Bulletin of Environment, Pharmacology and Life Sciences
Bull. Env. Pharmacol. Life Sci., Vol 10 [5] April 2021 : 289-304

Online ISSN 2277-1808
Journal's URL:http://www.bepls.com
CODEN: BEPLAD
REVIEW ARTICLE **OPEN ACCESS**

Zinc Oxide Nanoparticles in Agriculture: A Critical Review

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ABSTRACT
Over the recent times, Zinc Oxide nanoparticles (ZnONPs) are being utilized in agricultural practices as nanofertilizers, nanoherbicides and nanopesticides etc. ZnONPs are also extensively used in commercial applications so it is expected to find its way into various fields. Green synthesis of ZnONPs is ecofriendly and safe for agriculture use when compared to chemically synthesized nanoparticles (NPs). Plant responses to ZnONPs depends on the type of plant, its developmental stage, and specific growth conditions. Also, uptake, translocation and accumulation of ZnONPs depend on physical characteristics of ZnONPs in dose-dependent pattern and internal structure of the host plants. This review suggests that bioengineered ZnONPs are interacting with meristematic cells such as embryonic cells, xylem and phloem of the plant cells which triggers biochemical pathways and enhances seed germination and biomass production. On the contrary, negative effects of ZnONPs on plant growth and metabolism have also been reported at various developmental stages of the plants. The extensive use of ZnONPs is negatively affecting the environment. The surplus application of NPs provokes reactive oxygen species (ROS) in living organism. Imbalance in ROS production in cell creates oxidative stress in plants. Excess ROS production causes oxidative damage to DNA, proteins, lipids and finally leads to cell pre-mature death. This review will be helpful in understanding the favourable and detrimental effects of ZnONPs in agriculture and on environment.
Keywords: *Zinc Oxide nanoparticles (ZnONPs); Nanoparticles (NPs); encapsulated; biosafe; dose-dependent pattern; reactive oxygen species (ROS); Oxidative stress.*

Received 09.02.2021 Revised 12.03.2020 Accepted 12.04.2021

INTRODUCTION

Paul Ehrlich called Nanomaterials (NMs) magic bullets (1,2). NMs are tiny particles ranging from 1nm to 100mn in diameter (3,4) having unique properties which are completely different from there chemical parental composition because of their minute size (5,6). These small magic bullets find a lot of application due to small size, high surface to volume ratio, crystal phase, electrical and optical properties (7) and have been used in different fields of Science like Chemistry, Botany, Physics, Electronics, Material Science, Agriculture, Life Science, Medical Science and Pharmaceutical branches. The applications are found in waste water treatment, water purification, food industry and packaging, environmental remediation, smart sensors, medical treatments, disease prevention and treatment by using various nanocides for examples nanopesticides and nanofertilizers, precision farming and plant growth and protection (8,9,10,11,12,13,14). Different range of materials are used to manufacture various type of NPs like metal, metal oxide, ceramics, magnetic materials, semiconductor quantum dots, carbon, silicates polymers, proteins, silicates, lipids, dendrimers and emulsions (15,16).
The applications and uses of nanotechnology in agriculture and industries started only in recent year (17), but research in this field started about half a century back (18). In India almost 43% workforce is involved in Agriculture (19). Indian agriculture mainly relies on monsoon. Monsoon unpredictability has a huge impact on agriculture. Also, problems like depletion in soil fertility, unevenness of water distribution, climatic changes, global warming, and surplus use of chemical fertilisers, depletion in natural resources, various diseases and pests affect agriculture. Though after green revolution, food production drastically increases (20) but it is still not sufficient to feed population which is increasing exponentially .Thus, technology interventions are badly needed in agriculture that too with reduced inputs of harmful pesticides, fertilizers and herbicides. Although extensive use of chemical fertilizers enhances the crop productivity however, its use over a long period has negative effects which disturb the soil mineral balance, reduce soil fertility, adversely affect soil microbial flora and cause eutrophication in water bodies (21,22). In this sequence, fertilizers also disrupt the food chains in ecosystems (174) which can lead to

heritable mutations in consumers. Thereby fertilizers are considered as double-edged sword which should be used wisely.
Many technologies are amalgamating with nano science to play crucial role in increasing food production and for quality improvement. Recently, Chitosan NPs are reported to be used as bio-pesticides in agricultural field (23). These NPs shows antifungal and antibacterial activity (24, 25, 26, 27). The effects and efficiency of NPs differs among diverse plants. The resultant growth, germination, physiological and morphological characters of the plants seems to depend upon the concentration of different NPs (28, 29, 30, 31) used in treatment. Nano encapsulation is a method which aids NPs to be used as nanofertilizer, nanopesticides and nanoherbicides for crops without causing damage to environment by reducing leaching and evaporation of these substances (32, 33). This new mode of using NPs decreases the worldwide consumption of huge amount of chemical pesticides which is almost two million tonnes per annum (34). Continue use of these pesticides deteriorate increasing pathogen and pest resistance, reduces soil fertility and biodiversity, declines pollinators and birds and also causes bio magnification (35). Thus, nano formulation based chemical methods efficiently increase productivity, insect pest management and smartly allow slow and steady release of nutrients and water into soil, in addition to reducing adverse effects of conventional fertilizers and pesticides on soil biodiversity and soil fertility (36, 37). This review will focus on the beneficial and harmful effects of ZnONPs on plants, soil and environment.

