the transport of AuNPs through plasmodesmata-endoplasmic reticulum route where they likely accumulated as the channels narrowed. Presence of AuNPs in the xylem within the leaves indicated that the NPs were transported during nutrients and water uptake (Zhai et al. 2014). Similar observations were previously reported for AgNPs which aggregated within the plasmodesmata and were likely transported via apoplastic pathway (Geisler-Lee et al. 2013).

Direct penetration of NPs through cell wall can be envisioned for smaller size NPs as the pore size on the cell wall (2–20 nm) may limit the passage to the NPs larger than 20 nm (Zhai et al. 2014). Furthermore, cell membrane acts as yet another barrier for extraneous agent to pass through. To test this hypothesis, Sabo-Attwood et al. (2012) investigated uptake and distribution of 3.5 nm or 18 nm sized citrate-coated AuNPs in tobacco (*Nicotiana xanthi*), where the authors observed uptake of Au only from 3.5 nm AuNPs treatments (see Fig. 1 in Sabo-Attwood et al. 2012), unlike with 18 nm sized AuNPs treatments, and that the larger sized particles were found adhered to tobacco root surfaces. Furthermore, exposure to 3.5 nm sized AuNPs resulted in leaf necrosis culminating in plant death, which did not occur with 18 nm AuNPs treatments (Sabo-Attwood et al. 2012). Another study suggested that a size threshold may occur for NPs translocation to the leaves which they reported to be <36 nm; while accumulation of TiO₂NPs in the wheat root could only occur if NPs are <140 nm in diameter, with higher accumulation that occurred when NPs were much smaller (in the size range 14–22 nm) (Larue et al. 2012). Combined these observations from chemically different ENMs bolster the premise that particle size could be an important factor regulating ENM biouptake in plants.

8.4 Potential Factors and Mechanisms of Nanoparticle Toxicity

More recently, measuring the seedling growth in *Phaseolus radiatus* and *S. bicolor*, Lee et al. (2012) reported particle-mediated toxicity of citrate-coated AgNPs (Citrate–AgNPs) in soil, while free Ag⁺ toxicity was found to be more pronounced when tested in agar medium. A concentration-dependent inhibition of two different sized (20 nm vs. 100 nm) AgNPs on the biomass growth and frond number, including the greater effects of free Ag⁺ compared to AgNPs, were observed in *Lemna minor* (Gubbins et al. 2011). However, the toxicity of gum Arabic-coated AgNPs was higher compared to the same concentration of dissolved Ag⁺ in *L. multiflorum*, with greater Ag bioaccumulation observed with AgNPs treatment compared to Ag⁺ (Yin et al. 2011).

Negatively charged, anionic carboxylated AuNPs conferred protection to the model lipid membrane against the extreme pH (=12) via shielding effects, whereas positively charged, cationic amino-AuNPs could penetrate and disrupt the model membrane (Tatur et al. 2013). Silva et al. (2014) have experimentally shown interaction between surface charge and particle size to influencing AgNPs toxicity in both the prokaryotic and eukaryotic model organisms, and developed highly precise predicative models based on empirical data to explain nanotoxicity. However, potential surface charge effects and its interaction with particle size in influencing ENM phytotoxicity have not received much attention and therefore what potential effect surface charge density might have remains to be tested in plants.

Amongst the types of ENMs used in commerce, AgNPs are the ones which have undergone high scrutiny as they are widely used in various antimicrobial applications and thus more information is available on potential toxicity mechanisms. Such information would be useful to regulators and industry partners to make informed decision while addressing potential health and safety issues of ENMs. As AgNPs can act as a reservoir for continual ionic Ag⁺ release into the environment (Liu and Hurt 2010), it has been argued that AgNPs toxicity could likely be a combined effect of ENMs and the released ions (Pokhrel et al. 2013, 2014b). Direct change in lipid-bilayer structure leading to formation of pits on the cell wall and subsequently altering membrane permeability have been linked to AgNPs exposure (Fabrega et al. 2009). Literature suggests that antimicrobial properties apparently retained in AgNPs might be due to cellular internalization of particulates, thereby causing DNA damage, while potential ionic Ag⁺ release within the cell from internalized AgNPs can inhibit ion exchange and cellular respiration (Ratte 1999). Physical interaction of AgNPs with the cell surface has also been implicated as an important factor mediating AgNPs toxicity (El Badawy et al. 2011). Furthermore, AgNPs are known to inhibit β-galactosidase activity leading to cell death (Pokhrel et al. 2012). Reactive oxygen species (ROS) release followed by oxidative stress have also been linked to AgNPs toxicity (Choi et al. 2008).

8.5 The Path Forward

Thorough review of current literature indicates that ENMs, when available in the environment (air, soil, and water), can be taken up by plants including by the food crops, and can potentially transfer from one generation of plants to next (e.g., CeO₂NPs in soybean; Hernandez et al. 2013). Although phytotoxicity of ENMs have been associated with the dissolved ions released from the ENM surfaces, higher toxicity of ENMs themselves have been reported for various types of metal-based ENMs, regardless of whether they tend to release toxic ions (e.g., AgNP, ZnONP) or not (e.g., CeO₂NP and TiO₂NP).

Phytotoxicity investigation using high-purity ENMs is critically important, and to this end, application of ultrapurification techniques such as tangential flow filtration (TFF) coupled with hollow fiber membranes have enabled separation of dissolved ions and impurities from the ENM suspension (El Badawy et al. 2011; Flory et al. 2013; Dorney et al. 2014; Pokhrel et al. 2012, 2014a, b). Use of commercially procured ENMs without further purification (as has been routinely reported in the literature) would complicate the mechanistic understanding of ENM toxicity to biologic receptors, including plants, owing to potential confounding effects of toxic impurities (e.g., heavy metal ions in CNT samples, and dissolved Cd/Se ions in commercial quantum dots samples) already present in the nanosuspensions.

To date, studies have mostly addressed acute toxicity (short-term, high dose) of ENMs at single plant species level and in controlled laboratory setting, providing valuable information on individual species responses to, and basic mechanistic understanding of, ENM stress. However, research investigating ecosystem-level responses, including the field trials, to chronic (long-term, low dose) ENMs exposure has not been fully realized and should be the focus of future research. More research is warranted to assess whether standard USEPA OPPTS 850.4200 bioassay could be adequately used for screening ENMs toxicity (Pokhrel and Dubey 2013), or if molecular endpoints (although less economical) could serve as a more sensitive screening tool. More focused research is needed to elucidate the biological basis of ENM toxicity and how ENMs' and biologic surface characteristics would interact in influencing fate and toxicity of ENMs and of modified by-products both in vivo and ex vivo (Silva et al. 2014). Also, important for nanotechnology to be sustainably used in agriculture, emphasis should be on biouptake, effects on food quality, and crop yield before more nanotechnology-based products (e.g., nano-enabled fertilizer, pesticides, growth stimulant, etc.) find routine applications in our farms.

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