Review Article

Potential Toxic Effects of Engineered Nanoparticles and Heavy Metals on Growth and Development of Plants

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Abstract

 Nanoparticles (NPs) interact with plants causing many morphological and physiological changes, depending on their properties. Their positive and negative effects on plant growth and development could be determined by chemical composition, size, surface covering, reactivity and dose. The impact of engineered nanoparticles (ENPs) on plants depends on the form, density, comprehensiveness and physical and chemical properties of ENPs as well as the interacting plant species that varies from plant to plant. A considerably large area of land is contaminated with inorganic heavy metals (HM) contaminants due to use of sludge or municipal compost, pesticides, fertilizers and emissions from domestic waste incinerators, car exhausts, residues from metalliferous mines and smelting industries etc. Since the onset of the industrial revolution, concentration of these contaminants has increased drastically, posing threats to health and environment due to their persistent and non biodegradable nature. The metals accumulate in vital human organs like kidneys, bones and livers with associated serious health disorders. Moreover, plants experience oxidative stress upon exposure to HM that lead to cellular damage. In addition, plants also accumulate metal ions that disturb cellular ionic homeostasis. To minimize detrimental effects of HM exposure and their accumulation, plants have evolved detoxification mechanisms. The focus of this review is to determine the effects of both engineered nanoparticles and HM on growth development of some selected plant species.

Keywords: Cellular Damage; Detoxification Mechanism; Engineered Nanoparticles; Heavy Metals; Plant Growth

Introduction

 The term nanotechnology was coined by Freynman (1959) for the first time and it was used by [40]. The "Nano-Era" started in the late 1990's propelled by the worldwide increase in governmental investments into nanomaterials (NMs) and their applications [49].

The National Nanotechnology Initiative of the United States, created at the beginning of 2000, had coordinated the research and improvements in this sector [51]. Since then, a number of carbon-based and metal based NMs have been produced and are currently used in many areas. NMs are commonly referred to as small objects

with one or more external dimensions in their size range 1–100 nm. At these dimensions, materials exhibit a distinctive behaviour in comparison to larger particles of the same composition. Dissimilar types and compositions of NPs could be existing and selected according to the size of their application. In plant science, gold, silver, titanium and zinc NPs are mainly used compared to others, but it is not point out that other NPs (e.g., Cd, Cs and Yb) can/may not be used for plant growth and development. There is a conformity that the outcomes created by these materials is dependent on the type of NPs, the plant species and the plant substrate (e.g., culture medium, hydroponics, aeroponics and soil substrate). Therefore, many theme, reports and challenges linking the biological belongings of NPs stay unresolved [49].

Over 450 metric tons of silver nanoparticles (nAg) were produced in 2014 and they made an important component in the area of NMs market [38]. A number of reports have confirmed that NPs can induce phytotoxicity [49]. The mechanisms of nanotoxicity remain unknown; however, it is assumed that their chemical composition, chemical structure, particle size and surface area matters. The toxicity of the NPs may be attributed with: (i) a chemical toxicity based on the chemical composition, for example, their release of (toxic) ions; and (ii) stress or stimuli caused by the surface, size and/or shape of the particles. It has been also been confirmed that the solubility of NPs oxide significantly affect cell cultures negatively [49]. Whereas, other evidences have suggested that the nanoparticle-mediated toxicity cannot be solely explained by the release of the dissolved components of the NPs [38].

The term 'heavy metal' (HM) is somewhat imprecise; it includes most metals with an atomic number greater than 20, but excludes alkali metals, alkaline earths, lanthanides and actinides [3]. defined the HM as those metals that have a density greater than five; (thirtyeight elements). However, in general terms, metals may be found in the lower-left side of the diagonal of semi-metals or metalloids (from Boron to Polonium) in the periodic table, which may act as both metals and non-metals. Metals are distinguished from non-metals by their capacity to lose electrons, forming positively charged ions, or Lewis acids and by their speciation-dependent affinity for abiotic and biological inter-action [4,21]. Some metals are essential for biological life in trace amounts, and their accumulation in excessive amounts could be poisonous and could lead to death of living organisms including plants. Accumulation

of HM in agricultural soils is of increasing concern because of food safety issues, potential health risks and its injurious effects on soil ecosystems [5]. Their excess results in chlorosis ensued by necrosis, weak plant growth, yield depression, accompanied by reduced nutrient uptake and disorders in plant metabolism [22]. A few of them like (Ni and Cu) are essential for growth and development of both plants and human beings; whereas, others (As, Cr, Cd and Hg) are highly toxic. Furthermore, these HM striking soil fertility, soil biomass and crop yields also contribute to bioaccumulation of metals in the food chain [32] and thus pose unwholesome threats to the health of animals and humans [32].

Environmental degradation due to unabated urbanisation, industrialization, (mining, power generation, transportation and intensive agriculture practices) with use of increased use of HM based products (pesticides including fungicides, insecticides, disinfectants, solid industrial wastes and application of phosphate fertilizers, land fertilized with sewage slug and sewage water) that constitute major environmental pollutions (in agricultural soils, their negative effects on soil, animal and plant ecosystems, environment, food safety issues and potential health risks) have become a major threat to human welfare since last couple of decades [6,16].