ROLE OF Zn

ZnO is an inorganic white powdered compound which is insoluble in water (38). In earth crust this is found in various mineral forms like zincite but for commercial purposes ZnO is prepared synthetically. ZnO is very good semiconductor as it has unique properties like having high electron mobility, being transparent and has wide band gap (39). Due to its physical, chemical, optical and antimicrobial properties ZnO is used in biosensor, sunscreen creams, solar cell, photo catalysis, and offers enormous potential in boosting agriculture production (40).
In living organism Zn play an essential role in plants metabolic pathway like synthesis of carbohydrate, lipid, nucleic acid and protein along with their degradation. It also has significance in metal protein complexes (41). Zn is a major integral component in all six types of enzymes classes (42). It also helps in gene transcription control and coordinates with many biological activities that are regulated by protein which contains DNA binding- Zn finger motifs (43). Zn is a major player in control and synthesis of indol acetic acid (IAA), a plant hormone that regulate plant growth and development. Beside this Zn also plays a major role in synthesis of chlorophyll, cytochrome and formation of leaf cutical (30). Within specific range of concentration, Zn resists metal toxicity in plants, by regulating various mechanisms involved in recognition and response to stress in plants. Zn has also been reported to improve scavenger oxygen reactive species and protect the plant cell against oxidative stresses (44).
Zn is an essential micronutrient and its deficiency affects approximately one third of the world population especially children and pregnant women. Zn deficiency may lead to decrease in growth and yield and its excess accumulation can cause toxicity. Therefore intake, accumulation and translocation of Zn should be regulated (45). Zn deficiency in plants is a major concern in India and all over the world. In India, the average level of Zn deficiency is almost 50% and it will increase to 63% in 2025 (46). Zn insufficiency is influenced by so many factors like soil pH, pesticides, herbicides and organic nutrient present in the soil. Zn deficiency cause stunting in growth and development of plants and also reduces productivity by dropping grain yields (47).

