Factors affecting ENMs toxicity towards terrestrial plants

Lessons learned: Are engineered nanomaterials toxic to terrestrial plants?

P. Venkata Laxma Reddy^{ac}, JA Hernandez-Viezcas^{bcd}, J.R. Peralta-Videa^{abc}, Jorge Gardea-Torresdey^{abc*}

^aEnvironmental Science and Engineering PhD Program, The University of Texas at El Paso,
500 West Univ. Ave., El Paso, TX 79968, USA.

^bChemistry Department, The University of Texas at El Paso,
500 West Univ. Ave., El Paso, TX 79968, USA

^cUniversity of California Center for Environmental Implications of Nanotechnology (UC CEIN),
The University of Texas at El Paso, 500 West Univ. Ave., El Paso, TX 79968, USA

*Corresponding author: jgardea@utep.edu (J. Gardea); P: 915-747-5359; F: 915-747-5748

Abstract

The expansion of nanotechnology and its ubiquitous applications has fostered unavoidable interaction between engineered nanomaterials (ENMs) and plants. Recent research has shown ambiguous results with regard to the impact of ENMs on plants. On one hand, there are reports that show hazardous effects, while on the other hand, some reports highlight positive effects. This uncertainty whether the ENMs are primarily hazardous or whether they have a potential for propitious impact on plants, has raised questions in the scientific community. In this review, we tried to demystify this ambiguity by citing various exposure studies of different ENMs (nano-Ag, nano-Au, nano-Si, nano-CeO₂, nano-TiO₂, nano-CuO, nano-ZnO, and CNTs, among others) and their effects on various groups of plant families. After scrutinizing the most recent literature, it seems that the divergence in the research results may be possibly attributed to multiple factors such as ENM properties, plant species, soil dynamics, and soil microbial community. The analysis of the literature also suggests that there is a knowledge gap on the effects of ENMs towards changes in color, texture, shape, and nutritional aspects on ENM exposed plants.

Key words: Nanoparticle-plant interactions, Nanotoxicity, Fate, Transport, Transformation

1. Introduction

Nanotechnology industry is progressing and it has rapidly emerged into a technological sensation in the last two decades. This industry is operating in numerous fields of science and is constantly expanding its applications (Barkalina et al., 2014; Ditta et al., 2015). Engineered nanomaterials (ENM) are the building blocks of nanotechnology. Their unique properties and new characteristics, compared to their bulk counterparts, are the reasons behind their industrial and scientific success. Although nanotechnology is already a billion dollar industry globally, extensive ongoing research proves that this technology is still in the exploration stage and it has been projected to grow further (Shapira & Youtie, 2015). To meet the ever increasing industrial demand, NMs are manufactured expansively. This massive and unrestricted use of ENMs in recent years has led researchers to ponder the issues, questions, challenges, and consequences of their environmental impact (Gottschalk et al., 2015; Tolymat et al., 2015). Amongst the diverse studies that are been carried out, the impact of ENMs in ecosystems and their involvement in the food chain has conveyed some alarming discoveries. For the most part, experimental studies have proven that ENMs can pose undesirable effects to the food chain producers. There are some excellent reviews which have thoroughly emphasized these findings (Rico et al., 2011; Gardea-Torresdey et al., 2014). The most compelling evidence is primarily attributed to the tendency of the plants to uptake ENMs through their roots, followed by translocation, biotransformation, and perturbation of physiological functions (Li et al., 2015). Impairment in physiological functions can affect seed germination, seedling growth, increase reactive oxygen species (ROS) generation, disrupt cell walls, and modify biomolecules such as: proteins, carbohydrates, lipids, pigments, and hormones (Rico et al., 2014; Majumdar et al., 2014; Siddiqui et al., 2014). Conversely, reports show the positive effects of ENMs as they are proven to act as pesticides and

fertilizers. There are some excellent reviews on the beneficial effects of ENMs on plant growth as well (Adhikari et al., 2010; Gopal et al., 2012; Tiwari et al., 2014). Overall, the impact of ENMs on plants is still debatable, and there is no conclusive explanation pertaining to this situation. In this review we explore various factors that have probably determined both the positive and negative responses (Figure 1). We include a brief discussion on two important facets of the ENMs-plant studies: The interactions of ENMs with environmental components (soil, water) prior to their interaction with plants and the corresponding responses as an outcome of ENMs exposure. Accordingly, it is expected that this review will be helpful to expand our knowledge about implications and impact of ENMs on terrestrial plants.

2. Fate and transformations of ENMs' in environmental matrices and their impact

Generally, upon disposal into the environment, the ENMs tend to interact with various environmental components and usually, undergo aggregation, dissolution, sedimentation, and transformation (Markus et al., 2015). The most recent estimates indicates that in 2010, between 8 to 28% of the ENMs released into the environment ended up in soils and 4 to 7% in water (Keller et al., 2013). Furthermore, several factors influence their levels of accumulation in various environmental compartments. According to Liu and Cohen (2014), accumulation of ENMs in sediments increases as their attachment to suspended solids in water increases. For instance, in a study carried out by Mueller and Nowack (2008), they reported that predicted environmental concentrations of TiO₂ NPs in water bodies around Switzerland was 0.7–16 µg/L. These levels can vary geographically as they are in direct correlation with the degree of utilization of ENMs. In a similar study carried out on surface sediments of Xiamen Bay, China, it was reported that titania-based nanomaterial concentration was around 2.74 g/kg (Luo et al.,