Each HM has numerous unspecific and a few specific effects on plant metabolism that are greatly dependent on the type of plant species and mode of HM action [40]. Crop plants take up these metals and accumulate them in their edible and nonedible parts in various forms and concentrations. The intake of these elements by edible parts of plants could significantly harm human health. Therefore, it is very important to limit the HM accumulation in agricultural products [6,29].

Thus, this review summarizes the toxic effects of engineered nanoparticles and HM on plant growth and development.

Engineered nanoparticles uptake and effect on plant growth and development

Nanoparticles are atomic or molecular aggregates with at least one dimension between 1 and 100 nm [9, 51] which are having different physico-chemical properties compared to their bulk counter parts [45]. Nanoparticles can be categorized according to their origin in to natural, incidental and engineered types. Natural nanoparticles have existed from the beginning of the earth's history and

continue to occur in the environment (Volcanic dust, mineral composites etc.) [45].

Incidental nanoparticles are produed after manmade industrial processes (diesel exhaust, welding, furnaces etc.). [38] has divided engineered nanoparticles into four groups:

(i) Carbon based materials (Single wall, Multiwall carbon nanotubes, Fullerene etc.),

(ii) Metal based materials (Quantum dots, nanogold, nanozinc etc.),

(iii) Dendrimers which are nano-sized polymers built from branched units, capable of tailoring to perform specific chemical functions,

(iv) Composites which combine nanoparticles with other nanoparticles or with larger bulk type materials present in different morphologies like tubes, rods, spheres and prisms.

Recent exploration of engineered nanoparticles in consumer products is expected to find their way into terrestrial, atmospheric and aquatic environments in which the fate, transport and behaviour mechanisms are largely unknown. Studies on the toxicity of engineered nanoparticles are still emerging and primarily evidence several negative effects on growth and development of plants. Engineered nanoparticles could reach in plants through direct application, contaminated soil/sediments, accidental release and atmospheric occurance, which outcomes in a substantial negative effect on food crops and food chains [38].

The effect of magnetic nanoparticles coated with tetramethylammonium hydroxide on the growth of *Zea mays* plant ontogenetic stages was reported by [49]. These engineered particles were used as source of iron in culture medium. Interestingly, the results revealed that these iron based nanoparticles have both chemical and magnetic influence on the enzymatic structures implied in the different stages of photosynthesis. Small concentrations of these have stimulating effect on the growth of plantlets while the enhanced concentration of ferrofluid solution induced an inhibitory effect. Five types of multi-walled nanoparticles at the stages of seed germination and root growth in six higher plant species (*Zea mays, Lactuca sativa, Lolium multiflorum, Brassica napus, Raphanus sativus and Cucumis sativus*) were applied and were analysed

for phytotoxic symptoms. Inhibition of root growth varied greatly among nanoparticles and plants and it is partially correlated to nanoparticles concentration [38]. [37] analysed toxicity and bioavailability of Cu nanoparticles to the plants Phaseolus radiates and *Triticum aestivum*. The growth rates of both plants were inhibited and the seedling lengths of tested species were negatively related to the exposure concentration of the nanoparticles. *Triticum aestivum* showed a greater accumulation of Cu nanoparticles in its roots.

[11] studied the behaviour of Palladium (Pd) nanoparticles in nutrient solutions used to grow plants. They reported the uptake of Pd by *Hordeum vulgare*. Smaller and larger Pd particles were comparatively assessed and the results revealed that Pd uptake through roots depends on size of the particles. Smaller Pd particles showed stress effects in leaves at low concentration. An increase in the shoot/root ratio compared to that of control was observed when metal nanoparticles were applied to Lactuca seeds [53] after 15 days of incubation. Some of the plant species showed their ability in accumulating engineered nanoparticles without considerable physiological damages. This may lead to recognition of these species as potential and cost-effective candidates for cleaning up the nanoparticles contamination. *Medicago sativa* and *Brassica juncea* were reported to be hyperaccumulators of silver [41] whereas *Cucurbita maxima* [64] is capable to take up significant quantities of magnetite nanoparticles from liquid growth medium and to accumulate them with in roots and leaves.

Plant growth and development as influenced by heavy metals

Toxicity of HMs is expressed in terms of inhibition in seed germination and alterations in plant growth variables, photosynthesis, mineral nutrition and water relations. Thus, HMs adversely affect plant growth and development parameters, which are described below.

Seed germination

Germination assay is a basic procedure to determine HMs toxic effects on plants [39]. Seed germination is highly sensitive to metal pollution because of lack of well establish defence mechanism [6,39]. It is one of the most sensitive physiological processes in plants, regulated by several hormonal interactions and environmental factors [39].

When plants are exposed to excess As, either in soil or in liquid culture, they exhibit toxicity in form of seed germination inhibition [1,5]. Arsenite was more toxic and hence more restrictive to wheat seed germination than arsenate [39]. In Indian mustard As reduced seed germination up to 40% [5]. In the case of Beet Greens, Cd caused variable degree of germination inhibition [38]. In *Phaseolus vulgaris* var. Pinto Americano, Cd treatments decreased the percent germination with an increase in the concentration of the metal. Cd-EDTA treatments that also reduced their germination percentage [38].

