Chapter 13
Nanotechnology in Soil-Plant System

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Abstract Opportunities for applications of nanotechnology in soil-plant system are fast emerging as an alternative to Green Revolution technologies, which need to be phased out due to their limitations in breaking yield barriers and environmental compliances, and ever escalating shortage of farming inputs, especially P- and K-containing fertilizers and irrigation water. Literature and patent applications on nanotechnology applications in soil-plant system encompass novel materials containing nutrients and stimulators of plants, and pesticides. Compatibility of nanomaterials to farming, food and environment is essential because agricultural production functions in open system, where both energy and matter are freely exchanged in the realm of geosphere–biosphere–atmosphere. Apart from nanomaterials intended for farming, thousands other engineered nanoproducts are entering in soil-plant system, which have been altering the pristine state of soil-plant continuum, and therefore calls for framing of regulations on their use. One of the treasures in soil-plant system could be nanofabricated materials containing plant physiologically suitable nutrient ion(s) in clay minerals receptacles. The areas that need further attention in the success of nanotechnology applications in soil-plant system are founding of impeccable paradigms for concepts that govern farm production system, nanofabricating novel materials so as to improve input use efficiency and environmental compliance, interventions in soil fertility and damaged ecosystems, nutrient and water transport mechanisms in soil-plant system, and biosafety of engineered nanomaterials.

Keywords Nanomaterials · Biosafety · Clay mineral · Environmental compliance, farming system · Nano-inputs · Physiological response · Nutrient use efficiency · Ecosystems · Soil fertility

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13.1 Introduction

Application of nanotechnology in the discipline of agriculture is about a decade old initiative. As of now, research works are largely confined in literature and patent applications. But nevertheless, it promises revolutionary changes in farming with time. Encouraging results have already been noticed for a few novel materials based on clays (Table 13.1). The promise could be judged from the fact that there are a good number of claims of utility of the novel nanomaterials for their use as fertilizers, and surely, it is a matter of little more time for at least a few of them to be approved by the fertilizer regulatory authorities for their use in farmers' field.

For agricultural production system, compatibility of nanomaterials to farming and environment is essential because of unique nature of agriculture, which functions as open system, where both energy and matter are freely exchanged in the realm of geosphere–biosphere–atmosphere. Due to the rigors of agricultural production system, neither the manufacturing processes nor their applications meant for industrial purposes can be copied for agriculture. Also economic returns from agriculture are low. It is therefore understandable that nanotechnology research aimed agricultural applications could be minuscule in volume and its translation to reality could be slow compared to other disciplines such as electronics, drug development and security devices. It is worthwhile to remember that the editors of

Table 13.1 Some clay-based nanotechnology ventures for agriculture (adapted after modification from Kalpana-Sastry 2007)

Product	Application	Institution
Nanocides	Pesticides encapsulated in nanoparticles for controlled release	BASF
	Nanoemulsions for greater efficiency	Syngenta
Buckyball fertilizer	Ammonia from buckyballs	Kyoto U., Japan
Nanoparticles	Adehesion-specific nanoparticles for removal of *Campylobacter jejuni* from poultry	Clemson U.
Food packaging	Airtight plastic packaging with silicate nanoparticles	Bayer
Use of agricultural waste	Nanofibres from cotton waste for improved strength of cotton	Cornell U.
Nanosensors	Contamination of packaged food	Nestle, Kraft
	Pathogen detection	Cornell U.
Precision agriculture	Nanosensors linked to GPS for real-time monitoring of soil	USDA
Livestock and fisheries	Nanoveterinary medicine (nanoparticles, buckyballs, dendrimers, nanocapsules for drug delivery, nanovaccine, smart herbs, nanocheck for cleaning fish ponds, iron nanoparticle-feed for fish	Cornell U., Nanovic, Australia

Nature (2011) estimated that any technology takes some 20 years to emerge from the laboratory and be commercialized.

Historically, scientific discoveries happened in those areas, where sound theoretical frameworks, called paradigms had already laid the foundations (Kuhn 1970). This incidentally is a serious hardship for revolutionizing farming. For example, many concepts (e.g., available plant nutrient, soil health, pest control, nutrient transport) are still rudimentary in nature and do not conform to the scientific diligence. Some other important issues pertaining to agriculture are that use of nanomaterials does not guarantee a control framework that we have in electrical machines, or in satellites, or in chemical or synthetic reactors. However, it could possibly be an erudition-predicated passive framework. Similarly, the requirement of inputs in agriculture is gigantic compared to industrial use. For example, requirement of carbon nanowire for 50 million cell phones might be restricted to 50 mg, but for every hectare of land, requirement of nitrogen fertilizer could be 100 kg at optimum level (Mukhopadhyay 2014a). This is true for all inputs (seed, fertilizer, water, pesticide etc.). Whether we use nanomaterials or bulk materials, the optimum requirements of plants to achieve yield cannot be curtailed (First law of thermodynamics). At the same time, it must also be kept in mind that 100 % use efficiency of inputs is not achievable (Second law of thermodynamics).

