



## Uptake and impacts of metal oxide nanoparticles on plants-A review

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### Abstract

As the demand for NPs based goods has increased, near environmental concentrations of metal and oxide nanoparticles have risen. This poses a serious problem for sustainable agriculture. There has been evidence that metal NPs and metal oxide NPs have adversely affected growth, yields and quality of important agricultural crops. Numerous studies have shown that NPs have negative effects at biochemical, physiological, and molecular levels. Under low NPs toxicity, antioxidant enzyme activities in crops increased while the activities decreased at higher NPs toxicity. NPs altered mineral nutrition, photosynthesis, and caused oxidative stress as well as genotoxicity. The exposure of crop plants to NPs caused the concentration of NPs in different plant parts, including fruits and grains, which could be passed on to humans through the food chain. Therefore, the vast majority of NPs have both positive and negative effects on crops at the physiological, morphological, biochemical, and molecular levels. Plants react differently to NPs depending on various factors such as the species, stages of growth, conditions, and method of exposure, in addition to the dose and duration. Nanotechnology in various industries may cause a huge environment dispersion of nanoparticles. Concerns about nanoparticles interaction with flora and fauna is raised due to a growing load of it in the environment. Findings suggest oxidative burst as a general mechanism through which the toxic effects of nanoparticle are spread in plants. This review article also recommends future research directions.

**Keywords:** metal oxide NPs, NPs Uptake, NPs toxicity

### Introduction

Nanoparticles are classified as a material in which at least one dimension is <100 nm in diameter (Auffan *et al.*, 2009)<sup>[2]</sup>. Nanoparticles are not new to the environment and occur naturally in the form of minerals, clays, and products of bacteria. The nanoparticles have been used since ancient times as a colorant for metals (Maurer-Jones *et al.*, 2013)<sup>[30]</sup>. A new type of nanoparticle has been developed which could be used in the production of fuel. The nanoparticles are designed to have the properties which are not present in bulk samples of the same materials (Auffan *et al.*, 2009)<sup>[2]</sup> they are more efficient than conventional nanoparticles. Engineered nanoparticles are distinct from naturally occurring materials in which they are composed of a variety of materials and occur in different sizes and shapes with a suite of synthetic surface molecules (Radad *et al.*, 2012; Maurer-Jones *et al.*, 2013)<sup>[38, 30]</sup>. Metal and metal oxide nanoparticles have distinct physiochemical properties and differ from their original bulk constituents in a number of ways, including their surface, optical, thermal, and electrical properties. During the creation of metal and metal oxide nanoparticles, reducing or oxidizing/precipitating agents are added (Sanchez-Dominguez *et al.*, 2009)<sup>[44]</sup>. Nanoparticles reactivity with biomolecules is influenced by a number of parameters, including their size, core composition, shape, surface characteristics, purity, stability, and production technique (Teske and Detweiler, 2015; Wang P. *et al.*, 2016)<sup>[50, 6]</sup>. There is a considerable possibility that nanoparticles will retain the major characteristics of their bulk material; consequently, while studying nanoparticle interactions in the environment, it is necessary to examine the impact of bulk material, for example, heavy metals are toxic to plants

whereas silicon as a metalloid was observed to be beneficial for plants (Yadav, 2010; Tubana. *et al.*, 2016)<sup>[60, 54]</sup>.

In the last decades, nanoparticles have been used in various household and industrial products. Different industries are developing novel nanoparticles for the improvement of their services and products. They can also be used in food and pharmaceuticals.

Nano nanoparticles can contaminate the environment through improper management of industrial waste and improper disposal of products by the users. Several mathematical models are being developed to estimate the release of nanoparticles to the environment. (Keller and Lazareva, 2014; Dumont *et al.*, 2015)<sup>[20, 8]</sup>. The release of silver and zinc oxide nanoparticles in Europe has been assumed to be significant and broadly distributed in European territory (Dumont *et al.*, 2015)<sup>[8]</sup> by some experts. Keller and Lazareva (2014)<sup>[20]</sup> predicted that a large amount of nanoparticles were released into the environment. In varied environmental conditions, nano nanoparticles can vary their aggregation state, oxidation state, secondary phase precipitation, and so on. Furthermore, they are affected by environmental factors and might change when exposed to water or air (Levard *et al.*, 2012)<sup>[24]</sup>. The stability of nanoparticles is influenced by physical characteristics and chemicals present in various environments. As a result, nanoparticles may behave differently depending on the situation affecting their availability and reactivity in the ecosystem. The composition of nanoparticles can alter their properties, such as reactivity, penetration, and translocation inside the plant, resulting in variable plant responses to the same nanoparticle in various plants (Levard *et al.*, 2012)<sup>[24]</sup>.