Ability of a seed to germinate in a medium containing Cr is an indicator of its level of tolerance to this metal [48]. Seed germination of the weed *Echinochloa colona* [52], the bush bean (*Phaseolus vulgaris*) [48] and Lucerne (Medicago sativa cv. Malone) was reduced upto 25% with 200 µM Cr, 500 mg kg^{-1} of hexavalent Cr in the soil upto 48% and 40 mg kg^{-1} of Cr-VI respectively [48].

The rice seeds were exposed to different concentrations of Cu to determine their effects on germination. The germination rate of the rice seeds significantly decreased with the increase of Cu concentrations, ranging from 1.0 to 2.0 mM. The shoot growth of the germinating seeds was significantly inhibited at 0.2 mM Cu. It decreased further at higher Cu concentrations [2]. The Cu based decline up to 18% in seed germination was noted in Brassica Juncea [4].

The germination and seedling growth of turnip was relatively resistant to HgCl$_2$ exposed to mercurials [3]. The toxic effect of mercury on germination, growth and yield has been studied on different plants [41]. [40] found that mercury caused an inhibition of seed germination in wheat and cucumber (*Cucumis sativus*) seeds.

Nickel also inhibits seed germination like other HMs. The germination stage is considered as the most sensitive particularly to nickel toxicity [60], i.e. the increasing concentration of nickel has been shown to inhibit seed germination and seedling growth of different plant species [60]. The Ni-induced growth inhibition has been ascribed to down-regulation of protein synthesis and activities of some key enzymes responsible for mobilization of food reserves during seed germination [6]. In addition, Ni is also known to be an active competitor of a number of essential micro and macro-elements and it may reduce uptake of elements in germinating

seeds thereby resulting in poor germination and seedling establishment [47]. [6], has also validated the significant reduction in germination in Brassica genotypes after nickel application.

Root growth

Root is the main organ of plants for mineral nutrient uptake and its growth undoubtedly affects the nutrient uptake and transport in plants. The micronutrient uptake depends largely on root activities, which affects root characteristics controlling uptake rate [4]. Decrease in root growth is a well-documented effect of heavy metals on trees and crops [54].

Studies on arsenate toxicity have shown that plant species that are non-resistant to As suffer considerable stress on exposure with symptoms ranging from inhibition of root growth to death [41]. Differential root length responses to arsenite and arsenate were noted at different concentrations among wheat varieties. Relative root length (RRL) decreased significantly when the concentrations of arsenate and arsenite were more than 2 mg L^{-1} for wheat varieties. Although no varieties showed a specific particular resistance to arsenic in terms of root growth, differential responses were noted among the wheat (*Triticum aestivum* L.) hexaploids varieties [38] and some Brassica genotypes [5]. However, root inhibition at higher concentrations may be linked with lower mitotic activity in the root meristematic zone or inhibition of cell enlargement in the elongation zone as a consequence of decreased cellular turgor [5], as root lengthening is controlled by the cell-division rate in the apical meristems and by expansion and elongation of the newly formed cells. A dose-dependent inhibition of root growth (and of the whole plant), has been demonstrated in wheat, mung bean, arabidopsis, broad bean and rice [5].

Cd caused inhibition of root growth, which was significant at concentrations > 2.5 µM. The degree of root growth inhibition was positively correlated with Cd concentration and the length of roots treated with 250 µM CdCl$_2$ was about 25% that of the controls. The diameters at the root-apex base were only slightly influenced, whilst the highest Cd concentration (250 µM) caused a significant increase at 0.5 mm from the root tip; the apex and length of the meristems were significantly reduced when exposed to 25 and 250 µM Cd [28]. Furthermore, 10 mg L^{-1} Cd reduced root size by 6.0% as compared to the control in Alfalfa plant [48]. A significant reduc-

tion due to Cd was observed in wheat seedlings [48] and barley genotypes (*Hordium vulgare*) [7].

Chromium shows its deleterious effects towards plants in terms of reduction in root length and dry weight of plants grown under dry conditions. The root length of the *Caesalpinia pulcherrima* –a woody perennial plant, was inhibited by 100 mg L^{-1} Cr [31]. Total root weight and root length of wheat was affected by 20 mg Cr (VI) kg^{-1} soil as K$_2$Cr$_2$O$_7$ [18,25]. Treatment with 150 μM of dichromate caused a 50% primary root growth inhibition and root hair growth induction, as compared to control [14].

[17] showed the effect of CuSO$_4$ on the growth of rice seedlings. Increasing concentration of CuSO$_4$ from 20 to 50 μM progressively decreased the root length. The differential effect of Cu on root and shoot growth could be due to Cu accumulation mainly in roots and to a minor extent in shoots [53]. The Cu toxicity is largely noted on root growth and morphology because of Cu tends to accumulate in the root tissue with little translocation to the shoots [53]. The tendency of Cu to retain largely in root is indicates that roots are more sensitive and more exposed to metals than shoots [53]. The similar results were also observed in Indian mustard genotypes [5].