A few things that are important for a productive venture into the nanotechnology are as follows: (i) knowledge and understanding of nanomaterials and ability to nanofabricate novel materials, (ii) understanding behavior of nanomaterials in soils, and their interaction with plants, (iii) improving use efficiency and availability of plant nutrients, especially phosphorus and micronutrients, and (iv) biosafety and environmental compliance.

13.2 Defining Nanotechnology

Nanotechnology is defined by the US Environmental Protection Agency (2007) as a science of understanding and control of matter at least in one dimension of roughly 1–100 nm where unique physical properties make novel applications possible. The inherent problem-solving capacity of the material is the driving force in imploring nanotechnology in applied disciplines such as agriculture. Therefore, Nakache et al. (1999) and USDA (2002) suggested that the size dimensions of nanoparticles could be between 10 and 1000 nm that are simultaneously colloidal particulates. More appropriate definition could be the one offered by Hall (2006), who described nanotechnology as the science of designing and building machines in which every atom and chemical bond is specified precisely. To him, it was not a set of particular techniques, devices, or products, but the set of capabilities that we will have when our technology gets near the limits set by atomic physics. He emphasized that nanotechnology aims at achieving for control of matter what computers did for our control of information.

13.3 Limitations of Green Revolution Technologies

Green Revolution Technologies have manifold farm productivity to the extent that it successfully addressed global food demand. But, it also brought along with it, degradation of environmental qualities such as causing excessive load of toxins in soils and water bodies, damage to C, N, and P cycles in soil-plant system, loss of biodiversity, declining groundwater levels, rapid weathering of soil minerals, soil acidification, and salt buildups. Together, they have threatened life and life-supporting systems (Mukhopadhyay 2005; Bhalla and Mukhopadhyay 2010; Mukhopadhyay and Sharma 2013; Mukhopadhyay 2014a). One of the root causes of this alarming situation is unrestraint and inappropriate use of farm inputs.

On the other hand, alternate farming ventures such as "Conservation Agriculture," "organic farming," "rainfed/dryland farming," and similar attempts have fallen short of our productivity expectations. The situation becomes worrisome with rising population and accelerated pace of climate change, depleting resources, and shrinking landscape. Under such situation, there exists opportunities for transcending existing farming technologies by novel use of nanotechnology that complies with the farm production system. The novelty of farming-compliance nanotechnology lies in the transcribing of nature (Naik and Stone 2005; Kuzma and VerHage 2006; Mukhopadhyay and Brar 2006; Khot et al. 2012; Mukhopadhyay 2014a).

13.4 Nanomaterials and Their Application Potential in Agriculture

Classes of materials: Four classes of nanomaterials, viz., (i) carbon based, (ii) metal based, (iii) dendrimers, and (iv) composites are recognized by US Environmental Protection Agency (2007). In this chapter, we would try to highlight what could possibly be done with these materials with special emphasis on clay minerals.

Advantages of nanomaterial over its corresponding bulk material: At the nanoscale, matter shows extraordinary properties that are not exhibited by bulk materials. For example, in the case of clay; surface area, cation exchange capacity, ion adsorption, complexation, and many more functions of clays will multiply, if they are brought to nanoscale. One of the principal ways in which a nanoparticle differs from bulk material is that a high proportion of the atoms that are associated with a nanoparticle are present at the surface (Maurice and Hochella 2008). Nanoparticles may thus have different surface composition, different types and densities of sites, and different reactivities with respect to processes such as adsorption and redox reactions (Waychunas et al. 2005).

Nanofabrication with clays as receptacles: Clays have become popular material for nanofabrication. For centuries, they are used in ceramics, computer hardware, oil refinery, filtration, pharmaceuticals, pesticide, cosmetics, construction, cement, and paper industries, to name a few. In nanoform, they have been used since ages in ceramics in China. Since time immemorial, naturally occurring nanoparticles found in soil system have been cleaning surface and ground water bodies, and regenerating life by changing harmful substances dumped on it (Sparks 2004; Maurice and Hochella 2008). Clays are inherently self-regulatory (functions in non-linear dynamical system). They are safe to life and environment, and address many other challenges of synthesis and applications in nanotechnology. Chien et al. (2009) described soils as nature's great electrostatic chemical reactor and suggested that clays could be used to clean up high pollution load in soils and water bodies arising from low use efficiency of fertilizers. The advantages of use of clay in nanofabrication are because of their: (i) ordered structural arrangements, (ii) huge adsorption capacity, (iii) capacity to shield from sunlight (ultraviolet radiation), (iv) ability to concentrate organic chemicals, and (v) ability to serve as polymerization templates. Clay-nanofabricated materials could be used in controlling release of nitrogen by trapping N in zeolites and hydroxylapatites, and in controlling release of plant nutrients, nature, and population of microflora in soil rhizosphere, ion transport in soil-plant system, and emission of dusts and aerosols from agricultural soil. They are potentially useful in precision water farming and zeoponics.