Plants are constantly in contact with air, soil, and water, all of which may contain nanoparticles engineered by humans. Compared to bare nanoparticles, encapsulating nanoparticles affects plant responses. (Barrios *et al.*, 2016)<sup>[3]</sup>. It is possible that nanoparticles can be passed into the food chain through grazing animals. If nanoparticles get into the food chain, they may harm humans. In the last few years, a few studies have confirmed the trophic transmission of several nanoparticles via a terrestrial or aquatic food chain (Unrine *et al.*, 2012; Tanga *et al.*, 2016)<sup>[55, 49]</sup>.

Despite the fact that plants are producers and play an important role in the environment, the effects of nanoparticles on them have not been thoroughly investigated (Rico *et al.*, 2011; Feng *et al.*, 2013)<sup>[42, 37]</sup>. The lack of appropriate detection tools for nanoparticles in the environment complicates nanoparticle research (Navratilova *et al.*, 2015; Mahdi *et al.*, 2017)<sup>[33, 27]</sup>. Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most reliable techniques for detecting nanoparticles among the various options (Hadioui *et al.*, 2015; Navratilova *et al.*, 2015; Mahdi *et al.*, 2017)<sup>[17, 33, 27]</sup>. Nanoparticles can have both a good and detrimental impact on plants, depending on their size, concentration, chemical composition, zeta potential, stability, and shape, according to study conducted on various plants (Nhan *et al.*, 2015; Tripathi *et al.*, 2015, 2017; Costa and Sharma, 2016; Wang Z. *et al.*, 2016)<sup>[34, 53, 6]</sup>. Several studies have shown that nanoparticles have a deleterious influence on plants, resulting in decreased plant growth, productivity, and pigments (Landa *et al.*, 2016; Tripathi *et al.*, 2017)<sup>[23, 52]</sup>. Nano nanoparticles can be used for growth stimulators, nanopesticides, nanofertilizers, soil improving agents, or sensors for monitoring different agricultural parameters in the field. Nanoparticles can also be used to improve crop yields and yield of food crops (Wang P. *et al.*, 2016)<sup>[58]</sup>.

The influence of industrial nanoparticles on plants has been studied in recent years. The purpose of this review is to systematically present and analyze the research performed in the last years to give an overview of the recent advancement in the field. Different types of nanoparticles that exist in the environment, how they affect plants, and a concise discussion and a general mechanism through which nanoparticles have an impact on plants will be discussed in the following section.

### Effect of Nanoparticles on Plants

Although nanoparticles can be made from a wide range of materials, only a few are widely used, and the environment is at risk of being contaminated by them. The most commonly used nanoparticles are titanium dioxide (TiO<sub>2</sub>), silver, zinc oxide, cerium dioxide, copper, copper oxide, aluminium, nickel, and iron. These are typically used in industries, and their effects on plants are mostly studied (Santos *et al.*, 2015)<sup>[45]</sup>. Nano nanotoxicity is a chemical reaction between metal and non-metal nanoparticles. Some of the most well studied nanotoxins, such as carbon nanotubes and fullerene, have been shown to be highly toxic in some cases. Under exposure to single-walled carbon nanohorns (SWCNHs), it was shown that corn, tomato, rice, and soybean grew more effectively and germination rates elevated (Lahiani *et al.*, 2015)<sup>[22]</sup>.

Nanoparticles have recently been produced for use as nano pesticides and nano fertilizers in agriculture, which include the use of nanoparticles as nanocarrier for pesticides,