[63] found negative effects of Hg on young barley root growth. Alfalfa root growth was sensitive to the exposure of Hg^{2+}. The treatment with Hg^{2+} at 1, 5, 10, 20 and 40 μM external concentrations gradually inhibited the root growth, as expressed in dry weight. The biomass of roots treated with 20 μM Hg^{2+} decreased by 54% as compared to the control (Hg-free). Therefore, 20 μM concentration of Hg^{2+} was used for the estimation of physiological responses. To evaluate the Hg^{2+} toxicity to the roots of alfalfa, the oxidative damage to membranes was examined by measuring the content of thio-barbituric acid reactive substances (TBARS), an indicator of lipid peroxidation [63]. Exposure of seedlings to Hg^{2+} caused a general increase in the TBARS content. The significant increase in TBARS level was observed at 50 μM Hg^{2+} and attained a peak at 20 μM Hg^{2+}, where the TBARS value was four-fold higher than the control. Treatment of roots with 20 μM Hg^{2+} significantly enhanced TBARS content in a time-dependent manner. Formation of TBARS was maximal after 12 h of Hg exposure; a further incubation of roots with Hg resulted in a decreased TBARS content in roots [3,63].

[6] have shown that Ni inhibits root growth in part by inhibiting the cell division in the root apex, yet they were unable to determine whether the effect was primary or secondary. Nickel at a concentration of 25 mg L^{-1} had an effect on growth of hairy roots of the Ni-hyperaccumulator, Alyssum bertolonii. By contrast, *Nicotiana tabacum* roots induced necrosis (became dark brown) within 7-10 d of exposure to Ni and the growth was severely inhibited [1]. The reduction in roots due to Ni was 5% in *Pusa Jai Kisan* genotype of Indian mustard [6].

Stem growth

Exposure of As to plant reduces shoot growth [1] and sometimes leads to plant death [33].

Cd pre-treatment also decreased the stem length of uninoculated seedlings with 10 mg Cd kg L^{-1} and that of *Sorgham bovinus*-inoculated seedlings with 100 kg L^{-1} [36]. Adverse affected Cr on plant height and shoot growth [36]. When Cr was added at the rate of 2, 10 and 25 mg L^{-1} to nutrient solutions in sand cultures in oats, by 11%, 22% and 41% plant height was reduced respectively, over the control [36]. [10] reported reduction in plant height due to Cr (VI) on *Curcumas sativus, Lactuca sativa and Panicum miliaceum*. [10] observed that addition of Cr (III) inhibited shoot growth in lucerne cultures.

[2] reported that plant height reduced significantly in wheat cv. UP 2003 in a glasshouse trial after 32 - 96 days under 0.5μM sodium dichromate sown in sand. There was a significant reduction in plant height in *Sinapsis alba* on soils containing 200 or 400 mg kg^{-1} Cr along with N, P, K and S fertilizers [2]. The shoot growth of the germinating seeds was significantly inhibited at 0.2 mM Cu that decreased further at higher concentrations [2].

Hg-exposure was noted to induce a significant reduction of root and shoot length in cucumber seedlings and this effect varied with the time of exposure and the concentration of exogenous Hg [58].

The average length of shoots was reduced by 40% in seedlings exposed to Ni throughout the growing period. The growth rate of the seedlings was also affected by treatment with 0.05 μg Ni day^{-1} in the comparison to control seedlings [6].

Leaf growth

The presence of metals in the leaves can affect plant metabolism even at very low concentrations. The oldest leaves of metal-exposed plants exhibit highest metal content [58]. The researchers

showed further reduction in plant dry matter production [6]. Leaf growth, area development and total leaf counts decisively determine the yield of crops. The presence of As in the environment at an elevated level could hamper the growth of plants with the toxicity symptoms such as wilting and necrosis of leaf blades [5], reduction in leaf area [4] and lower fruit and grain yield [5]. The effect of different Cd^{2+} concentrations (100, 200 and 300 mM CdCl2) was evaluated on the growth of sunflower leaves collected at different times between days 1-4. Although 200 and 300 mM Cd^{2+} inhibited leaf expansion from the beginning of the treatment, leaf area was significantly decreased only at day 4 under 100 mM Cd^{2+}. Day 4 of the treatment was selected to perform the analysis of growth parameters in plants grown for 4 days in the nutrient solution with or without Cd addition [47]. In the presence of 6 mg kg L^{-1} Cd, there occurs a significant desiccation of cotyledons and leaves, while the changes in stem and root are not statistically significant. Salicylic acid (SA) in concentrations applied here did not lead to significant changes of water balance. However, Cd effect on leaves insignificantly decreased in the presence of SA. Thus, at 6 mg kg^{-1} Cd and 10^{-4} M SA, leaves are equally hydrated as in control plants [29].

A leaf count per plant was reduced by 50% in wheat, when 0.5 mM Cr was added in nutrient solution [25]. [25] reported that the various concentrations of tannery effluent decreased leaf area and leaf dry weight in *Oryza sativa, Acacia holosericea and Leucaena leucocephala*. The severity of reduction in leaf size increased with increasing Cr^{6+} concentration and the duration of exposure. Similar observations with reference to Cr (VI) were made in *Phaseolus vulgaris* [55], *Pisum sativum* [24] and *Vigna radiata* [55]. The Cu content of leaves of maize cultivars increased with increasing Cu concentration [23].

Visible symptoms of Hg stress include leaf chlorosis, necrotic leaves and leaf tips and the stunted growth [35]. Hg stress may result in decreased foliar chlorophyll content and/or damage to internal leaf structure, strongly correlated with biomass of vegetation and leaf area index [30].