2011). It must also be noted that ENM concentrations at disposal sites such as wastewater treatment plants (WWTP) can vary in comparison to surface sediments. According to recent findings, the concentration of ENMs varies from 0.003 (fullerenes) to 21 ng/L (TiO₂ NPs) for surface waters. However, the same ENMs at sewage treatment facilities were around 4 ng/L (fullerenes) to 4 µg/L (TiO₂ NPs), respectively (Kunhikrishnan et al., 2015). In this context, wastewater treatment plants (WWTPs), as biosolid generators, are important intermediate conduit of ENMs from industry to arable land. Thus, there is a strong possibility for ENMs transformation prior to their interaction with plants. There are some critical reviews which have briefly discussed the stability, toxicity, fate, and transformation of ENMs in terrestrial ecosystems (Klaine et al., 2008 ; Peralta-Videa et al., 2011; Gardea-Torresdey et al., 2014; Keller et al., 2015).

2.1 Physiochemical properties of ENMs

Engineered nanomaterials are very diverse and offer extreme benefits in comparison to their bulk forms. Although there are beneficial advantages in the industry, nanostructured forms are also proven to be toxic in comparison to the bulk forms (Musante and White., 2012). The enhanced toxicity in comparison to the bulk is primarily attributed to the high surface area and ability to penetrate the tiny pores. In addition, the size also determines the fate and behavior of the ENMs. Bian et al. (2011) reported that the dissolution of ZnO NPs increase with the decrease in size of the NPs in the range of 15-240 nm diameter. The shape and morphology also affect the activity of ENMs. For example, the ionic strength strongly affected the aggregation of spherical ZnO NPs but had little or no impact on irregular ZnO NPs (Zhou et al., 2010). Ghosh et al. (2008) reported that humic acids, in combination with pH, affected the colloidal behavior of aluminum oxide NPs. The surface charge of the NPs decreased as the pH increased. The surface

charge can be a significant factor in the plant nanotoxicity studies. Zhu et al. (2012) concluded that small sized positively charged Au NPs were usually confined to the roots of terrestrial plants, whereas the negatively charged NPs were easily translocated to shoots and leaves. The fate of ENMs is also affected by surface coating (Buzea et al., 2007; Unrine et al., 2012). The nanomaterial stability can also be influenced by the light irradiation coupled with other chemical variables. The aggregation behavior of C₆₀ NPs, before and after UV-A irradiation, was studied in solutions varying in ionic strength, ionic composition, and humic acids. Qu et al. (2010) reported that under UV illumination, the stability of C₆₀ NPs increased, whereas their aggregation decreased in a medium containing NaCl. The enhancement in stability was attributed to an increase in the negative surface charge and a reduction in the hydrophobicity of the NPs. Although it is clear that various physiochemical properties of ENMs have proven to determine their effects on plants, their optimization is yet to be known.

Chemicals present in the media can also trigger the transformation of ENMs. According to an experimental work, it was reported that Ag NPs have a tendency to combine with inorganic ligands, like sulfur, forming Ag₂S NPs. The sulfidation reduces the toxicity as the Ag₂S have lower solubility in environmental matrices. ZnO NPs also tend to combine with sulfur, forming ZnS (Ma et al., 2013). Although this transformation enhanced the stability, it is not clear if ZnS pose more or less toxicity than the reactant ZnO NPs. This study explains that inorganic ligands play a crucial role in the transformation as well as have the potential to influence the outcome of studies (Levard et al., 2012). As a matter of fact, inorganic ions have the potential to carry out redox reactions, triggering surface changes in ENMs. Liu et al. (2015) observed that CeO₂ NPs have the tendency to carry out a redox reaction with ferrous ions. This improved the colloidal stability by enhancing the zeta potential and hydrophilicity of CeO₂ NPs. The increase in

hydrophilicity of ENMs could have a potential impact on their transport. The presence of heavy metals/metalloids such as lead and arsenic in soil, and their impact on ENMs, is still unknown. There are potential knowledge gaps about how metal pollution in soil can affect the ENMs fate.

On the other hand, other factors like cationic valence also affect the behavior of ENMs. For example, monovalent and divalent cations enhance the aggregation of TiO₂ NPs in soil and water, but higher aggregation is produced by divalent species (French et al., 2009). Extra polymeric substances (EPS) derived from phytoplankton affected the stability of Cu-based NPs. The EPS also have a significant impact on the dissolution of ENMs in the presence of other chemical variables like ionic strength and pH. Recent studies have suggested the potent role of EPS in the speciation of Cu-based NPs, which results in formation of additional free Cu²⁺ ions, producing other forms of Cu toxicity (Adeleye et al., 2014). The environmental media also play an important role in the toxicity of ENMs. For instance, photochemical reactions can modify the transformation of CNTs in aqueous media. Moreover, under UV irradiation in the same medium, MWCNTs had the highest ROS production, compared to C₆₀ and SWCNTs (Chae et al., 2011). Since the UV irradiation is proven to affect the toxicity of ENMs, it would be interesting to find out the impact of natural weather conditions such as temperature, humidity, and precipitation. The composition of media also influences the surface chemistry, causing unexpected behavior of ENMs (Ottofuelling et al., 2011). Keller et al. (2010) studied the behavior of TiO₂, ZnO, and CeO₂ NPs in water from a lagoon, a river, ground water, and sea water. These researchers found that the electrophoretic mobility of the three ENMs was highly influenced by the organic matter content and ionic strength but not by the pH. However, it is not clear whether similar behavior will be exhibited by carbon-based ENMs such as CNTs.