Mukhopadhyay et al. (2014a) have developed a novel process of nanofabrication involving clay minerals as receptacles, developed four advanced Zn-based nanomaterials containing zinc in plant-available form (Zn^{2+}) using clay minerals as receptacles, and then embedded them into a polymer matrix. The four nanoproducts were nanofabricated Zn^{2+} in fuller's clay receptacles, in fuller's clay nanocomposite, in kaolin clay, and in kaolin clay nanocomposite for their use as novel fertilizers (Singh et al. 2013). Mukhopadhyay (2014b) also made novel nanophosphorous products by intercalating phosphate ion (PO_4^{3-}) in kaolin clay mineral. The nanoproduct, when applied to soil as fertilizer, would release either phosphate ions (PO_4^{3-}), or get converted to hydrogen phosphate ions (HPO_4^{2-}) or dihydrogen phosphate ions (H_2PO^{4-}). All three forms are available to plants, and the release of phosphate ion would be through diffusion process. The novelty in this invention lies in the use of clay minerals as receptacles (Mukhopadhyay 2014a) and extracting phosphates from phosphorous minerals free from toxic materials (Mukhopadhyay 2014c). These and many other clay-based nanoproducts are expected to work in the soil system due to their colloidal and charge properties (Singh et al. 2013; Mukhopadhyay 2014a, b, c).

Nanotechnology involves synthesis of nanomaterial and its application to achieve a particular task. For example, if it is nanofertilizer, it has to supply nutrient ions in plant-available forms, and would remain in the soil system for a long time. Similarly, a nanoherbicide has to be specific against targeted weeds, but safe to the crop, and so on. Other requirements of nanosynthesis for agricultural applications would be that the raw materials and processes of synthesis must be cheap because farming requires large amount of inputs, and farmers must be able to afford them! Such scenario calls for innovative routes that are tuned to agriculture, and in all probability, they are likely to be different from the courses followed for manufacture of industrial nanoproducts. The routes of fabrication could rely on charge properties: (a) such as density, origin, and nature of charges, (b) intensity and degree of manifestation of charge in nanoscale, and (c) the nature (geometry) and extent of interface available for reaction (Mukhopadhyay 2013). Historically, nanosynthesis has come a long way from the top-down and bottom-up approaches to what Zubarev (2013) has titled, "Any way you want it". This should be the essence for nanofabrication as well.

Manipulation of bonds in clays: Manipulation of bonds could be an effective means for nanofabrication involving clays. Such manipulations are commonly observed in soil clays, especially in silicates. Covalent and ionic bonds simultaneously coexist in many clay minerals. They can be changed from one form to other through isomorphous substitution or insertion of small ions (e.g., Li^+), or by the use of organic compounds (for transforming of van der Waal's force to a stronger covalent or, metallic bond). Such phenomenon could be implored for improving nutrient supply mechanism in soil-plant continuum through passive control system. It is worthwhile to recognize that the control system that we observe in electrical machines, or in satellites, or in chemical reactors is not implementable in soil-plant system. The only viable system for them could be founding knowledge-based passive control system so as to create millions of rhizospheres in an acre of land to support the growth of millions of plants of a crop; a breakthrough to transcend agriculture into new millennium.

13.5 Fundamental Concepts

The origins of nanoscience can be traced to clay mineralogy and crystallography as clay minerals are crystalline and of nanometer size in all three axes (x, y, and z) (Lower et al. 2001). In nature, transformation and supply of nutrient ions to plants and microbes, fate of accreted materials that get into soil system, and purity of ground and surface water are regulated by clay minerals. The use advantage of clay minerals in nanofabrication over other colloidal material lies in their structural properties such as high anisotropic and often irregular particle shape, broad particle size distribution, different types of charges within the unit cells, heterogeneity of layer charges, pronounced Cation Exchange Capacity (CEC), disarticulation and flexibility of layers, different modes of aggregation, and high surface/mass ratio. Colloidal properties of clay minerals enhanced when bulk material is scaled down to nanoform. Another key feature of use of clay minerals for nanofabrication is their compatibility to life forms, because of their well-documented roles in the genesis of life on Earth and evolutionary diversification of Neoproterozoic life.

13.6 Public Acceptance

Risks and benefits analysis showed that nanotechnology (NT) is neutral, and better placed than genetically modified organisms (GMO), stem cell, biotech, nuclear power etc. (Currall et al. 2006).

13.7 What Are the Opportunities in Soil-Plant System

Improving farm-input use efficiency: Nanotechnology has opened up new opportunities to improve nutrient use efficiency and minimize costs of environmental protection. A disturbing fact is that the fertilizer use efficiency is only 20–50 % for nitrogen, and 10–25 % for phosphorus (<1 % for rock phosphate in alkaline calcareous soils). DeRosa et al. (2010) opined that emergence of nanofertilizers as alternative to conventional fertilizers would eliminate nutrient build ups in soils, which would eventually do away with eutrophication and drinking water contamination. Recent findings have established that plant roots and microorganisms can directly lift nutrient ions from solid phase of minerals (that includes so-called susceptible (i.e., easily weather able), as well as non-susceptible minerals (Mukhopadhyay and Brar 2006). The low solubility and the consequent excess application of P fertilizer, which have been practiced, have led to its build-up in soils and surface water bodies. This problem can be addressed by use of phosphorus-containing nanofertilizers, which have opened new avenues to improve P use efficiency (Mukhopadhyay 2014b, c, d). The central idea is to keep the ratio of applied and plant uptake P around unity by improving efficiency of native and applied phosphorus in soils, regulation of essential and toxic elements associated with phosphorous in pedosphere–hydrosphere continuum as almost all P fertilizers contain heavy metals, and most importantly, supply P to plants in available forms. Singh et al. (2013) developed a high-charge Zn^{2+} nanofertilizer in clay mineral receptacles. Similar to P, Zn^{2+}nanofertilizer would release Zn^{2+} in plant-available form. Micronutrient-based nanoproducts (i) can be applied at the time of sowing by which there will not be any need to wait for deficiency symptoms to appear and thereby no loss of potential yield, (ii) will supply nutrients directly to plant-available forms, and (iii) because of compatible capacity of holding ions on receptacles and their transfer to crops, untargeted loss will minimized (Mukhopadhyay 2014a, b, c). Similarly, nitrogen nanofertilizers will be able to check nitrate pollution and emission of green house gases. Tarafdar et al. (2013) found that nanofertilizers improved quality of agricultural products, removed environmental hazards, and required in lesser amount than conventional fertilizers. Another advantage of nanofertilizers is that the elemental purity in them is very high.