Nickel concentrations greater than 200 mmol and 20 mmol agar, depressed seedling growth. At 80 mmol Ni, the seedlings showed Ni toxicity symptoms, such as production of short (1 mm) lateral roots with black tips, chlorotic shoot tips, scaled distal portions of young leaves and purple base of older leaves [6].

Photosynthesis

One of the most important physiological processes in plants is photosynthesis. HMs reduce the photosynthesis drastically and invariably [6]. [49] explained some hypotheses concerning the possible mechanisms of HM toxicity on photosynthesis and presented a list of key enzymes of photosynthetic carbon reduction, which were inhibited in the HM treated plants (mainly cereal and legume crops). Increased As concentration cause alteration of chloroplast shape, manifested in its rounding and shortening of the longitudinal axis. Other manifestations are concaving of membrane, binding and partial destruction as well as changes in the accumulation and flow of assimilates which results in the decrease of chlorophyll content in rice leaf [42] and hence, decrease in photosynthesis [49].

It was found that Cd toxicity caused notable reduction in photosynthetic rate in different plant species [32]. In *Zea mays*, Cd altered the photosynthesis and enzymes of photosynthesis and the sulphate and nitrate assimilation pathways [32]. Cr stress is one of the important factors that affect photosynthesis in terms of CO_2 fixation, electron transport, photophosphorylation and enzyme activities [32]. The decrease in the chlorophyll a/chlorophyll b ratio [54] brought about by Cr indicates that Cr toxicity possibly reduces the size of the peripheral part of the antenna complex. The decrease in chlorophyll b due to Cr could be due to destabilization and degradation of proteins of the peripheral part. The inactivation of enzymes involved in the chlorophyll biosynthetic pathway could also contribute to reduction in chlorophyll contents in most plants under Cr stress.

Higher concentration of Cu is an effective inhibitor of photosynthesis in higher plants. The results of several studies on the photosynthetic apparatus in excessive Cu-treated plants showed that Cu has a toxic effect on the primary reactions of photosynthesis and electron transport [4]. The action of excess Cu in photosynthesis may primarily target the reaction centre of photosystem II (PS II), which is more susceptible to Cu toxicity than photosystem I (PSI) [60]. Both the donor and acceptor sides of PSII have been proposed as Cu inhibitory sites [12, 62].

The main site of action of mercury damage appears to be the chloroplast thylakoid membranes and photosynthesis. Organo-mercurial compounds have been shown to strongly inhibit electron transport, oxygen evolution [62], hill reaction, photopho-

sphorylation and quenching of chlorophyll fluorescence in photosystem [62].

Mercury affects photosynthesis by disturbing both light and dark reactions of photosynthesis [4,46]. Several studies have been conducted on higher plants grown in Ni contaminated soil and media that show reduction of plant growth and disturbance of metabolic and physiological processes, like photosynthesis [46]. Physiological processes, such as photosynthesis and water status, are sensitive to heavy metals such as Ni in several plants, [44]. Heavy metal, especially Ni, has been found to inhibit electron transport in photosynthetic systems [6] and the regenerative phase of the Calvin cycle [6]. Ni caused an oxidative stress consequential peroxidation of membrane lipids of *Brassica oleracea* [46]. Reduced chlorophyll contents in leaves of Ni-tempered *Brassica* plants, such as chlorosis may result from both Fe and Mg deficiency and also suppression of chlorophyll synthesis [57].

Mineral nutrition composition

One of the non-specific mechanisms of HMs toxicity is the decrease of cation and anion absorption by plant roots [57]. Arsenic may also influence nutrient uptake and distribution in plants through direct competition with nutrients and/or altering the metabolic process. Arsenate affects P uptake because they are taken up via the phosphate transport systems [41].

Cd is phytotoxic, as it can interfere with mineral nutrition and growth regulators balance (Chien and Kao, 2000). Cd may also interfere with nutrient uptake by affecting the permeability of plasma membranes [18]. Interactions between Cd and other nutrients are seen as changes in the nutrient content of the plant [7] and manifested by physiological disorders with negative effects on growth and yield.

Cr affects mineral nutrition of plants in a complex way [56]. Interactions of Cr with uptake and accumulation of other inorganic nutrients have received maximum attention of researchers. Plants take up Cr (III) and Cr (VI) by different mechanisms [56]. [25] reported that tannery effluent irrigation caused micronutrient deficiencies in several agricultural crops. Excess of Cr (0.5 mM) caused a decrease in the concentration of Fe and affected the translocation of P, S, Mn, Zn and Cu from roots to tops in cauliflower [15]. Another study showed that 0.5 mM Cr application resulted in 20% loss of total P in sunflower hulls 30 days after