A key point to be noted is the possible change to occur in ENMs during the extended stay (aging) in environmental matrices. Reports indicate that AgO and ZnO NPs have the tendency to undergo alterations during the aging process in different suspensions. In one of these studies, the influence of aging on the speciation and chemical stability of Ag and ZnO NPs in kaolin suspensions was examined for 18 months. According to the study, Ag NPs remained unchanged in sodium nitrate suspensions; however, silver chloride was identified with the metallic Ag NPs in sodium chloride suspensions. On the other hand, ZnO NPs were rapidly converted via destabilization/dissolution mechanisms to Zn^{2+} inner-sphere sorption complexes within one day of reaction, remaining in the same form for almost 12 months (Scheckel et al., 2010). However, various other factors may have the potential to influence the outcome. For instance, impurities and additives used in the nanomaterial synthesis can be released when ENMs interact with environmental matrices. Liu et al. (2013) carried out a study to examine the phosphorous released from impurities in the synthesis of five different TiO_2 NPs. Authors reported that 50 nm anatase TiO_2 had higher phosphorous, which seemed to peak at pH of 11.2. Likewise, silicon, which had a similar role as mentioned above, was found to be released into aqueous media attached to TiO_2 NPs during the synthesis process (Liu et al., 2014). As phosphorous is believed to be essential nutrient for plant growth, the consequences of the elevated phosphorous levels in soil can lead to undesirable effects. Nonetheless, the existence of phosphorous is believed to affect the structural and morphological aspects of some other nanomaterials. Rathnayake et al. (2014) reported that ZnO NPs have the tendency to interact with phosphate in the media and transform into two structurally and morphologically heterogeneous products. The two products formed were crystalline zinc phosphate phase (hopetite) and nanoscale zinc, which contains the core ZnO with a shell of $\text{Zn}_3(\text{PO}_4)_2$. The role of solubility of available phosphorous also seemed

to play a part. In an experimental work, the impact of insoluble phosphorous on ZnO was studied by using hydroxyapatite (HAP) mineral. It was observed that under acidic conditions, 80% ZnO was transformed into scholzite in a span of 4 hours. In contrast, under neutral or alkaline conditions, the adsorption of Zn^{2+} on HAP was observed and, eventually, resulted into a structural transformation of over 60% ZnO NPs to amorphous inner-sphere Zn adsorption complexes in a span of 30 days (Lv et al., 2014). In summary, it must be observed that same ZnO NPs transformed into different structural forms, based on the type of phosphorous form and pH conditions. Thus, it can be summarized that various factors can influence the degree of toxic impact of ENMs (Figure 2). The impact of different ENM synthesis methods as well as their post modification on the stability and potential phytotoxicity towards plants is yet to be studied on a broader scale.

2.2 Soil properties and their role in the effects of ENMs in plants

Soils are one of the major disposal sinks for ENMs. Thus, it is expected that terrestrial plants will be in contact with ENMs deposited in places reached by plant roots. Currently, our knowledge about the interactions of ENMs with soil is very limited. Once ENMs reach the soil, they will be either physically or chemically adsorbed onto the surface of the soil particles. They may also undergo chemical transformations triggered by soil organic matter. ENMs can enter the pores of large sized soil particles remaining suspended for longer periods (Jaisi and Elimilech, 2009). The mobility and retention dynamics of ENMs in the soil determine their overall uptake and bioavailability. Column experiments with loamy sand soil have shown that the retention of Ag NPs was higher in the presence of soil cations such as K^+ and Ca^+ . The authors concluded that the retention was due to a decrease in ionic strength and the release of more clay into soil (Liang et al., 2013). The soil texture also affects the mobility of ENMs. In a

work carried out by Zhang et al. (2012), it was observed that fullerene NPs exhibited different transport behavior in two different media, i.e Ottawa sand (quartz) and Lula soil (containing a mixture of soil organic components and quartz). The size of the nanomaterials has also proven to impact their retention in the porous media. Column experiments with silicon NPs of 8 and 52 nm demonstrated that larger NPs (52 nm) had lower retention (Wang et al., 2012). The coating of the ENMs also has an impact on the transport in the soil media. In a work carried out by Zhao et al. (2012), the transport distances (cm) for bare ZnO NPs and coated ZnO was studied in both sandy and sandy loam soils. It was observed that the distances travelled by bare ZnO in either soils were 19.2 and 5.3 cm, while distances for coated NPs were 21.4 and 6.9 cm, respectively. It could be inferred from this study that the surface coating of ZnO reduced its deposition rates in soil. Lastly, the pore water velocity in the porous media was also proven to significantly influence the transport of the nanomaterials. In a one dimensional flow through column experiment carried out by Liu et al. (2009), it was reported that the transport and mobility of MWCNTs was greater at a pore water velocity greater than 4.0 millidarcy (m/d). The above literature clearly shows the need for more research in this direction. As it could be inferred, the soil habitat has a huge impact on the ENMs fate and uptake. Soil associated factors such as texture, pH, and organic matter content are factors to be included in ENM-based studies.