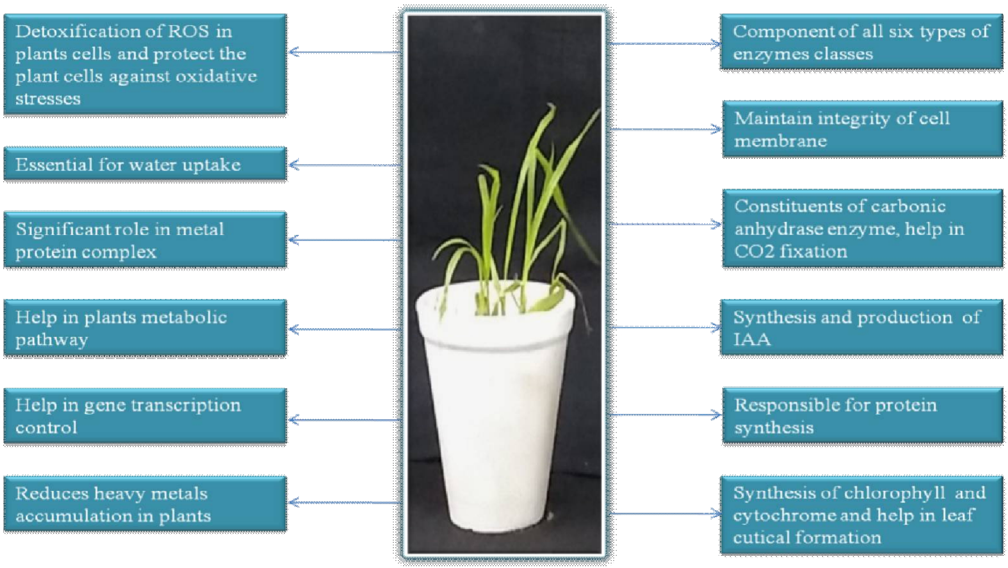

Figure 1 : Major functions of Zn

Mechanism of uptake and translocation

Zinc present in soil is available in the form of Zn^{2+} ion, which is absorbed by plant roots (Figure.2). Zn is also present in the form of complex with organic acid chelates. Xylem in plants helps in translocation of Zn ion into various plant parts (48). Zn transportation is done via protein transporter of heavy metals, which belongs to ZIP family (Zinc regulatory transporter-Iron regulatory transporter like protein). These transporters were identified in barley (*Hordeum vulgare*), rice (*Oryza sativa*) and in thale cress (*Arabidopsis thaliana*). These transporters were found in cell plasma membrane and tonoplast of vacuoles (49). Eight transmembrane domains are present in ZIP proteins, with amino- and carboxyl-terminal ends, which are situated on the outer surface of the cell membrane (50). The ZIP proteins differ considerably in overall length because of the variable regions. These regions are present between the transmembrane domains. TM^{-3} and TM^{-4} transmembrane domains are situated on the cytoplasmic side. These domains provide a potential metal-binding domain rich in histidine residues. Guerinot, (2000) have reported most-conserved region of these proteins lies in a variable region, which has been anticipated to form an amphipathic helix. This helix contains completely conserved histidine that possibly forms part of an intramembranous metal-binding site involved in transportation of Zn ions. Zn transport is done from soil to rhizodermal and cortical cells. These cells transport Zn into xylem cells with the help of specific protein transporter of heavy metals like HMA2 and HMA4 (Heavy Metal ATPase). These specific protein transporters are located on the cell membrane of the vascular bundles of the stem and root (51, 41). Zn cation can also be transported by extracellular apoplastic pathway through the area of undeveloped casparian strip (52). The Zn transportation from shoot to seed is done with the help of phloem. Other than this Zn is also symplastly bound to chelate of nicotianamide (53). The phloem protein transporter is not yet identified therefore they are considered being a part of yellow strip like transporter (YSL) group that is made with oligonucleotides (54).

In Gramineae family, mugineic acid (MA) is excreted under condition of iron deficiency and help in solubilising iron from the root environment. This solubilised iron can be up taken by the plants from the rhizosphere (55). Mugineic acid is an amino acid which is closely related to its biochemical precursor, nicotinamine and a number of other compound that also were identified as phytosiderophores in Gramineae family. Welch& Shuman (1995) also reported that beside iron, MA may also help in the acquisition of Zn and other metal nutrients. In conditions of Zn deficiency the secretion of MAs from wheat (*Triticum spp.*) and barley (*Hordeum vulgare*) roots into the rhizosphere is reported to increase (56, 57, 58). In RIL46 line of rice, Zn deficiency is tolerated by plant to some extent, due to the increased efflux of MAs (59). Nanoparticles are also taken up by the plant through leaf stomata or base of leaf trichomes (60), but the rate of absorption is influenced by the leaf surface properties such as leaf thickness, chemical composition of cuticle, density of stomata, number of epidermal layers, and structure of trichomes (61,62). Various environmental factors like humidity, temperature, pH and light intensity also play an important role in Zn absorption (60, 63). Zn is also absorbed via stomata and cuticles of leaves which usually diffuse nonpolar lipohilic compound. In several plants, the effectiveness of foliar application of Zn in the form of fertilizer has been studied (64,65). In pistachio (*Pistacia vera*) there is no significant result of Zn foliar application (66) but in tomato (*Solanum lycopersicum*) and mandarin orange (*Citrus reticulatus*), foliar spray of Zn has been reported to be very effective (67). In another study in mung bean (*Vigna mungo*), the plant was exposed to insufficient zinc nutrition, which caused growth retardation but foliar spray of Zn in the form of $ZnSO_4$ increased plant growth (68). In maize plant, increased Zn translocation was observed when phosphorus application was increased (69). Nitrogen supply to Wheat plant is reported to dramatically influence Zn uptake, its movement via Xylem and further re-deployment via Phloem (70), it was also reported in another study that in maize plants, nitrogen administration can be a good economically cheap alternative to increase Zn in the grain (71). On the contrary in rice plant it has been reported that intrinsic factors within the plant decides about Zn allocation and various rice genotypes may differ in terms of deployment of Zn via Phloem from leaves to grain (72). It was observed that root to shoot Zinc translocation in rice plants using solution culture experiment was mainly affected by timing of Zn application (73)). Very few studies have investigated the correlation between fertilizer Zn dosage and root-to-shoot Zn translocation efficiency under field conditions. It was noted that Zn translocation from root to shoot under field condition is yet uncertain.

The uptake and translocation of ZnONPs in plants is a growing field of research interest. The NPs intake, accumulation, along with translocation is mainly dependent on the type of plant species, its age, the internal structure of the host plant , growth environmental conditions and its physical and chemical property, functionalization of NPs and their stability and the mode of delivery. The intake, translocation, as well as biological conversion pathway of various NPs along with possible modes of cellular uptake in plant system have been investigated by many researchers and scientists (74, 75, 76, 77, 78). The pore size of cell wall ranges from 5–20 nm (79) and entry of NPs via cell wall depends on their pore size and shape (80). Several reports have discussed that uptake of different types of NPs into plant cell via binding to carrier proteins (such as aquaporin), ion channels, or endocytosis (81, 82). Beside the cell wall pore and leaf opening, NPs can also be transported by forming complexes with membrane transporters or root exudates into the plant system. But at higher concentration the entry of NPs into the plant cell is inhibited due to agglomeration of NPs which prevent it to enter inside the seed through cell wall pores (83, 84, 85). In tomato (*Solanum lycopersicum* L.), effects of two NPs of similar size (25 ± 3.5 nm) over a range of concentrations (0 to 1000 mg kg−1) have been studied and comparison was done in terms of translocation, intake and accumulation of NPs and also their effect on physiological parameters. It was observed that till a specific concentration of TiO_2 and ZnONPs treated tomato plants showed favourable growth and development and also aerosol mediated application uptake of NPs was more productive than the soil mediated application in plants (86).