Chinnamuthu and Boopathi (2009) observed that the honeycomb-like layered crystal network of zeolites when filled with nitrogen, potassium, phosphorous, calcium, and a set of minor and trace nutrients slowly released nutrient ions “on demand.” They felt that this property of zeolite can be employed to increase fertilizer use efficiency and eliminating nitrate contamination of ground and surface water bodies that arise from the application of soluble N fertilizers and their fast mineralization. Leggo (2000) opined that zeolites could be used for nitrogen capture and storage because the rate of release of absorbed nitrogen (or, fertilizers compounds) is much slower than the adsorbed ionic forms of N. Millan et al. (2008) observed that zeolite chips containing urea in their cavities can be used as slow-release nitrogen fertilizer material. They also found that there was synergic relationship of ammonium ion holding zeolites in solubilization of phosphate minerals that led to improved uptake of phosphorus and crop yield. Li (2003) used hexadecyltrimethylammonium surfactant to modify zeolites. He observed that zeolites were effective fertilizer carrier and suitable sorbent for nitrate, whose rate of release was slowed down.

Slow/controlled release-nanofertilizers: Jinghua (2004) showed that application of a nanocomposite containing of N, P, K, some micronutrients, mannose, and amino acids enhanced the uptake of nutrients in grain crops. Liu et al. (2006) implored zinc–aluminum-layered double-hydroxide nanocomposites containing plant growth regulators and found that the products released chemicals in controlled manner. DeRosa et al. (2010) also observed that that fertilizer incorporated into cochleate nanotubes (rolled-up lipid bilayer sheets) improved crop yield. These reports demonstrated that nanotechnology could be successfully applied to develop advance supply tools, and materials can be synchronized to comply the mechanisms of nitrogen release from nanofertilizer materials in accordance with the demand of crop provided that the nanomaterials must supply chemicals that can be directly internalized by the plants.

Al-Amin Sadek and Jayasuriya (2007) and Sultan et al. (2009) aimed to manufacture nanofertilizers and to develop their delivery mechanisms in such a manner that they would release nutrient ions in controlled manner (slowly or quickly) in response to environmental signals such as heat and moisture. In nutrient-deficient environment in soils, crops secrete carbonaceous compounds into rhizosphere that enable biotic mineralization of N and/or P from soil organic matter, and P from soil inorganic colloids. Authors suggested that since these root exudates can be considered as environmental signals, they may be used for making nanobiosensors, which may be incorporated into novel nanofertilizers.

Opportunities of nanotechnology intervention in salt-affected soils: Some of the possible areas, where research may be initiated are as follows:

(i) *Reducing salt concentration in soil solution*: Nanocomposites and nanopolymers may be explored.

(ii) *Improving drainage*: Sodium salts are most soluble. If drainage can be facilitated, then leaching of these salts will help crop growth. Drainage may be improved by improving structure in subsurface and sub soils. Nano-Ca^{2+}, nanoferrites, and biofriendly nanopolymers might be exploited for this purpose.

(iii) *Replacing Na^+ by Ca^{2+}*: All clay minerals show high to very high selectivity and spontaneous reactions (negative ΔG^0) for Ca^{2+} over Na^+. Can then nano-Ca^{2+}, nano-Mg^{2+}, and nano-K^+ be useful to remove Na^+ from exchange complex?

(iv) *Changing carbonate chemistry*: Sodium carbonates are more soluble than other carbonates. Capping/encapsulating sodium carbonates with nanocomposites and nanopolymer selectively may yield products which are insoluble and may be leached through preferential flows. It is a common knowledge that organic materials are strongly selective on clays (inorganic substances). Formation of nanoorganic carbonates could be other possibility.

(v) *Prevention of Na_2CO_3 formation*: Nanomaterials such as nanocalcium carbonates, nano-Ca^{2+}, nano-Mg^{2+}, nano-K^+, and nano-iron oxides may be explored to prevent Na_2CO_3 formation in soils.

(vi) *Addition of K^+*: It is proven that potassium has beneficial effect in countering adverse effect of sodium. Illite is most common clay mineral in most of salt-affected soils of India, US, Australia, and many other places in the world. Illite has a very strong preference for K^+ over Ca^{2+}, Mg^{2+}, Na^+, and some other ions. Therefore, nano-K^+ in illite receptacle could be beneficial for accelerating ion exchange reactions to reduce exchangeable sodium saturation.