In order to better understand the interaction of soil-landed ENMs with plants, it is necessary to understand their fate, mobility, and transformations in soil. Firstly, the aging of nanomaterials in the soil can have a dramatic impact on their toxic potential. Mc Shane et al. (2014) reported that the potential toxic activity of various ENMs changes with their residence (aging) in soil. These authors compared the Cu^{2+} activity from CuO (nano), CuO (micro), and $\text{Cu}(\text{NO}_3)_2$ for 56 days. They found that nano CuO had higher Cu^{2+} release than micro CuO but lower than the salt form.

In addition, the Cu^{2+} activity was very high in the initial 11 days. On the other hand, the silver-based ENMs exhibited a different behavior during the aging process in the soil. It was reported that Ag NPs have strong sorption with soil ligands in the first few hours. As time passed, the Ag ion release increased by more than 10 times (Benoit et al., 2013). These results suggest the need for further studies on all the types of ENMs, as it seems that the aging triggers varied responses. As previously mentioned, the colloidal stability of ENMs is affected by the pH and humic acids present in the soil. Humic acids induce the aggregation of ENMs in the soil (Mashayeki et al., 2012). The reviews by Grillo et al. (2015) and Pachapur et al. (2015) have provided crucial information pertaining to the interactions between ENMs and organic matter in various environmental media. The reviews suggest that ENMs such as TiO_2 have higher mobility in the mineral soil in comparison to soil rich in organic colloids.

2.3 Sorption behavior of ENMs

The chemical nature of ENMs allows different types of bondings with soil components such as hydrophobic interactions, hydrogen bonding, and electrostatic interactions, along with others. In addition, ENMs tend to either adsorb or absorb the chemicals present in the soil matrix, which may modify their effects on plants. The research in recent years have proven that a wide range of toxic chemicals such as radioactive metals, pesticides, polychlorinated biphenyl (PCBs), and heavy metals have the tendency to undergo sorption on the ENMs surface. A work carried out by Feng et al. (2012) showed that nano CeO_2 exhibits a strong adsorption tendency towards extremely toxic elements such as arsenic. TiO_2 NPs have also shown adsorption tendency towards radioactive elements. In a study carried out by Tan et al. (2007), it was proven that the pH, in combination with humic and fulvic acids, altered the sorption of thorium and TiO_2 . The sorption process has shown to modulate the transport of contaminants. An experiment performed

in two sandy soil columns showed that at a low concentration (1.55 to 12.8 mg/L), C₆₀ increased the mobility of PCBs and phenanthrene (Zhang et al., 2011).

Recent studies have shown that almost all the well-known carbon-based nanomaterials have sorption tendency for carcinogenic pesticides such as lindane and atrazine. The SWCNTs can bind dimethyl phthalate and diethyl phthalate. However, this sorption is reduced by humic acids due to the competition effect (Wang et al., 2010). It is believed that the sorption of nano metal oxides is higher than bulk metal oxides due to the higher surface area. This was proven in one experimental study, where pyrene was more absorbed onto the nanoscale zinc, aluminum, and titania oxides, in comparison to their bulk counter parts (Wang et al., 2008). Recent studies have shown that personal care products and pharmaceuticals such as ketoprofen, carbamazepine, and bisphenol A can be bound to carbon-based ENMs such as MWCNTs and graphene (Liu et al., 2014). Although there is no concrete evidence on how personal care products will affect terrestrial plants if they are taken up along with ENMs, it is speculated that they can pose a risk. On the other hand, there is experimental evidence that the sorption properties of carbon-based ENMs decrease in the presence of oxygen and irradiation (Shen et al., 2014). In fact, the European Commission and the EPA (Petrie et al., 2015) have created a list of emerging contaminants that could potentially interact with the sorption properties of ENMs, changing their impact on plant toxicity.

2.4 Soil microbial community

Soil is a vital habitat for large number of organisms, including plants, nematodes and microbes that are essential in nutrient cycling, matter decomposition, and nitrogen fixation. Any disturbances to these organisms can potentially have huge implications in ecosystems. Studies have shown that ENMs can cause serious perturbations to soil microbiota. Rodrigues et al.

(2012) reported that bacteria eventually recovered from adverse effects of SWCNTs, whereas the fungal microbiota showed no signs of recovery. Another study showed that NPs of FeO and Ag decreased fungal biomass in clover arbuscular mycorrhizal fungi (Feng et al., 2013). This study highlights the implications of decreased nitrogen fixation in terrestrial plants and the potential deterioration of soil fertility.