fertilizers (Wang P. *et al.*, 2016)<sup>[58]</sup>. Herbicide was encapsulated with chitosan nanoparticles, which resulted in a considerable increase in herbicide efficiency (Maruyama *et al.*, 2016)<sup>[29]</sup>. Mesoporous silicon nanoparticles have also been utilised to transfer DNA, proteins, and other substances in plants as metalloids nanoparticles (Torney *et al.*, 2007). Nanozeolites (basic building blocks of silicate [SiO<sub>4</sub>]<sup>-</sup> and aluminates [AlO<sub>4</sub>]<sup>-</sup> tetrahedrons), hydrogels (consisting of different polymers such as, chitosan and alginate), which helps in the improvement of soil quality, and nanosensors (used in agriculture for monitoring plant and soil health.) They can be used to monitor the quality of plants and soil in a variety of ways including as fertilisers and pesticides. (Fraceto *et al.*, 2016)<sup>[29]</sup>. Silica nanoparticles were shown to be innocuous to plants, while some scientists noticed a harmful effect as a result of changes in the pH of the media after nanoparticles were added (Slomberg and Schoenfisch, 2012)<sup>[48]</sup>. Silica nanoparticles were found to be effective in reducing chromium (VI) phytotoxicity in *Pisum sativum* (L.) seedlings (Tripathi. *et al.* (2015)<sup>[53]</sup>. Metal and metal oxide nanoparticles have a harmful effect on plants, however some studies have also demonstrated that they can improve plant growth indices and productivity (Tripathi *et al.*, 2017)<sup>[52]</sup>. The zeta potential is an important reliable indicator of nanoparticle coagulation and reactivity in solution. The analytical selection of information is needed regarding size, concentration, zeta potential, up take by a certain type of plants and effects on the plant, could be used to determine whether the metal and metal oxide nanoparticles represent a risk to plant organisms and the environment. Changes in pH or ionic strength affect zeta potential, which represents the total electric potential of all particles and ions in solution (Teske and Detweiler, 2015)<sup>[50]</sup>. Plants are affected by nanoparticles in a variety of physiological, morphological, and genotoxic ways. As a result, understanding the role of certain nanoparticles is critical for the effective use of nanotechnology in agriculture (Nair *et al.*; 2014)<sup>[31]</sup>.

### Mechanism of Nanoparticle-Plant Interaction

Most of the nanoparticles are toxic to the plants in high concentration. The uptake of nanoparticles by plant and their translocation into different tissues is needed for exhibiting the toxic effect, it is hypothesized. Based on their transportation, properties, and reactivity, the particles may interfere with different metabolic activity to produce an impact.

### Nanoparticle Uptake

When nanoparticles are present in higher concentrations, they cause damage to the plant cell wall and plasma membrane, allowing them to penetrate and interact with many plant processes (Mazumdar and Ahmed, 2011). Nanoparticles can penetrate plant tissue via the root or above-ground components such as root junctions and wounds. Nanoparticles must pass through a variety of chemical and physiological barriers in order to be taken up and transported. When nanoparticles interact with plant, cell wall is the first barrier it has to cross. Plant cell walls are a structure composed of cellulose which permits the entry of small particles and restricts larger ones. Cell wall sizes between 5 and 20 nm are excluded from plant cell walls (Dietz and Herth, 2011)<sup>[7]</sup>. A recent study has found that nanoparticles can cause cell wall cells to form larger pores

which further facilitate the entry of large nanoparticles into the cell walls. Some of the nanoparticles have been reported to induce the formation of larger pores in cell wall (Navarro *et al.*, 2008) [32]. Nanoparticles are thought to move at various rates from the cell wall to different plant tissues via endocytosis and symplastic transport (Etxeberria *et al.*, 2006; Ma *et al.*, 2010) [10, 26]. A plant's roots are more vulnerable to damage from nanoparticles than its shoots, which take in more particles from soil/water (Qian *et al.*, 2013; Shaw *et al.*, 2014; Tripathi *et al.*, 2017). Wong *et al.* 2016 has published a mathematical model that suggests a lipid exchange mechanism for nanoparticle transport into plant cells. The size, magnitude, and zeta potentials of nanoparticles are important in controlling their transit inside

the plant, according to the study. Although most NPs have a greater size than plant cell wall pores (3.5–5 nm) (Chichiriccò and Poma, 2015) [4], it has been shown they can enter plant root cells through different mechanisms, including aquaporins (Takano *et al.*, 2010), endocytosis (Eggenberger *et al.*, 2009), membrane transport systems (Gojon *et al.*, 2009) [16], by binding to carrier proteins or organic chemicals in the environmental media (Rico *et al.*, 2011) [42], creating new pores by crosslinking of components of the cell wall (Fleischer *et al.*, 1999) [13]. According to the type of NPs, they can be accumulated in roots or be translocated to other tissues via xylem and phloem (Cifuentes *et al.*, 2010) [5].