flowering [29]. Cr (VI) is actively taken up and is a metabolically driven process in contrast to Cr (III), which is passively taken up and retained by cation-exchange sites of the cell wall [55]. Dichromate and chromate, due to their structural similarity with some essential anions, can affect mineral nutrition of plants in a complex way [14]. Reports have shown that Cu and other heavy metals can induce deficiency of essential elements in plants [44]. A deficiency of these elements in plants is often a manifestation of toxic effects [44]. However, compared to the sensitive plants, the metal-tolerant plants are more tolerant to mineral deficiency [44]. Cu-tolerance in Shiny Elsholtzia (*Elsholtzia splendens*), is perhaps correlated with its ability to maintain high mineral nutrient level in plants under Cu stress [61]. Mercury affects membrane structural integrity [44] and thereby mineral nutrient uptake [19]. Nickel inhibited the uptake of some macro and micro-nutrients in various plants species including wheat (*Triticum durum* Desf.). In the drought sensitive cultivar seedlings of wheat, reduced concentrations of Cu, Mg and Mn were observed in roots even at low Ni concentration [44]. At the higher Ni treatment, Fe and Zn root levels were also lowered in durum wheat. Ni concentrations of 35 μM reduced the level of all the mineral nutrients in wheat (*Triticum durum* Desf.) [44]. Mineral nutrients in plant organs may increase, decrease, or remain unaffected in the presence of Ni. One of the probable mechanisms for decreasing the uptake of macro- and micro-nutrients by Ni relies on the competition for common binding sites due to comparable ionic radii of Ni^{2+} and other cations. Such mechanisms may have operated when the uptake of Mg^{2+} (78 pm), Fe^{2+} (82 pm) and Zn^{2+} (83 pm) decreased in the presence of Ni^{2+} (78 pm) [13].

Water relation

Plant water relationship as affected by HMs and has been critically reviewed by [2]. Cd induces decrease in water stress resistance of *Phaseolus vulgaris* cv. Contender by affecting endogenous ABA level, water potential, relative water content and cell wall elasticity [4]. Changes in plant water relations due to excess of Cd and Pb [2] and wilting of various crops to Cr toxicity is reported by [59].

[2] observed a decrease in leaf water potential in Cr-treated bean plants. Excess of Cr decreased the water potential and transpiration rates and increased the diffusive resistance and relative water content in the leaves of cauliflower [15]. Cu is known to decrease water content significantly in the germinating seeds [2]. It generates osmotic stress in germinating rice seeds [2]. Mercury has

been reported to inhibit water flow, mainly through the blockage of water channels [3]. Nickel treatment has produced a decrease in water potential (Ψw), turgor pressure (Ψp), osmotic potential ($\Psi \pi$) and RWC in wheat [56]. The diminution in Ψw was around twice in the drought sensitive variety (-0.59 MP) when compared to drought tolerant cultivar (-0.31). Correspondent deportment was found for Ψp and $\Psi \pi$. Approximately 16% and 10% reduction in the relative water content was recorded in the drought sensitive and drought tolerant cultivars, respectively. Osmotic potential at full turger ($\Psi \pi 100$) and ε (absolone) did not vary in either wheat cultivar [56].

Conclusions

This review furnishes rapid access to views allied to the toxicity of engineered nanoparticles and HMs towards plants growth and development. Notable progress has been made in developing nanotechnology but there are many gaps in our knowledge on the ecotoxicity of engineered nanoparticles. Since, nanoparticles properties largely depend on their chemical composition size and /or shape therefore, behaviour, reactivity and the toxicity could vary depending on the penetration and transport of nanoparticles in plants.

Metals like Ni, Cu in plentiful quantities plays a vital role in an immense range of physiological and morphological functions, right from seed germination to seed set. However, excess HMs (As, Cd, Cr, Cu, Hg and Pb) toxicity is supposed suppression of lateral seed germination, growth variables, photosynthesis, mineral nutrition and water relation. Thus, the exceeding amount of HM could alter plant growth and development negatively.

Acknowledgements

Bibliography

1. Abedin MJ., *et al*. "Relative toxicity of arsenite and arsenate on germination and early seedling growth of rice (Oryza sativa L.)". *Plant Soil* 243 (2002): 57-66.

2. Ahsan N., *et al*. "Excess copper induced physiological and proteomic changes in germinating rice seeds". *Chemospere* 67.6 (2007): 1182-1193.

3. Ansari MKA., *et al*. "Mercury-induced changes in growth variables and antioxidative enzymes in Indian mustard (Brassica juncea L)". *Journal of Plant Interactions* 4.2 (2009): 131-136.

4. Ansari MKA., *et al*. "Identification of the phytoremediation potential of Indian mustard genotypes for copper, evaluated from a hydroponic experiment". *Clean-Soil Air Water* 41.8(2013): 789-796.

5. Ansari MKA., *et al*. "Screening Indian mustard genotypes for phytoremediating arsenic-contaminated soil". *Clean-Soil Air Water* 41.2 (2013): 195-201.

6. Ansari MKA., *et al*. "Genotypic variation in phytoremediation potential of Indian mustard exposed to nickel stress: A hydroponic study". *International Journal of Phytoremediation* 17.1-6 (2015): 135-144.

7. Ansari MKA., *et al*. "Tolerance capacity of Turkish genotypes of barley (Hordium Vulgare L.) for cadmium stress". *Journal of Environmental Botny* 39 (2018): 1027-1035.

8. Arruda SCC., *et al*. "Nanoparticles applied to plant science: A review". *Talanta* 131(2015): 693-705.

9. Ball P. "Natural strategies for the molecular engineer". *Nanotechnology* 131 (2002): 15-28.

10. Barton LL., *et al*. "Inhibition of ferric chelate reductase in alfalfa roots by cobalt, nickel, chromium and copper". *Journal of Plant Nutrition* 23 (2000):1833-1845.