Paradoxically, ENMs may not have a similar inhibitory effect on the pathogenic fungi. For instance, Rispaill et al. (2014) reported that quantum dots and super paramagnetic nanoparticles have proven to exhibit little or no toxic effects on *Fusarium oxysporum*. Amongst the various bacteria that persist in the soil, it must be noted that nitrifying bacteria are more susceptible to ENMs toxicity than nitrogen fixing and denitrifying bacteria. Different types of coated quantum dots were exposed to soil bacterial and affected their gene expression pertaining to the nitrogen cycling (Yang et al., 2012). There are also reports that suggest that ENMs affect ammonia oxidizing bacteria. Luo et al. (2015) reported that TiO₂ NPs have significant inhibitory effects on ammonia oxidizing bacteria, while CeO₂ NPs showed to affect soil denitrifying bacteria. Likewise, ZnO NPs showed toxicity to the amylolytic activity, denitrification, and urea degradation in *Bacillus subtilis* and *Pseudomonas aeruginosa* (Santimano and Kowshik, 2013). Our knowledge about the impact of these ENMs in methanogenic and sulphur oxidizing bacteria is still limited. In addition to the microbial biota, other life forms such as nematodes are shown to be affected by ENMs. Hu et al. (2010) reported that ZnO exhibited higher toxicity on the nematode *Eisenia fetida* than TiO₂.

Conversely, chemicals extracellularly released by soil microbes can influence the stability and toxicity of ENMs persisting in the soil. Metz et al. (2009) reported that lignolytic fungus-based extracellularly released compound has proven to facilitate the hydroquinone driven Fenton's

reaction on NPs, having huge impact on the transformation of CdSe core/ZnS shell quantum dots (QD) functionalized with poly(ethylene glycol). The QD was transformed to Se aggregates. This study has proven that the biologically-driven natural redox conditions can have an impact on the fate and transformation of ENMs in soil.

3. Impact of ENMs exposure to terrestrial plants

Several studies have shown that ENMs affect terrestrial plants in different ways. Disturbances in physiological aspects such as seed germination, stunted growth, yield, crop quality, and biochemical aspects like abiotic stress, lipid peroxidation, and cell wall disruption have been extensively reported (Table 1).

3.1 Growth and development

The impact of the ENMs on plant growth and development is being extensively studied. The survey of the recent literature indicates that the impacts of ENMs in plants have been assessed at germination and seedling growth, and during the entire life cycle. Studies at germination stage and seedling growth seem to begin in the middle 2000's with a study on soybean germination (Lin and Xing, 2007). After that, several studies have explored the effects of various ENMs in different plant species. Lin and Xin (2007) studied the effects of MWCNTs aluminum, alumina, zinc, and zinc oxide NPs at 20, 200, and 2000 mg/L on six plant species (radish, rape, ryegrass, lettuce, corn, and cucumber). Authors concluded that ENMs had little impact on seed germination, except for Zn NPs that at 2000 mg/L had an inhibition effect on ryegrass, whereas the ZnO NPs had a similar effect on corn. The inhibition of root length was observed for either Zn-based ENMs at concentrations such as 2000 mg/L. However, concentrations higher than 500

mg/L would be rare in environments away from ENM factories or where these ENMs are not intentionally used.

On the other hand, exposure of TiO₂ NPs to mungbean (*Vigna radiata*) seeds in Murashigi and Skoog (MS) medium at concentrations from 250-2500 mg/L did not yield any abnormal result (Theerakarunwong & Chouychai, 2013). In contrast, the same TiO₂ NPs at concentrations ranging from 0.2 to 4.0 % delayed germination progression for the first 24 h in *Zea mays* L. and *Vicia narbonensis* L. (Castiglione et al., 2011). Likewise, TiO₂ NPs at 0, 5, 20, 40, 60 and 80 mg/L, along with the bulk counterpart, were tested on fennel seed germination and early growth. It was reported that after 14 days of seed incubation, the overall germination percentage increased with exposure to 60 mg/L (Feizi et al., 2012). Twelve nm SiO₂ NPs at 8 g/L also increased tomato seed germination in terms of mean germination time, seed germination index, seed vigor index, seedling fresh and weights (Siddiqui and Waihibi, 2014). Reports also show that CNTs increase rice seed germination (Nair et al., 2012). Likewise, MWCNTs improve the growth of tobacco seedlings (Khodakovskaya et al., 2012). CNTs at a concentration of (10–40 µg/mL) were found to penetrate tomato seeds and affect their germination and growth rates (Khodakovskaya et al., 2013). These results emphasize the impact of concentration and provide evidence that different plants react in different ways to a specific nano exposure. Another important aspect is that ENM exposure to seeds may yield misleading conclusions. For example, graphene at low concentration showed mixed results on tomato seed germination and seedling growth. On one hand, it increased seed germination, but on the other hand, reduced plant biomass with taller seedlings (Zhang et al., 2015).