(vii) *Solubilizing of $CaCO_3$*: Calcium carbonate could possibly be solubilized by the application of nano-Ca^{2+}, nano-Mg^{2+}, and nano-iron oxides.

(viii) *Precipitation*: Nanopolymers and nanoorganic substances may be used so that they form complexes or insoluble salts with harmful ions and precipitated.

(ix) *Common ion effect*: This is a well-known phenomenon. Nano-Ca^{2+}, nano-Mg^{2+}, and nano-iron oxides may be applied to counter adverse effect of Na^+.

Fabricating novel fertilizer materials: Existing fertilizers are known to cause soil acidity, damage soil carbon profile, harm beneficial microflora, weather clay minerals, and accumulate heavy metals resulting in irreparable damage to soils and food quality, and as a consequence, it is detrimental to human health. Literatures is flooded with the reports of adverse consequences of fertilizer use (Khan et al. 2013), but without suggesting viable long-term alternate pathways. One of the key problems of existing fertilizer materials is that most of them are salts, one component consisting of plant-nutrient ion(s), while counter component is not very useful or toxic. It is possible to manufacture novel nanofertilizers using plant-nutrient ions intercalating or adsorbing on clay minerals, which function as receptacles.

13.8 Observing Behavior of Nanomaterials in Soils

Nanotechnology could be a useful venture to obviate some unique problems of soils. In soil system, nanoparticles may be introduced intentionally (e.g., nanofertilizer) or unintentionally (e.g., TiO_2). In soils, the nanomaterials are perceived to move to rhizosphere, because of small size and direction of force from soil to plant, but their participation in ion exchange, adsorption–desorption, and other reactions, and complexation with organic matter cannot be ruled out. Ming and Boettinger (2001) opined that nanoscale ion capture–release mechanism would not let nutrient ions to be lost due to leaching. Also, the ions would be permanently fixed or adsorbed or precipitated and thereby would be retained on soils (including clays) surface by sequestration inside their porous structures. There is no control on the fate, transformations, reactions, and mobility of the nanoparticles once they enter in soil system. However, this need not worry us, because right from the inception of agriculture, knowledge-based passive control system has been pursued to the height of today's level of sophistication to achieve productivity in conformation with environmental standards. The effect of nanomaterials in the physiology of plants is not yet studied. Some nanoform metal oxides increased yield of crops (Tarafdar et al. 2013). The study of effect of nanomaterials in soils and plants remains unresolved because of technological limitations. For example, at one hand, radioisotopes cannot be studied under conventional nanotechnology tools and instruments such as electron microscopes and spectroscope, and on the other hand, radioisotope measuring counters cannot measure nanoparticles.

13.9 Biosafety and Environmental Compliance

Our expanding ability to synthesize nanoparticles for use in electronic, biomedical, ceramic, pharmaceutical, cosmetic, energy, environmental, catalytic, and similar materials has caused concern over the role of these particles in environmental safety. The gravity of situation may be assessed from the data provided by Nowack and Bucheli (2007), who expected use of engineered nanomaterials to the tune of 58000 tons during 2011–2020 from mere 2000 tons in 2004. Apart from native soil materials, many new nanoproducts are entering into soil system, some of which are used for agricultural production and some others for many other purposes. All these materials eventually land on soil. Bernhardt et al. (2010) advocated that nanotechnology interventions must adhere to environmental ethos to be useful to the society.

13.10 Opportunities for Application of Nanotechnology and Nanoscience in Environmental Cleanup Operation

Nanoscience (also nanotechnology) has found applications in controlling release of nitrogen, understanding weathering of soil minerals, soil development, and nutrient ion transport in soil-plant system, nature of dusts and aerosols from agricultural soil, zeoponics, and precision water farming. As it strides forward, nanotechnology has converged soil mineralogy with imaging techniques and artificial intelligence. A fascinating aspect of remediation of pollution is how nanoparticles may affect the fate, transport, and bioavailability of pollutants in soils. There is a long-standing and rich literature on the importance of Fe-hydroxide nanoparticles and nanomaterials interactions with nutrients and pollutants in the subsurface, including sorption and redox phenomena (Brown and Parks 2001; Brown et al. 1998). Cheng et al. (2009) found that depending on the conditions, nanosized carbon such as C_{60} or nanotubes could either enhance or inhibit the mobility of organic pollutants. Hydrophobic organic compounds could potentially sorb into C-based nanoparticles such as fullerenes, thus affecting fate, transport, and other processes such as biodegradation pathways. Amendments to nanoparticles to alter their surface properties may affect interactions with pollutants. In addition, fullerol ($C_{60}(OH)_{24}$) has been demonstrated to produce reactive oxygen species (ROS), which may affect redox processes and stabilities of organic pollutants (Pickering and Wiesner 2005). This may also play a role in disinfection capabilities of engineered nanoparticles. Nanophase minerals also influence the movement of heavy metals in surface and shallow subsurface environments through complex biogeochemical interactions.