11. Battke F., *et al*. "Palladium exposure of barley uptake and effects". *Plant biology* 10.2 (2008): 272-276.

12. Bernal M., *et al*. "Copper effect on cytochrome b559 of photosystem II under photoinhibitory conditions". *Plant Physiology* 120.4 (2004): 686-694.

13. Boominathan R. "Ni-induced oxidative stress in roots of the Ni hyperaccumulator, Alyssum bertolonii". *New Phytology* 156.2 (2002): 205-215.

14. Castro RO., *et al*. "Effects of dichromate on growth and root system architecture of Arabidopsisthaliana seedlings". *Plant Science* 172.4 (2007): 684-691.

15. Chatterjee J., *et al*. "Phytotoxicity of cobalt, chromium and copper in cauliflower". *Environmental pollution* 109.1 (2000): 69-74.

16. Chehregani A., *et al*. "Effect of heavy metals on the developmental stages of ovules and embryonic sac in Euphorbia cheirandenia". *Pakistan Journal of Biological Science* 8 (2005): 622-625.

17. Chen LM., *et al*. "Copper toxicity in rice seedlings: changes in antioxidative enzyme activities, H2 O2 level and cell wall peroxidase activity in roots". *Botanical bulletin of Academia Sinica* 41(2000): 99-103.

18. Chen H., *et al*. "EDTA and HEDTA Effects on Cd, Cr and Ni Uptake byHelianthus annuus". *Chemosphere* 45.1 (2001): 21-28.

19. Cho UH., *et al*. "Mercury-induced oxidative stress in tomato seedlings". *Plant Science* 156.1 (2000): 1-9.

20. Cui YL., *et al*. "Transfer ofmetals from soil to vegetables in an area near a smelter in Nanning, China". *Environmental International* 30.6 (2004): 785-791.

21. D'Amore JJ., *et al*. "Methods for speciation of metals in soils: a review". *Journal of Environmental Quality* 34.5 (2005):1707-1745.

22. Dan T., *et al*. "Toxicity thresholds for oat (Avena sativa L.) grown in Ni-impacted agricultural soils near Port Colborne, Ontario, Canada". *Canadian Journal of Soil Science* 88 (2008): 389-398.

23. Deniz T., *et al*. "Ünalan.Changes in photochemical and antioxidant enzyme activities in maize (Zea mays L.) leaves exposed to excess copper". *Chemosphere* 67.1 (2007): 89-98.

24. Dixit V., *et al*. "Chromium ions inactivate electron transport and enhance superoxide generation in vivo in pea (Pisum sativum L. cv: Azad) root mitochondria". *Plant Cell Environment* 25.5 (2002): 687-693.

25. Diwan H., *et al*. "Chromium-induced modulation in the Antioxidant defense system during phenological growth stages of Indian mustard". *International Journal of Phytoremediation* 12.2 (2010): 142-158.

26. Duffus JH., "Heavy metals" a meaningless term? (IUPAC technical report)". *Pure and AppliedChemistry* 74 (2002):793-807.

27. Finster EM., *et al*. "Lead levels of edibles grown in contaminated residential soils: a field survey". *Science Total Environmental* 320.2-3 (2004): 245-257.

28. Fusconi A., *et al*. "Effects of cadmium on rootapical meristems ofPisum sativum L: cell viability, cell proliferationand microtubule pattern as suitable markers for assessment of stress pollution". *Mutation Research* 632.1-2 (2007): 9-19.

29. Glorennec P., *et al*. "Analysis and reduction of the uncertainty of the assessment of children's lead exposure around an old mine". *Environmental Research* 100.2 (2006): 150-158.

30. Hansen PM., *et al*. "Reflectance measurement of canopy biomass and nitrogen status in wheat crops using normalized difference vegetation indices andpartial least squares regression". *Remote Sensing Environment* 86.4 (2003): 542-553.

31. Iqbal MZ., *et al*. "Effects of chromium on an important arid tree (Caesalpina pulcherrima) of Karachi city, Pakistan". *Ekológia, Bratislava* 20.4 (2001): 414-422.

32. Iqbal M., *et al*. "Improving the phytoextraction capacity of plants to scavenge metal(loid)-contaminated sites". *Environmental Reviews* 23.1 (2015): 44-65.

33. Jahan I., *et al*. "Effects of arsenic on some growthparameters of rice plant". *Dhaka University Journal of Biological Sciences* 12 (2003): 71-77.

34. Jain CK., *et al*. "Arsenic: occurrence, toxicity and speciation". *Water Research* 34.17 (2000): 4304-4312.

35. Kabata-Pendias A., *et al*. "Trace Elements in Soils and Plants (3rd ed)". CRC Press, Boca Raton (2001): 413.

36. Kim MV., *et al*. "Some properties of human small heat shock protein Hsp22 (H11 or HspB8)." *Biochemical and Biophysical Research Communications* 315.4 (2004): 796-801.

37. Lee WM., *et al*. "Toxicity and bioavailability of copper nanoparticles to the terrestrial plants mungbean (Phaseolus radiates) and wheat (Triticum aestrivum): Plant agar test for water-insoluble nanoparticles". *Environmental Toxicology and Chemistry* 27.9 (2008): 1915-1921.