The transformation of ENMs in the plants is also an important aspect. In the majority of cases, the transformed products could be more potentially toxic or beneficial for plant growth and

development. In a study carried out by Hernandez-Viezcas et al. (2013), soybean seeds were germinated and cultured in organic soil in the presence of ZnO and CeO₂ NPs at a concentration of 500 mg/kg and 1000 mg/kg, respectively. As per the study, both ZnO and CeO₂ NPs were taken up and biotransformed, to a certain extent, within the plant. The micro-X-ray absorption near edge structure (μ -XANES) showed that the ZnO form was completely absent inside of the plant. Instead, the observed form was Zn-O resembling the Zn- citrate. On the other hand, most of the cerium content existed in the form of CeO₂; however, a small portion of oxidized form of cerium(IV) was also observed. There are also some experimental evidences showing that ENMs, in addition to changing their chemical form, change their shapes during the transformation inside the plant. In a study carried out by Ma et al. (2011), lanthanum oxide (La₂O₃) NPs were exposed to cucumber plants at specific conditions explained in the study. TEM coupled to EDS, STXM, and NEXAFS were used to assess the results. As per authors observations, La₂O₃ NPs and LaCl₃ were both transformed to needle-like LaPO₄ nanoclusters in the intercellular regions of the cucumber roots. TiO₂ NPs have also proven to affect plant growth in a positive way. An experiment carried out on wheat with bulk and TiO₂ NPs at five different concentrations showed that TiO₂ NPs at concentrations of 2 and 10 ppm, respectively, enhanced the seedlings and shoot length, in comparison to the bulk TiO₂ (Feizi et al., 2012). Similarly, the exposure of tomato plants to CeO₂-NPs (0.1–10 mg/ L) seemed to exhibit inconsequential or slightly positive effects on plant growth and tomato production (Wang et al., 2012).

There are also some research findings showing that at certain concentrations and conditions, ENMs have beneficial impacts on plant growth. Water soluble carbon nanotubes (wsCNTs) were experimentally proven to improve the growth of common gram (*Cicer arietinum*). At 6.0 μ g/mL, the wsCNTs had a positive effect on every part of the plant. According to the authors, the

positive effects were primarily attributed to the better water absorption and retention by the plant (Tripathi et al., 2011). Furthermore, in a typical study carried out by Tripathi and Sarkar (2015), water soluble carbon nano-dots (wsCND) upon exposure to wheat plants under dark and light conditions proved to enhance the growth of roots and shoots.

3.2 Reactive oxygen species (ROS) production and other biochemical perturbations

In general, reactive oxygen species (ROS) production is part of the normal plant biochemical processes (Suzuki et al., 2012). Generally, ROS include free radicals such as superoxide anion ($O_2^{\bullet-}$), hydroxyl radical ($\bullet OH$), as well as non radical molecules like hydrogen peroxide (H_2O_2), and singlet oxygen (1O_2) (Gill and Tuteja, 2010). Generally, in normal plants, ROS are formed by the inevitable leakage of electrons onto O_2 from the electron transport activities of chloroplasts, mitochondria, and plasma membranes; or as a byproduct of various metabolic pathways localized in different cellular compartments. In a healthy plant, ROS act as signaling molecules (Thannikal and Fannburg, 2000). In other instances such as abiotic and biotic stresses, there is an excessive production of ROS. In the case of elevated ROS levels, the plant has innate scavenging mechanisms for the depletion of ROS. These mechanisms can be enzyme-based and include superoxide dismutase (SOD), guaiacol peroxidase (GPX), ascorbate peroxidase (APX), and catalase (CAT) (Mazhoaudi et al., 1997); or non-enzyme-based anti-oxidants including ascorbate (AsA), glutathione (GSH), carotenoids, tocopherols, and phenolics. In the absence or ineffectiveness of the scavengers, the excess ROS could lead to various effects such as protein oxidation, DNA damage, lipid peroxidation, electrolyte leakage, and membrane damage, among others. The overall process will eventually trigger oxidative damage and ultimately cell death (Sharma et al., 2012). There are several works reporting that ENMs have a

tendency to induce ROS generation (Hong et al., 2005; Navarro et al., 2008; Lee et al., 2010; Rico et al. 2015). Other reports show results pertaining to genetic, hormonal, and other biomolecule disruptions (Atha et al., 2012; Zhao and Liu, 2012). It has yet to be proven whether these biomolecule perturbations are only consequence of excess ROS or if there are other ways that ENMs directly affect the biomolecules. Furthermore, researchers must be sure that factors such as light, water, and temperature, which also contribute to ROS generation and affect biomolecular functions, are not having any impact on the experimental studies.

In a work reported by Faisal et al. (2013), nickel oxide nanoparticles (NiO NPs) were exposed to tomato seedlings in the concentration range of 0.025–2.0 mg/mL. In comparison to control, it was reported that oxidative stress, indicated by elevated activity of catalase (CAT), glutathione (GSH), and superoxide dismutase (SOD), was produced. Authors concluded that the dissolution of Ni ions from NiO NPs triggered a mitochondrial-dependent intrinsic apoptotic pathway, leading to cell death. In another work, CeO₂ NPs exposed to cilantro (*Coriandrum sativum*) at 125 mg/kg increased CAT contents in the shoots, whereas the level of ascorbate peroxidase was higher in the roots (Morales et al., 2013). In another study, *Arabidopsis* and rice leaf protoplasts were exposed to SWCNTs at 25 µg/mL, resulting in cell death. Exposure to SWCNT caused adverse cellular responses, including oxidative stress, cell aggregation, chromatin condensation, and H₂O₂ accumulation, eventually leading to cell death (Shen et al., 2010).