13.11 Behavior of Nanomaterials in Plants

During the last decade, advances have been made in the study of fundamental characteristics of nanomaterials and their utilization for many applications. There is, however, scanty information available on the effect of nanomaterials on plant cells, and the way they influence the physiology and development of plants. Plants are the producers of food and oxygen that sustain life. The plants are also the most affected by the unprecedented human activities leading to environmental degradation. The area of nanoscience that has its implications in plant growth and development and ultimate productivity is of current interest (Srinivasan and Saraswati 2010).

The effect of nanoparticles on plant growth is relatively less explored and is an emerging area of research which needs to be meticulously explored. Recent research has focused on engineered nanoparticles as potential candidates for improvement of crop yield (Barik et al. 2008), and their use has been made particularly for efficient nutrient utilization, disease resistance, and enhancement of growth (Nair et al. 2010). However, limited information is available on the mode of action of these nanoparticles on crop plants.

The metal nanoparticles provide more surface area for valence electron exchange with the biomolecules, due to more surface area-to-volume ratio. These metal nanoparticles therefore pose changes in the antioxidant status of plant treated with it as they can participate in cellular redox reactions (Arora et al. 2012). Water-soluble nanotubes can become aligned due to endo-osmotic root pressure in the xylem vessel of plants that enhances water and nutrient uptake capacity. In the presence of CNTs, lignin biosynthesis suggests the formation of more biomass of xylem vessels than is shown to be directly related to the growth of the plant. The essential nutrients required for the plant interact with the hydrophilic groups attached to the surface of carbon nanomaterials by H-bonds and by electrostatic interaction in the temporal periphery of carbon nanoparticles and remain attached there on a temporal basis; thus, the carbon nanomaterial works as storage house for micronutrients. Such retention allows a sustained and slow release of these micronutrients for the facile transport inside the xylem vessel.

Nanoscale carriers: The nanoscale carriers can be used for efficient delivery of fertilizers as well as plant growth regulators. The mechanisms involve mainly encapsulation and entrapment. It may also be in the form of polymers or dendrimers. Such mechanisms help to reduce the input amount and also in alleviating environmental load.

Why nanoparticles?: Usually a very low amount of growth-promoting chemical reaches the target site of plants. This concentration is much lower than the concentration required for plant growth promotion. This happens due to leaching of chemicals, its degradation by photolysis or hydrolysis, or its degradation due to microbial activity. Hence, the repeated applications are required which may cause soil or water quality degradation. Therefore, there is need of nanoencapsulated agrochemicals which may have high stability and effectiveness along with being highly soluble. Such nanoencapsulated agrochemicals must be released in response to specific stimulus and must be safe ecologically (Boehn et al. 2003).

Nanoparticle entry into plants: The plant cells provide a barrier for entry of any external agent into it. This is because of pore diameter of cell wall that ranges between 5 and 20 nm (Fleischer et al. 1999). Hence, nanoparticle aggregates with diameter less than the size of pore diameter of cell wall can pass through cell wall and reach plasma membrane (Moore 2006). The engineered nanoparticles may interact with the pores of cell wall and increase the size of the pores of cell wall or may also give rise to new pores. These engineered nanoparticles may cross the plasma membrane using embedded transport carrier proteins or though ion channels. In the cytoplasm, nanoparticles may bind with different cytoplasmic organelles and interfere with the metabolic processes at the site (Jia 2005). When nanoparticles are applied though leaves, they enter through stomatal opening or through the base of the trichome and then get translocated to the other tissues (Eichert et al. 2008). The accumulation of nanoparticles on the photosynthetic surface may cause foliar heating, which may lead to changes in gas exchange.

13.12 Impact of Nanoparticles on Plants

Carbon-based NPs: The effects of nanoparticles on plants can be beneficial (e.g., seedling growth and development) or non-beneficial as they have been reported to prevent root growth (Zhu et al. 2008). Carbon nanotubes (CNT) have single or multiple layer of carbons established in a cylinder (Wz et al. 1996). Carbon nanotubes behave as fibers, and the properties of CNT are different from the properties of bulk carbon and graphite. They are the strongest small fiber and have been reported to transport to systemic sites, viz., fruits, leaves, and roots, and thus cause a significant change in gene expression. It is important to pre-establish the optimum dose of CNTs because these may have phytotoxic effects on plant cells and may cause death by causing excessive electrolyte leakage. The multiwalled CNTs (MWCNTs) are taken up by the roots and the seeds through the creation of new pores and water uptake for the development of tomato seedlings (Checkin et al.