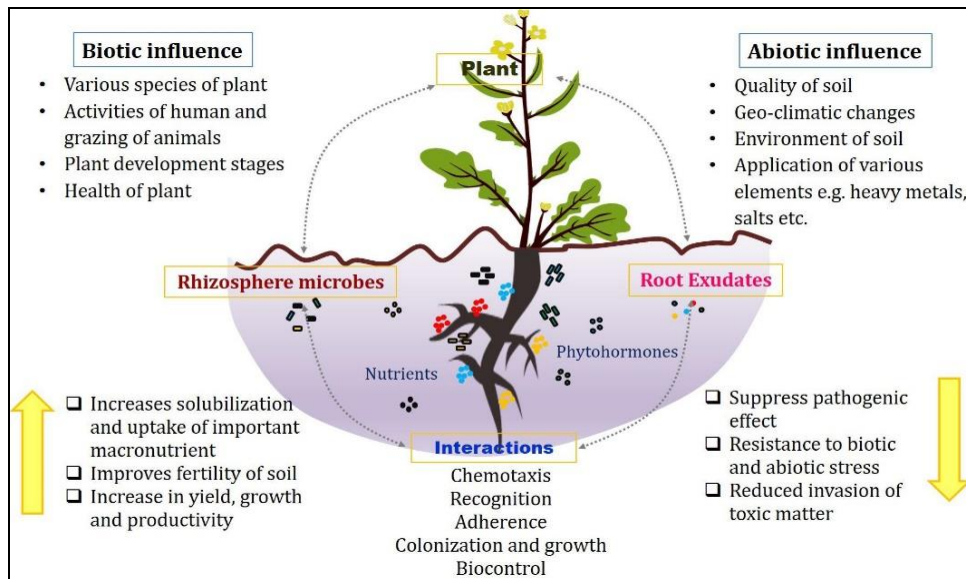
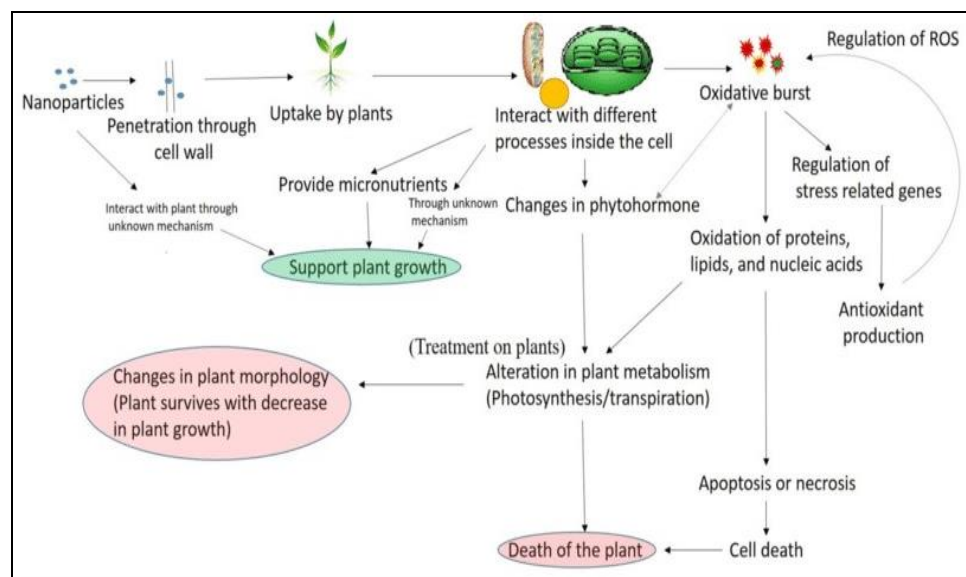


Fig 1: Various factors influencing the uptake of NPs by plants

**Nanoparticle-Plant Interaction Pathways**

Plant metabolism can be influenced by nanoparticles in a variety of ways, including delivering micronutrients (Liu and Lal, 2015) [25], gene regulation (Nair and Chung, 2014) [31], or interfering with several oxidative processes in plants, resulting in oxidative bursts (Hossain *et al.*, 2015) [18]. The

preceding portion of this article stated several nanoparticles when present in excess cause ROS production, and interfere with the oxidative pathway, but not all the interactive pathways have been identified, and more research is needed to determine the others.



(Adopted from reference No.41)

Fig 2: A general mechanism of nanoparticles interaction with plant.