38. Lin D., *et al*. "Phytotoxicity of nanoparticles:inbibition of seed germination and root growth". *Environmental Pollution* 150.2 (2007): 243-250.

39. Liu X., *et al*. "Toxicity of arsenate and arsenite on germination seedling growth and amylolytic activity of wheat". *Chemosphere* 61.12 (2005): 293-301.

40. Madyima S., *et al*. "Cumulative effects of sewage sludge and effluent mixture application on soil properties of a sandy soil under a mixture of star and kikuyu grasses in Zimbabwe". *Physics and Chemistry of the Earth* 27.11-12 (2002): 747-753.

41. Mcgrath SP., *et al*. "Phytoextraction of metals and metalloids from contaminated soils". *Current Opinion in Biotechnology* 14.3 (2003): 277-282.

42. Miteva E., *et al*. "Response of chloroplasts and photosynthetic mechanism of bean plants to excess arsenic in soil". *Bulgarian Journal of Agricultural Science* 8.2-3 (2002): 151-156.

43. Monni S., *et al*. "Copper resistance of Calluna vulgaris originating from the pollution gradient of a Cu-Ni smelter in southwest Finland". *Environmental Pollution* 109.2 (2000): 211-219.

44. Monni S. "Ecophysiological responses of Empetrum nigrum to heavy metal pollution". *Environmental Pollution* 112.2 (2001): 121-129.

45. Nel A. "Toxic potential of materials at the nano level". *Science* 311.5761 (2006): 622-627.

46. Patra M., *et al*. "Comparison of mercury, lead and arsenic with respect to genotoxic effects on plant systems and the development of genetic tolerance". *Environmental Experimental Botany* 52.3 (2004): 199-223.

47. Pena LB., *et al*. "Effect of different metals on protease activity in sunflower cotyledons". *Journal of Electronic Biotechnology* 9 (2006): 258-262.

48. Peralta JR., *et al*. "Study of the effects of heavy metals on seed germination and plant growth on alfalfa plant (Medicago sativa) grown in solid media". Proceedings of the conference on Hazardous Waste Research, Denver, Colorado (2000).

49. Racuciu M., *et al*. "TMA-OH coated magnetic nanoparticles internalized in vegetal tissues". *Romanian Journal of Physics* 52.3 (2007): 395-395.

50. Robertson AI., "The effect of nickel on cell division and growth of Brachystegia spiciformis seedlings". *Kirkia* 12.1 (1980): 115-125.

51. Roco MC., *et al*. "Broader societal issue of nanotechnology". *Journal of Nanoparticle Research* 5.3-4 (2003):181-189.

52. Rout GR., *et al*. "Effects of chromium and nickel on germination and growth in tolerant and non-tolerant populations of Echinochloa colona (L.)". *Chemosphere* 40.8 (2000): 855-859.

53. Shah V., *et al*. "Influence of metal nanoparticles on the soil microbial community and germination of lettuce seeds". *Water, Air and Soil Pollution* 97.1-4 (2009): 143-148.

54. Shanker AK., "Physiological, biochemical and molecular aspects of chromium toxicity and tolerance in selected crops and tree species". PhD Thesis, Tamil Nadu Agricultural University, Coimbatore, India (2003)

55. Shanker AK., *et al*. "Differential antioxidative response of ascorbate glutathione pathway enzymes and metabolites to chromium speciation stress in green gram (Vigna radiata (L.). R. Wilczek. Cv CO 4) roots". *Plant Science* 166.4 (2004): 1035-1043.

56. Shanker AK., *et al*. "Chromium toxicity in plants". *Environment International* 31.5 (2005): 739-753.

57. Sreekanth TVM., *et al*. "Occurrence, physiological responses and toxicity of nickel in plants". *International Journal of Environmental Science and Technology* 10.5 (2013):1129-1140.

58. Susan J., *et al*. "Nickel contamination affects growth and secondary metabolite composition of St. John's wort (Hypericum perforatum L.)". *Environmental Experimental Botany* 49.3 (2003): 251-257.

59. Tang SR., *et al*. "Heavy-metal uptake by metal tolerant Elsholtzia haichowensis and Commelina communis from China". *Communications in Soil Science and Plant Analysis* 32.5-6 (2001): 895-905.

60. Vinit-Dunand F., "Effects of copper on growth and photosynthesis on mature and expanding leaves in cucumber plants". *Plant Science* 163.1 (2002): 53-58.

61. Yang X., *et al*. "Sedum alfredii H: a new Zn hyperaccumulating plant first found in China". *Chinese Science Bulletin* 47.19 (2002): 1634-1637.

62. Yruela I. "Copper in plants". *Brazilian Journal of Plant Physiology* 17(2005): 145-156.

63. Zhou ZS., *et al.* "Metabolic adaptations to mercury-induced oxidative stress in roots of Medicago sativa L". *Journal of Inorganic Biochemistry* 101.1 (2007): 1-9.

64. Zhu H., *et al.* "Uptake translocation and accumulation of manufactured iron oxide nanoparticles by pumpkin plants". *Journal of Environmental Monitoring* 10.6 (2008): 713-717.