2012). They improved the seed water uptake, whereas no seed water uptake with single-walled CNTs (SWCNTs) was observed in cucumber seedlings after 84 h of treatment. A number of reports are published on the effects of MWCNTs on seed germination and plant growth. The stimulation of growth of tomato seeds has been reported by Villagarcia et al. (2012), whereas water-soluble MWCNTs have been reported to improve growth in gram plants (Tripathi et al. 2011). Tripathi et al. (2011) and Villagarcia et al. (2012) observed that CNTs stimulated water uptake and thus improved growth of plants, while Saxena et al. (2014) explained that SWCNTs, MWCNTs, and carbon nano-anions readily penetrated plants. The SWCNTs and MWCNTs enhanced rice seed germination when the seeds were germinated in the presence of these nanoparticles (Nair et al. 2012). In zucchini plants, there was no negative effect of MWCNT on seed germination, whereas decrease in biomass of plant was observed during further growth in the presence of SWCNTs (Stampoulis et al. 2009). The response of plants to nanomaterials depends on species of plant, the growth stage, and nature of nanomaterial. Some studies reported potential toxicity of MWCNTs in plant cells. The MWCNTs resulted in accumulation of reactive oxygen species causing increase in oxidative stress, decrease in cell proliferation, and thus cell death (Tan et al. 2009). The carbon-based nanomaterials are highly hydrophobic and thereby they interact with organic substances. Some plants take up specific carbon-based nanoparticles with specific uptake mechanism and accumulation. The toxic effects of CNTs have been reported by some workers. Begum et al. (2012) reported reduction in root fresh weight in rice and cucumber seedlings with the application of MWCNTs. They also induced reduction of germination rate in maize (Lin and Xing 2007) and increased fresh weight and root length in wheat seedlings (Wang et al. 2012). The effects of MWCNTs vary from one report to another because of involvement large number of factors such as concentration of MWCNTs and the process of obtaining it. The effect also depends upon the type of medium of growth used and type of plant material under study. It was concluded by Tiwari et al. (2014) that pristine MWCNTs at low concentration promote the growth of maize seedlings by enhancing water and nutrient transport, but their potency could be reduced by higher concentration of ions or polar species in the medium. They suggested that CNTs can be used for water transport in arid-zone agriculture and for the improvement of crop yields. The SWCNTs remain adhered to external surface of main and secondary roots as reported by Lou et al. (2011). Graphene, another carbon nanoparticle, is a two-dimensional allotrope of carbon. It can also be described as one atom layer of graphite. Graphene can cause phytotoxic effects in plant cells due to its accumulation and may lead to cell death.

The presence of black aggregate of fullerene is reported in seeds and roots of rice as compared to stem and leaves of rice (Torre-Roche et al. 2013). In mature plants, there is translocation of fullerene from roots to aerial parts. Fullerene aggregate is located near vascular system of stem and leaves. The roots do not show presence of fullerene aggregates. This suggested that the fullerene adopts the route of nutrients for translocation and make way through xylem (Torre-Roche et al. 2012). Fullerenols accumulate at interface between the cell wall and plasma membrane.

The accumulation was also between adjacent epidermal cells, which showed that fullerol had the apoplectic mode of transport (Gao et al. 2011).

Metal- and Metal Oxide-based nanomaterials: Metal and metal oxides show size-dependent properties such as fluorescence and photocatalytic degradation. They are used as agrochemicals (Franke et al. 2006). Tarafdar et al. (2012a) reported significant increase in yields with the foliar application of nanoparticles. They insisted on the scope of balanced nutrient uptake by the plants through the nanoproducts obtained through nanotechnology. Tarafdar et al. (2012b) observed increased uptake of nutrients, when fertilizers were encapsulated in nanoparticles.

The most studied metal-based nanomaterials are TiO_2, CeO_2, Fe_3O_4, and ZnO. Higher aggregation of Fe_3O_4 nanoparticle was observed by increasing pH of humic acid. Similar effect was also observed in CeO_2. The response of plant to metal nanoparticle application depends on the nature of plant, type of plant species, and stage of growth.

Titanium oxide (TiO_2): Titanium oxide nanoparticles are used in daily life, but information on their uptake and translocation in the plants is scanty. Titanium oxide nanoparticles produce reactive oxygen species when they interact with UV radiation (Feizi et al. 2013). Titanium oxide nanoparticles showed increase in enzyme nitrate reductase in soybean. They also enhanced the ability to absorb water and stimulated antioxidant system. The seeds which were treated with nano-TiO_2 produced plants with higher dry weight (73 %), increased photosynthetic rate, and 45 percent rise in chlorophyll 'a' formation than control (Mingfeng et al. 2013). Titanium oxide increases plant growth by improving nitrogen metabolism and promotion of adsorption of nitrate. On the contrary, negative effects of TiO_2 nanoparticles on seed germination and number of roots were observed in rice (Folete et al. 2011). The presence of TiO_2 does promote growth of plants through an involvement in nitrogen metabolism and photosynthetic rate. The nanoparticles improved the light absorbance and promoted the activity of Rubisco activity and thus accelerated growth in spinach (Lei 2007). Those nanoparticles enhanced nitrogen metabolism and promoted absorption of nitrate and thus increased fresh and dry weights. There was a decrease in the accumulation of superoxide radicals and promotion of antioxidant stress.