Moreover, nanoparticles can enter the mitochondria and chloroplast of cells and cause a burst of oxidative stress in the body. Consequently, exposure to nanoparticles could increase the level of ROS in the mitochondria (Faisal *et al.*, 2013; Pakrashi *et al.*, 2014) <sup>[11, 36]</sup>. The rate of carbon fixation is reduced under the effect of various stress conditions, which produces an increase in photoinhibition, potentially guiding the photosystem toward overproduction of superoxide anion radicals and H<sub>2</sub>O (Foyer and Noctor, 2005) <sup>[14]</sup>. It is known that once ROS is formed as a result of nanoparticle interaction, it interacts with practically all biological components, causing protein changes, lipid peroxidation, and DNA damage (Van Breusegem and Dat, 2006) <sup>[56]</sup>. Plant interaction with nanoparticles leads to increased levels of lipid peroxidation and DNA damage in plants-nanoparticle interaction (Atha *et al.*, 2012; Saha and Dutta Gupta, 2017) <sup>[1, 43]</sup>. When ROS are produced in excess, they can trigger apoptosis or necrosis, both of which result in the death of plant cells (Rastogi and Pospil, 2012; Faisal *et al.*, 2013) <sup>[11]</sup>. Although ROS are destructive, they are known to play an important role in a range of cellular functions, including the ability to handle stress (Sharma *et al.*, 2012) <sup>[6]</sup>. The balance between ROS generation and scavenging determines whether ROS plays a damaging or signalling role. Cell has evolved a powerful antioxidant mechanism to manage ROS levels in the cell's environment. Enzymatic (superoxide dismutase, catalase, and guaiacol peroxidase) and non-enzymatic (Ascorbate, glutathione, carotenoids, tocopherols, and phenolics) antioxidants are produced in the antioxidant process (Sharma *et al.*, 2012) <sup>[46]</sup>. To deal with stress, plants increase the production of antioxidant molecules (Rastogi and Pospíšil, 2010; Sharma *et al.*, 2012) <sup>[39, 6]</sup>.

There have been several studies showing that plants respond to nanoparticles by producing more antioxidant molecules (Faisal *et al.*, 2013, Costa and Sharma, 2016) <sup>[11, 6]</sup>, which confirms the regulation of the antioxidant system by nanoparticle interaction. When the antioxidants produced are unable to control ROS, the ROS oxidise cellular macromolecules, causing cell death through apoptosis or necrosis (Sharma *et al.*, 2012) <sup>[46]</sup>, which eventually results in plant death.

According to recent studies, phytohormones play a significant part in plant stress response signalling (O'Brien and Benková, 2013) <sup>[35]</sup>.

Hormonal control of plant development and stress tolerance is thought to be the result of a complex network of synergistic and antagonistic hormone interactions. ROS are intricately related to hormone signalling and influence one another's activity (Kwak *et al.*, 2006). Different hormonal pathways have been shown to be activated or deactivated in response to various stimuli.

The increase in cytokinin level in *Capsicum annuum* in response to Ag NP stress, as well as the decreases in IAA and ABA in a cotton plant in reaction to CuO NP, suggest that nanoparticles disrupt the hormonal balance in plants, affecting plant metabolism. As a result, the harmful action of nanoparticles in plants is mostly mediated by reactive oxygen species (ROS) (O'Brien and Benková, 2013) <sup>[35]</sup>. Because the electron transport chain in mitochondria and chloroplast occurs in an aerobic environment, excessive formation of reactive oxygen species (ROS) has an impact on the activities. (Foyer and Shigeoka, 2011) <sup>[15]</sup>. Photosynthesis is also thought to be a good indicator of a

plant's overall performance (Kalaji *et al.*, 2014) <sup>[19, 47]</sup>. Because it is the only source of energy for plants, it has an impact on all aspects of their metabolism and physiology. As a result, measuring photosynthetic pigment and activity is a useful tool for determining the impact of stressors. Several studies have found that nanoparticles have an impact on photosynthetic pigments (Qian *et al.*, 2013; Tripathi *et al.*, 2017) <sup>[37-52]</sup>. Plant growth may be suppressed or even destroyed when nanoparticle concentration is too high, resulting in reduced photosynthesis or plant death. Several reports have observed significant decrease in plant growth as the result of nanoparticle exposure.

### Conclusion and Future Perspective

Nanoparticles are widely employed in today's world and have become an integral element of human life. However, due to the demands of modern life, the environment cannot be overlooked.

According to studies, metal and metal oxide nanoparticles in excess are toxic to plants, but when present in minimal amounts, they can be beneficial. As a result, the concentration of nanoparticles in the environment is increasing. As a result, much research is required before nanoparticles may be used in the field. The majority of the research reveals that metal and metal oxide nanoparticles cause morphological changes in plants. The study also reveals a glaring lack of uniformity in the phytotoxic assay for nanoparticles. As a result, more research is needed to better understand the impact of metal and metal oxide nanoparticles. Nanoscience is garnering a lot of research funds, some of which needs to be diverted to raise public awareness regarding correct nanoparticle disposal. In addition, research in the domain of nanoparticle cleanup from agricultural soil and wastewater is required.

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