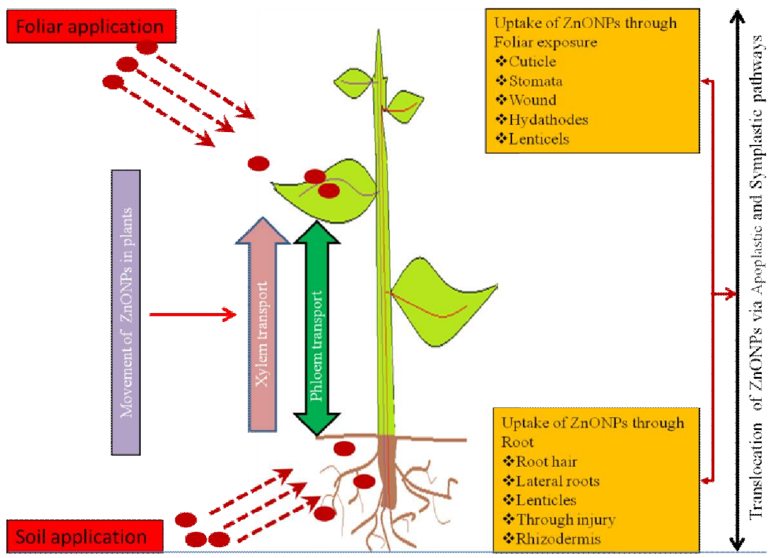

Figure 2: Mechanism of uptake and translocation of ZnONPs in plants

Green Synthesis of ZnONPs

ZnONPs are synthesized via various ways (physically, biologically plus chemically) and characterized by using many techniques like Ultra Violet–visible spectroscopy (UV-Vis), Fourier transform infrared spectrometer (FT-IR), Energy dispersive X-ray spectrometer (EDX), X-ray diffractometer (XRD), Field

Emission Scanning Electron Microscopy (FESEM) and High-Resolution Transmission Electron Microscopy (HRTEM)). Synthesis of NPs via plants is known as green synthesis. As we discuss earlier green synthesis is very important because this technique is ecofriendly, safe and use natural extract of plant in the form of solvent. This technique is less expensive and less toxic in comparison to chemically synthesised NPs. Plant extracts which contain phytochemicals like phenol, terpenoids, ketones, aldehydes and amide are responsible for synthesis of NPs (87). These functional molecules are responsible for reducing metal ion effects. ZnONPs have been biologically synthesized by via leaf extract of *Abutilon indicum, Aloe barbadensis, Melia azedarach, Indigoferatinctoria*, and many more plants and fungus (88, 89, 90, 91). It is reported that the biosynthesized ZnONPs have antimicrobial activities and can be effective for agricultural applications (92, 93). The antimicrobial efficiency of biosynthesized ZnONPs is directly related to its shape, size, surface to volume ratio and number of oxygen valence sites (94). Biological synthesised NPs showed less toxicity and quality growth as compared to chemically synthesized NPs. The accumulation of chemically synthesised ZnONPs in sesame plant was found to be more as compared to biologically synthesised NPs and it induced tremendous changes in the plant environment (95).

ZnONPs synthesized from $ZnNO_3$ via extracellular secretions of *Aspergillus fumigatus* TFR-8 and the foliar spray of this biological transformed ZnONPs enhanced plant biomass, morphological, physiological, biochemical, rhizospherical microbial population, acid phosphatase, alkaline phasphatase, phytase activity in 6 week old clusterbean plant (*Cyamopsis tetragonoloba* L). This also increased phosphorus mobilization in cluster bean and mung bean plant in addition to increase in gum content of the plant which has medical and industrial uses. These biological synthesized NPs also influence exopolysaccharide (EPS) production from *Bacillus subtilis* strain JCT1 which lead to increased soil aggregation, moisture retention and increased soil organic carbon in arid zone soil (28, 96, 97). ZnONPs were also synthesized by using plant extract of chamomile flower (*Matricaria chamomilla* L.), olive leave (*Olea europaea*) and red tomato fruit (*Lycopersicon esculentum* M.). These diverse biological NPs were examined on *Xanthomonas oryzae* pv.*oryzae* (strain GZ 0003) where ZnONPs synthesized from olive leaves showed greater antibacterial activity in the bacterial inhibition zone due to its small crystalline size compared to other two synthesized from Chamomile flower and Red tomato fruit. These ZnONPs affects bacterial growth, bioflim formation, swimming motility and cell membrane formation of bacteria therefore, it can be very effective rising bio control agent against the causal organism of bacterial leaf blight of rice disease (98). At a higher concentration (12mmol−1or higher), ZnONPs completely distort or damage *Escherichia coli* O157:H7 bacteria cell membrane and eventually the food borne bacteria die. It is an effective antibacterial agent to protect food, agriculture and industrial safety (24). Zn and ZnONPs are also reported to eliminate bacterial and fungal contamination and influence plant regeneration in Banana. In this study nine bacterial contaminants strains and four fungal contaminants species were observed in vitro cultures of banana having lethal effect on explants. When Zn and ZnONPs were employed in culture media , not only the microbial contaminants were successfully eliminated from in vitro culture of banana but percentage of somatic embryogenesis increased and plants thus produced had high proline contents, chlorophyll, antioxidant enzymes activity and accumulation of dry weight were also increased than the control. (99).