In depth analyses of various other cellular components such as DNA, proteins, lipids, and membranes have also been indicators of phytotoxicity due to ENMs' exposure. This has been primarily attributed to ROS formation upon exposure to ENMs. The genotoxic effects of ZnO and CuO NPs was studied on buckwheat (*Fagopyrum esculentum*). Random amplified polymorphic DNA assays showed different DNA polymorphisms at 2,000 and 4,000 mg/L of

ZnO and CuO NPs, compared to controls (Lee et al., 2013). In a similar work, ZnO NPs were exposed onto garlic (*Allium sativum* L.) and it was observed that mitotic index decreased in a concentration- and time-dependent manner. Other effects of ZnO NPs on garlic plants included mitotic aberrations, mainly consisting in chromosome stickiness, bridges, breakages, and laggings. It was observed that the overall percentage of abnormal cells proportionally increased as the ZnO concentration increased. The investigation provided new information for the possible genotoxic effects of ZnO NPs on plants (Shaymurat et al., 2009). In another genetic toxicity studies, *Allium cepa* roots were exposed to bismuth oxide NPs at 12.5, 25, 50, 75, and 100 mg/L for four hours. Results showed that at specific concentrations discussed in the work, there were various harmful effects such as increased mitotic index and total chromosomal aberrations (Liman, 2013). The oxidative stress on exposure to ENMs eventually has effects on the protein content. According to Vannini et al. (2014), exposure of *Triticum aestivum* L. seedlings to 10 mg/L of AgNPs resulted in the alteration of various proteins that are extensively involved in cell metabolism. Another work performed with *Oryza sativa* L. showed that twenty-eight responsive proteins were identified. The affected proteins were involved in various vital biochemical process such as oxidative stress tolerance, transcription and protein degradation, cell wall and DNA/RNA/protein direct damage, Ca^{2+} regulation, and signaling, cell division, and apoptosis, among others (Mirjazani et al., 2014). In order to enhance our understanding, advanced molecular approaches such as proteomics and genomics must be extensively implemented. According to Majumdar et al. (2015), proteomic analysis of kidney bean seeds from plants exposed to CeO_2 NPs has resulted in downregulation of essential proteins associated with nutrient storage and carbohydrate metabolism. It would be interesting to know if other ENMs affect the same or other proteins in beans.

In addition to having an effect on important biomolecules such as proteins, nucleic acids and other molecules, the exposure of MWCNT to *Allium cepa* has revealed that the uptake in root cells affects cellular morphology, membrane integrity, and mitochondrial functions (Ghosh et al., 2015). Furthermore, Nair and Chung (2015) carried out a study where AgNPs were exposed to mung bean (*Vigna radiate*) in half strength MS agar medium, at 0, 5, 10, 20, and 50 mg/L for 21 days. The experimental results, showed that at higher concentration of AgNPs, the total chlorophyll was reduced, whereas the hydrogen peroxide and lipid peroxidation levels were increased.

3.3 Nutritional quality

In addition to various effects on defense and growth aspects, ENMs are also proven to affect the nutritional quality of food crops. Rico et al. (2013) reported that rice grains from CeO₂ NP-treated plants exhibited less Fe, S, glutelin, lauric and valeric acids, and starch, in comparison to bulk CeO₂ treated plants. Rico et al. (2014) also reported that at 125 mg/kg, CeO₂ NPs altered the amino acid content, especially for the linoleic acid composition of wheat. Experimental results with ZnO NPs showed increased starch content at 400 mg/kg. Whereas, CeO₂ NPs at similar concentration affected sucrose content. According to the study, it must also be noted that, although ZnO NPs did not impact protein fractionation, there was a case where CeO₂ NPs at 400 mg/kg increased globulin and decreased glutelin as well as phenolic content (Zhao et al., 2014). Thus, the carbohydrate and protein value was affected. Likewise, other experimental studies have proven that CeO₂ NPs have potential to alter the carbohydrate levels in cilantro plants (Morales et al., 2013). The impact of ENMs on other nutritional aspects such as vitamins, fiber, taste, and texture of food crops must be carefully scrutinized.

4. Conclusions

Engineered nanomaterials are a vital part of the emerging nanotechnology industry. As of now, the research about the impact of ENMs on terrestrial plants is still an ongoing process and it demands further research. Based on the current knowledge, it could be concluded that ENMs' impacts on terrestrial plants depend on multiple factors. However, most often, but not always, concentrations less than 100 ppm, especially 10-40 mg/kg, have proven to exhibit beneficial effects on plant growth, whereas higher concentrations, at higher ranges, have inhibitory effects. TiO₂ and Si-based ENMs are either beneficial or have less negative impact on the plants. There are still a lot of knowledge gaps in our understanding of the impacts of ENMs in plants. Considering the potential benefits as well as threat posed by ENMs towards terrestrial plants, more in depth research must be carried out on the plant cell aspects such as membrane disruptions, cell wall lysis, susceptibility to biotic pathogens, signal transduction, gene expression, hormone release, and ROS production, among others. Furthermore, there is a need for studies about the impact of ENMs on color, texture, taste, and nutritional aspects of plants that are major components in the food chain.

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Figure legends

Figure 1. Biotic and abiotic factors contributing for ENMs toxicity towards plants.

Figure 2. Physicochemical properties determining the ENMs toxicity towards living organisms.

Table 1. Summary of the plant nanotoxicity/studies upon ENMs exposure.