Zinc oxide: Among the metal- and metal oxide-engineered nanomaterials, zinc (Zn) and zinc oxide (ZnO) are commonly applied on plants. One of the widely spread micronutrient deficiency in soil is zinc deficiency, and Stella et al. (2010) reported that it is the fourth most important yield-limiting nutrient after nitrogen, phosphorus, and potassium. Due to its extensive utilization in consumer products, it is likely that either through accidental release or deliberate applications, the Zn or ZnO might enter into atmospheric environments. This may further lead to considerable effect on many organisms, particularly plants which are the essential base component of all ecosystems (Dwivedi and Randhawa 1974). Zinc-containing nanomaterials are needed for chlorophyll production, fertilization, pollen function, and synthesis of auxins. Among the micronutrients, it is Zn that protects the plants from drought stress (Sharma et al. 2009). Zinc and ZnO may also affect the germination rate of the seeds. The effect of ZnO on root germination was observed for the species of Buck wheat (*Fagopyrum esculentum*) (Sooyeon et al. 2013). The ZnO nanoparticles had pronounced effect on onion (*Allium cepa*) root elongation, genetic composition, and metabolism. The seed soaking and incubation in the suspension of Zn/ZnO nanoparticles halted the growth of roots in corn. The toxicity of ZnO nanoparticle and Zn^{2+} could be driven by different theories, either it could be due to the chemical toxicity based on chemical composition or it could be due to the stress or stimuli imposed by size, shape, and surface of the ZnO nanoparticles. Both the theories affected the cell culture response of the plants. Depending on the plant species and the experimental conditions, the most important mechanism of action may be internal efficiency, i.e., Zn/ZnO utilization in tissues, or Zn/Zn uptake which is regarded as external efficiency (Dwivedi and Randhawa 1974). This deliberated the ZnO nanoparticles to enter the root cells and inhibit seedling growth.

The seed germination and root growth study of zucchini seed in hydroponic solution containing ZnO nanoparticles showed no negative response (Stampoulis et al. 2009), whereas seed germination in rye grass and corn was inhibited by nanoscale zinc and ZnO, respectively. It was confirmed by electron microscopy that the uptake of nanoparticles ZnO damaged epidermal and cortical cells and could also injure the endodermal and vascular cells causing growth inhibition in rye grass (Lin and Xing 2007).

Use of nanoparticles for seed quality enhancement has been achieved by Shyla and Natarajan (2014). The beneficial effects of ZnO NPs in improving seed germination could be due to higher precursor activity of nanoscale zinc in auxin production. Moreover, zinc is required for plant growth and is essential for various enzymes catalyzing various steps.

Iron oxide: The supraoptimal amount of iron oxide (Fe_3O_4) as a magnetic nanomaterial results in adverse effects on plant growth. The "Chlorophyll a" levels were amplified at low nano-Fe_3O_4 fluid concentrations, whereas at higher concentration of Fe_3O_4 nanoparticles fluid, the "Chlorophyll a" levels were inhibited. An inhibitory effect was discerned on the growth of the plantlets that led to brown spots on leaves at higher volume fractions of Fe_3O_4 nanoparticle fluids (Stephan 2004). The excess Fe_3O_4 nanoparticles treatment produced some oxidative stress, which in turn affected photosynthesis and resulted in decreased rates of metabolic process. The oxidative stress was induced by nano-Fe_3O_4 fluid concentration in the tissues of living plants (John 1988). Therefore, to overcome such limitations, the coating provides Fe_3O_4 nanoparticles a large adsorption surface as well as biocompatible properties. In pumpkin (*Cucurbita pepo*), the presence of carbon-coated Fe_3O_4 at specific concentrations within some cells or in extracellular space could reduce oxidative stress as well as the amount of chemicals released into the environment (Ionnis and Anastasios 2002). Further, a study on the effect of tetramethyl ammonium hydroxide-coated Fe_3O_4 nanoparticles on the growth of corn depicted that the chlorophyll level increased at low-Fe_3O_4 nanoparticle fluid, whereas, at higher concentration, the chlorophyll level was inhibited. Nanoparticles of Fe_3O_4 fluid induced oxidative stress in the living plant tissue, affected photosynthesis, and resulted in reduced metabolic rates (Ma et al. 2010).

Cerium oxide: The cerium oxide (CeO_2) nanoparticles have received attention due to their excellent catalytic activities. These nanoparticles have various industrial applications and serve as potential antioxidants toward intercellular reactive oxygen species. Nanoparticles of CeO_2 could possibly have dual role as an oxidation catalyst as well as reduction catalyst, depending upon the conditions of the reaction (Chekin et al. 2012). The natural environment may get an exposure to CeO_2 nanoparticle from exhaust catalysts after deposition on plant, when they get collected with road run off or, by industrial waste waters that contain CeO_2 nanoparticles. The CeO_2 nanoparticles are the only tetravalent metal oxides that exhibited different effects on various plant species. However, the possible causes of its toxicity, transport, and fate needs to be further investigated (Chekin et al. 2012).

13.13 Conclusions

Generation of data in most of the disciplines in agriculture is time-consuming and expensive, which is especially true for soil-plant system. In the farm production system, complex intrinsic relationship of nanomaterials with nature and involvement of large number of variables make success of nanotechnology intervention uncertain. Therefore, foresight and patience would be essential for applying nanotechnology in agriculture and assessing of effect of engineered nanomaterials that are steadily entering into soil-plant system. For sure, craving for environmentally clean, highly productive agriculture to mitigate crisis-ridden farm production system looks to nanotechnology. It is pertinent to remember that a large number of nanomaterials existed since time immemorial in the soils, plants, and atmosphere (Theng et al. 2008; Wilson et al. 2008; Li et al. 2012), and played their role in soil-plant system. Therefore, nanotechnology is not new to nature, which calls for inventing and expanding it for agriculture and food systems.

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