From the above discussion it is clear that ZnONPs have potential to increased seed germination and growth, nutrients intake and translocation, help in biofortification, protect plants from diseases, slowly and gradually release nutrient into the soil and prevent soil and environmental pollution. Green nanotechnology also reduces accumulation of pesticides and herbicides into the soil. Green synthesis of ZnONPs and its applications summarized in Table.1

Positive effects of ZnONPs on plants

There are different types of Zn nanofertilizers like ZnS, ZnSe, or quantum dots CdSe/ZnS, ZnSO4 and ZnO. Most of the Zinc NPs are utilized in the form of ZnONPs and used in agriculture in the form of Zn2+ ions. This is an eco-friendly, less toxic, bio-safe mode of use, all these characters makes them ideal for agriculture use and has a great potential to improve plant growth and yields (103).

TABLE 1:GREEN SYNTHESIS OF ZnONPs

Plant &Plant part extract	Shape	Size(nm)	Outcome	Significant aspect	References
Chamomile flower , Olive leaves, and Red tomato fruits	Pure crystalline	65.4, 48.2 (smallest), and 61.6	Highest inhibition zone of bacteria is 2.2 cm at 16.0 mg/ml via NPs synthesized through Olive leaves, Shrinking of bio film growth.	Due to bacterial cell membrane distortion through cytoplasm leakage.	98
Akra (*Calotropis gigantean)* leaf	Spherical	8–12	Neem, Karanj, and Milkwood-pine seedlings show noteworthy improvement in growth via foliar spray	Milkwood-pine demonstrates highest height improvement.	100
Russian olive *(Elaeagnus angustifolia)* flower	-	16	NPs were applied to tomato seeds. Plant germination and metabolic activities were concentration dependent.	Higher concentration was creating harmful effect.	101
Red clover *(Trifolium pratense)* flower	-	60–70	Successful antibacterial activity against every experimented strains (as concentration increases inhibitory effect also improved)	Bacterial cell membrane disturbs possibly due to the generation ROS.	102
Weed (*Lantana aculeata*) leaf	spherical	12 ± 3	Highest zone of inhibition at 100 µg ml−1	NPs able to do antifungal activity	93
Aquatic weed (*Eichhornia crassipes*) leaf	Spherical	32 ± 4	Aquatic weed leaf extract utilize as a reducing and capping agent	Aquatic weed removal and management.	92