ENMs	Size (nm)	Surface area (m ² /g)	Shape	Purity (%)	Concentration	Plant	Effects	Impact (positive or negative)	References	
n-ZnO	20	50 ± 10	Hexagonal	>99.5	1600 mg/L	Cucumber	Germination	+	Lin and Xing 2007	
	20	50 ± 10		>99.5	2000 mg/L	Corn	Plant Growth	-	Lin and Xing 2007	
	< 100	5.0		99.5	25-100 µg/ml	Onion	Genotoxicity	-	Kumari et al., 2011	
	8			100	2000 mg/L	Soya Bean	Plant Growth	-	Lopez-Moreno et al., 2010	
	<50			>97	500 mg/kg	Soya Bean	Seeds formation	-	Yoon et al., 2014	
	4				50 mg/L	Garlic	Genotoxicity	-	Shaymurat et al., 2012	
	10	>10.8	nonspherical	>97	500 mg/L	Desert Plant	Root Length	-	Hernandez et al., 2011	
	<50				2000 mg/L	Buckwheat	Genotoxicity	-	Lee et al., 2013	
	10				500 mg/L	Green Peas	Chlorolophyl/Stress	-	Mukherjee et al., 2014	
	100				100-1000 1000 mg/L	Rice	Root Length/Formation	-	Boonyanitipong et al., 2011	
	90				800 mg/kg	Maize	Stress	-	Liu et al., 2015	
	30 & 50				spherical and hexagonal	9950	1-80 mg/L	Chinese Cabbage	Root and Shoot formation	-
n-TiO ₂	21	50	Tetragonal	> 99.5	60 ppm	Fennel	Seed germination	+	Feizi et al., 2013	
	50				10-40mg/ml	Parsley	Germination, chlorophyll, growth	+	Dehkourdi & Mosavi 2013	
					0.25–4‰	Spinach	Seed germination	+	Zheng et al., 2005	
					0.05-0.2 g/L	Tomato	Photosynthesis	+	Qi et al., 2013	
	30.32				1200 ppm	Wheat	Root and Shoot length	+	Mahmoodzadeh & Aghili 2014	
	14 or 25				0-100 ppm	Wheat	Root and Shoot length	+	Larue et al., 2012	
	27 ± 4				750 mg/kg	Cucumber	Chlorophyll	+	Servin et al., 2012	
	27 ± 4 nm				polyhedral Semispherical semispherical	0.2-4%	Zea mayes	Germination	-	Morteza et al., 2014
						750 mg/kg	Cucumber	Stress	-	Servin et al., 2013
n-CeO ₂	8± 1	93.8	Rods	95.14	500 mg/kg	Barley	Biomass	+	Rico et al., 2015	
	7				2000 mg/L	Soya Bean	Genotoxicity	-	Lopez-Moreno et al., 2010	
	8 ± 1	93.8			20-320 mg/L	Cucumber	Stress	-	Hong et al., 2014	
	8± 1	93.8			62.5-500 mg/L	Rice	Stress	-	Rico et al., 2013	
	8± 1	93.8			62.5-500 mg/L	Wheat	Nutrition	-	Rico et al., 2014	
	10				400-800 mg/kg	Cucumber	Nutrition	-	Zhao et al., 2014	
n-Ag					50 mg/L	Pearl millet	Germination	+	Parveen & Rao 2015	
	10				2.5 mg/Kg	Wheat	Genetic expression	+	Dimpka et al., 2013	
	20				1000 ug/ml	Rice	Seed germination	-	Thuesombat et al., 2014	
n-CuO	<50		spherical		0.5 to 1.5 mM	Rice	Stress	-	Shaw and Hossain 2013	
	< 50	45		> 500 ppm	Chick pea and soyabean	Root growth	-	Adhikari et al., 2012		
	<50	29		100-500 mg	Green peas	ROS and plant growth	-	Nair & Chung 2015		

					2000- 4000 mg/L	Buckwheat	Genotoxicity	-	Lee et al., 2013
CNTs	8-15				0- 40 mg/L	Tomato and Turnip	Seed germination	+	Haghihi and Silva 2014
	10–30				6.0 µg m/L	gram	plant growth	+	Tripathi et al., 2011
	6–9			> 95	20 mg/L	Maize	Root growth	+	Tiwari et al., 2014
	6-13			99	80 ug/ml	wheat	cell length of root zones	+	Wang et al., 2012
	1 – 2			90	100 µg/mL	arabidopsis	defense	-	Shen et al., 2010
					0-1000 mg/L	spinach	cell damage	-	Begum & Fugestu 2012
n-Si	20-40			99.72	5-20 kg/ha	Maize	Growth	+	Suriyaprabha et al., 2012
	12	200			8 g/L	Tomato	Seed weight and Germination	+	Siddiqui & Al-Whaibai 2014
	50	361 ± 6.05	spherical	99.9	10 mg/L	Maize	Seed Germination	+	Karunakaran et al., 2012
n-Au	3.5		spherical			tobbaco	Necrosis	-	Sabo-Attwood et al., 2012
NiO	23.34		polyhedral		0.025-2.0 mg/L	Tomato	Stress, mitochondria, cell damage	-	Faisal et al., 2013
Graphene NP	3.8 to 15				500-2000 mg/L	cabbage, tomato, spinach	growth	-	Fugetsu & Begum 2011

Figure 1.

Factors affecting ENMs toxicity towards terrestrial plants

Figure 2.