In a study, ZnONPs treated tomato plants show improved growth and biomass production as compared with untreated ones, also improved antioxidant activity, photosynthetic rate and proline accumulation was observed in treated plants (104). ZnONPs alleviate imbalance between free radicals induced by the exposure to heavy metals like Cd and Pb in *Leucaena leucocephala*. It was also demonstrated that ZnONPs caused an augmentation in photosynthetic pigment and total soluble protein contents in *Leucaena leucocephala* whereas a considerable reduction in malondialdehyde (MDA-lipid peroxidation) content in leaves (105). In another study it was summed up that ZnONPs could indeed enter into the maize plant cells and influence the morphological traits (plant height, root length, root volume and dry weight) of the plants , also maize roots might have a particular way of absorbing nano-Zn and various enzyme activities of plant were somehow modulated by ZnONPs (47). In chicken pea seedling, overall biomass was increased after treatment of ZnONPs in a particular range of concentration (1.5ppm),owing to low reactive oxygen species levels produced which in turn lead to less lipid peroxidation but when concentration was increased to 10ppm, ZnONPs showed adverse effect on root growth (106). Seed treatment of Pearl millet with Green synthesized ZnONPs not only showed better performance in terms of growth and germination but also showed increase in activity of various defence enzymes and increased resistance against fungal attack (107). In *Triticum aestivum* L. and *Zea mays* L. ZnONPs enhanced quantitative, nutritional and physiological characters (108). Foliar application of Zn nanofertilizer enhanced physiological characters, yield of plant and Zn content in the seeds of Phaseolus vulgaris (109). Foliarly sprayed ZnONP-plants exhibited improved quantitative, nutritional, and physiological parameters in *Setaria italic* L. (110). The application of micro and macronutrient to field crops in the form of fertilizer to improve total yield is a regular practice in India as it improves availability of nutrients in nutrient deficient soil. To maximize yield these may be applied via various methods such as soil fertilizers, foliar spray, seed coating and seed priming. Where intense nutrient deficiencies occur in plants, foliar spray or direct soil fertilizer application is essential. While if the nutrient deficiency is less, seed coating and seed priming method is effective. Adhikari et al. (2016) applied ZnO fertilizer in the form of seed coated with pine oleoresin(POR), the percentage of seed germination in *Zea mays* L., *Glycine max* L., *Cajanas cajan* L. and *Abelmoschus esculentus* L. were increased as compared to the control. The most important benefit of seed coating is that ZnO do not exert any osmotic potential on germinating seed. Zn complex chitosan NPs (Zn-CNPs) are a noval nanofertilizer which boosts fertilizer use efficiency in plants. In wheat plant, Zn-CNPs nanofertilizer increased uptake, translocation and accumulation of Zn in grain (111). This is a method of agronomical bio fortification through which we can enhance Zn content in grains. Depkekar et al., (2018) also reported Zn complexed chitosan NPs for ferti-fortification of Durum wheat in field based experiment. Ferti-fortification of any plant with any vital micronutrient is one of the best strategies to prevent wastages of nutrient as well as to protect environment against pollution. This technique enriched nutrient content in grain without affecting agronomical parameters in wheat plant. Zn deficiency in human being imparts low immunity, retardation of physical growth and reproductive health (112, 113, 114). The intake of Zn in our diet is very low which create zinc deficiency which in India has caused a loss of 2.8 million DALYs (disability-adjusted life years) per annum (115). Thus, production and consumption of micronutrient loaded grain can overcome this problem and bio-fortification is the best technique to enrich cereals and grain content of micronutrient without causing any harm to soil and environment. Zn in the form of ZnONPs is considered as a bio safe material for all living organism together with environment. In coffee plants compared to conventional $ZnSO_4$salt, foliar application of ZnONPs increased photosynthesis ability with increased chlorophyll content due to their increased bioavailability to coffee plant leaves (116). In flooding and submerged soil, Zn availability is poorer to the plants due to the reaction of free Zn with sulphides (117) and as pH is raised for each unit, the Zn solubility decline 100 times with the onset of reducing conditions. To overcome this issue in flooded soil, Zn loaded inside a manganese carbonate hallow core shell was used for controlled release of fertilizer to improve low nutrient use efficiency and prevent environmental pollution. This method has many advantages over conventional fertilizers such as slow removal of fertilizer from the soil by irrigation or rain water, increased efficacy of fertilizer and sustained released of nutrient for a prolong time. It was proved that hollow core shell loaded with Zn nanofertilizer delivered to the rhizosphere of the rice (*Oryza sativa* L.) gave higher yield. This method improves Zinc use efficiency, beside the sustained released of zinc and prevention of ground water contamination and minimize environmental pollution (118, 119).This encapsulation method of nanofertilizer in such a way possess all desired properties such as enhanced targeted activity with effective concentration, easy mode of delivery and disposal, stability, solubility, less eco-toxicity and safe for all (120, 121, 122, 36). ZnONPs showed root elongation in *Glycine max* at lower concentration (84) while in *Cucumis sativus* fruit starch content and carbohydrate pattern were altered in plants grown in soils treated with ZnONPs and CeO_2NPs (123).

Negative effects of ZnONPs

Globally, agriculture sector has been facing lots of difficulties like soil fertility loss, desertification, climate changes and soil pollution. NPs have potential to overcome these difficulties because of its exceptional properties. NPs may reduce loss of nutrients during fertilization, minimize the applied amount of plants protection product, help in crop management and increase revenues through optimization of nutrients in agriculture (124, 7, 125, 126, 127, 128). Enhanced use of NPs in crop growing sector will ultimately lead to their discharge into environment, which may generate serious consequences on plant productivity. Although the mechanism of toxicity of ZnONPs against crops is not creditably known. Many researchers and scientists have studied toxicological effect of ZnONPs in last fifteen years and have reported that ZnONPs may put human beings and environment at risks. It imposes serious toxicity to micro flora (like bacteria, algae etc.), mice and even human cells (129, 130, 131). In peanut plant, seed were treated with various concentration of ZnONPs and zinc sulphate (ZnSO4) suspension, respectively and the results were compared to see effects on seed germination seedling vigour, plant growth, flowering, chlorophyll content, pod yield and root growth. It was reported that the application of 15 time lower dose of ZnONPs gives 29.5 % higher pod yield compared to recommended dose of chelated $ZnSO_4$ suspension. However, when the concentration is increased from 1000ppm to 2000ppm, inhibitory effects has been noticed on peanut plant (132). Enhancement in root elongation of *Glycine max* at a concentration of 500 ppm of ZnONPs was observed but with further increase in concentration, root size reduces (84). The investigations of phytotoxicity of various types of NPs such as multi-wall carbon nanotubes (MWCNTs), aluminum, alumina, zinc and zinc oxide were also observed on seed germination and root growth of diverse plants like radish, rape, ryegrass, lettuce, corn and cucumber. Out of these, seed germination in ryegrass as well as corn was inhibited by ZnONPs at a concentration of 200mg/L. Root elongations were completely inhibited in all plants at the similar concentration. This study shows that almost fifty percent inhibitory effect were noticed in radish and ryegrass at a doses of 50mg/L and 20mg/L concentration respectively (133). In *Hydrilla verticillata* and *Phragmites australis*, the phytotoxic effect and accumulation of ZnONPs was investigated using mesocosms technique. The submerged aquatic *Hydrilla verticillata* growth was reduced at a concentration of 1000mg/L during earlier stage of experiment but in emerged aquatic plant *Phragmites australis* the growth began to reduce after a few weeks of experiment at the same concentration. It was noticed that the measurement of antioxidant enzyme activity, chlorophyll content and accumulation of Zn is more in *Phragmites australis* as compared to *Hydrilla verticillata*. This result indicates that every plant show dissimilarity in the level of phytotoxicity depending upon their physiological differences for nutrient and water uptake (134). Therefore, NPs use and disposal should be monitoring carefully. The growth of most of the plants like peanut (*Arachis hypogaea*), corn (*Zea mays* L.), cucumber (*Cucumis sativus* L.), aquatic plants like *Hydrilla verticillata*, *Phragmites australis*, and wetland plant *Schoenoplectus tabernaemontani* was significantly inhibited at a doses of 1000mg/L (132, 135, 134, 136). Phytotoxic effect of four different metal oxide NPs, aluminium oxide (Al_2O_3NPs), silicon dioxide (SiO_2NPs), magnetite (Fe_3O_4NPs), and zinc oxide (ZnONPs), have been reported on the development of *Arabidopsis thaliana* (Mouse-ear cress) (137). The toxic level of NPs was evaluated on seed germination rate, root elongation rate and number of leaves per plant when exposed to three different concentrations: 400mg/L, 2,000mg/L, and 4,000 mg/Lof NPs and ZnONPs was found to be most phytotoxic, followed by Fe_3O_4NPs, SiO_2NPs, and Al_2O_3NPs due to its particles size and dissolution. The toxicity of metal and metal oxide NPs may be caused by their dissolution and subsequent release of toxic metal ions (138, 139). It was reported that seed germination was completely inhibition by ZnONPs above the concentration of 400mg/L. This experiment shows that compared to the larger sized (micron-sized) zinc metal oxide (ZnO), zinc oxide NPs (ZnONPs) exerts higher toxicity at equivalent concentrations (137). It is already known that heavy metals are widely known to inhibit plant growth, germination, development and also disturb their morphological, physiological and biochemical process in plants at higher concentration (140). ZnONPs are reported to display their toxic effect in mesocosms, hydroponic, agar medium as well as in soil. However, studies on toxicity of zinc based NPs on plants inoculated with symbiotic bacteria is limited, in one such study ZnONPs, bulk ZnO and $ZnCl_2$ differentially affected alfalfa (*Medicago sativa* L.) plant which is symbiotically associated with bacteria *Sinorhizobium meliloti* at concentrations ranging from 0 to 750 mg/kg soil. After treatment with particular concentration bioaccumulation of Zn in plant, dry biomass of root and shoot, leaf area, total leaf protein and catalase (CAT) activity in leaves, root and shoot were assessed in one month old plants. It was shown in this study that ZnONPs and ionic Zn decreased root and shoot biomass by 80% and 25%, at doses of 500-750mg/Kg soil but at the same concentration bulk ZnO increased shoot and root biomass by 225% and 10%, respectively. Both $ZnCl_2$ and bulk ZnO treatments altered total leaf protein and CAT levels in roots, stems, and leave at a concentration 500-750mg/Kg soil. Results showed 50% germination reduction by bulk ZnO at 500 and 750 mg/kg concentrations and $ZnCl_2$ concentration. Thus, the study showed less toxicity of ZnONPs compared to $ZnCl_2$ and bulk ZnO (141). Recent studies also reported the toxic effect of ZnONPs on varied plant species such as *Cicer arietinum, Arabidopsis thaliana, Brassica nigra, Zea mays, Pisum sativum*, and green alga *Picochlorum* sp. (106, 142, 143, 144, 145, 146). In *Allium cepa* treatment of cobalt and ZnONPs on root morphology, growth, cell morphology of a plant as well as their adsorption potential have been affected with increasing concentration resulting into severe accumulation of both NPs inside the plant cell and chromosomes in hydroponic medium. This leads to highly deleterious effect in plants (147).

To evaluate possible threat of NMs in food chain, five NPs (Ag, Cu, Si, ZnO, and MWCNTs) and their corresponding bulk counter parts were investigated using hydroponics to study their effect on various germination parameters in *Cucurbita pepo* (Zucchini) plants at a concentration of 1000 mg/L-1. It was reported that the seed germination was largely unaffected but plant root growth, transpiration rate and biomass have been severely affected by NPs and bulk material solution at given concentration (148).

A dose dependent harmful effect of Zinc NPs at various concentrations was observed in *Stevia rebaudiana* (Bertoni) plant when cultured in MS medium, also the production of stevioside was significantly reduced with undesirable effects on physiology of the plant (149).

Effects of ZnONPs on nine crops viz. wheat, maize, radish, bean, lettuce, tomato, pea, cucumber, and beet were investigated in two types of soil supplemented with ZnONPs and compared with control. After investigate found that the physiological and biochemical parameters affecting growth of these plants. It was finally concluded pH of soil and type of plant species are principal components defining the availability Zn and phytotoxicity of NPs in plants (150).

It has been reported that plant tolerance to various environmental stresses can be enhanced with the aid of nitric oxide (NO). Sodium nitroprusside (SNP) can be used in the form of NO donor which interacts with ZnONPs phytotoxicity and it has also reported that 10 μM SNP significantly inhibited the symptoms of toxicity in rice plant seedling by reducing Zn accumulation, reactive oxygen species production and lipid peroxidation. Due to NO-mediated antioxidant system, SNP help in reducing ZnONPs-induced oxidative damage by causing a decrease in superoxide dismutase activity, as well as an increase in reduced glutathione content, peroxidase, catalase and ascorbate peroxidase activity. NO can change gene expression level of the rice plant which enhances ZnONPs tolerance in plant using a NO excess mutant (noe1) and an OsNOA1-silenced plant (noa1) of rice (151).

In wheat plant seedling phototoxic effects of NPs in terms of reduced photosynthetic efficiency which increased accumulation of zinc (Zn) in the saps of xylem and phloem have been reported and nitric oxide has been shown to have an ameliorative effect against ZnONPs, by triggering the regulation of ascorbate–glutatione cycle (AsA–GSH) enzymes which reduces ZnONPs mediated oxidative stresses (152).

TABLE 2: NEGATIVE EFFECTS OF ZnONPs

Biological organism	NPs treatment	Concen-tration	Upshot	Cause of upshot	References
Wheat (*Triticum aestivum* L.) seedlings	ZnONPs solution	100 and 200 µM	Seedlings growth inhibits, photosynthetic competence decreased, increase in level of oxidative stress markers.	Enlarged accumulation of zinc (within xylem and phloem fluid)	77
Rockcress (*Arabidopsis*)	ZnONPs suspensions	200 and 300 mg/L	Decline in growth of *Arabidopsis* around 20 and 80%	Expression of chlorophyll synthesis genes and photo system genes inhibited.	145
Mustard (*Brassica nigra*)	ZnONPs with plain agar media	500 mg/L	Shoot length enhances but root length and elongation decreased.	Roots are in direct contact with NPs, agar media is non porous, less dissolved oxygen, water logging due to NPs.	146
Chickpea (*Cicer arietinum*) seedlings	Foliar spray aqueous solution of ZnONPs	10 ppm	Root growth negatively affected.	Physiological limitations, due to small particle size of ZnONPs. Dissolution rates enlarge thus solubility in water low down.	106
Peanut (*Arachis hypogaea*) seeds	ZnONPs suspension	2000 ppm	Decline in seedling vigor index.	Phytotoxicity	132
Onion (*Allium cepa*)	ZnONPs solutions	5 or 50 µg/mL	Cytotoxic as well as genotoxic effects on root meristems so reduce root development.	High Zn levels inside cytoplasmic plus nuclear fractions	147
Zucchini (*Cucurbita pepo*)	ZnO (under batch hydroponic Conditions)	1000 mg/L	Plant biomass decline.	Phytotoxicity	148
Ryegrass (*Lolium*)	ZnONPs	0-1000 mg/L	Shoot mass decrease approximately 50% at 1000 mg/L concentration.	Phytotoxicity	148

Mechanism of toxicity induced by ZnONPs in plants

Ambiguous results regarding the effects of diverse NPs on plants have been published time to time, where positive as well as negative effect of NPs on different growth stages have been observed and in addition NPs types, size, shape, structure, dimension, surface coating of with different coating materials other than this environmental factors, soil types and culture media have also shown to potentially affect the results in a different ways.

ATP is synthesized in living cells by reduction of molecular oxygen (O_2) to water (H_2O) through a sequence of coupled proton and electron transfer reactions in the mitochondria with the help of oxidative phosphorylation pathway. During this process, a small percentage of the oxygen is not completely reduced and it form reactive oxygen species (ROS) (153, 154). Thus, in mitochondria ROS are by products of cellular oxidative metabolism which play beneficial physiological roles in cellular signalling systems and induction of mitogenic responses in plants (155, 156). Besides cellular oxidative stress, there are several other biological reactions that can generate ROS in vivo, but overproduction of it can induce oxidative stress in plants which reduce normal physiological redox-regulated functions, (157, 158). ROS mainly damage cell organelles and nucleic acids (159). It has been reported that ROS and oxidative stress are associated with many havoc in cell like disruption of cell function and growth which includes oxidative modification of proteins to generate protein radicals, lipid peroxidation, breaks in DNA strands which lead to DNA damages and cell signalling, activation of redox-sensitive transcription factors which modifies gene expression into the cells and modulation of inflammatory responses through signal transduction leading to cell death (160, 161, 162, 163, 164, 165, 166). Therefore, it is very imperative to know the mechanism by which these NPs promote adverse effect? A dye DAB (3,3′-diaminobenzidine) which is ROS-sensitive dye have been used to find the accumulation of H_2O_2 in the plant roots treated with CeO_2 and La_2O_3 NPs. This dye gives insoluble deep brown colour product when treated with NPs which can be visualized easily by human eyes (167, 168). Some antioxidant enzyme like Superoxide dismutases, peroxidases, and catalases are found in plants that help in protecting plants species from damaging effect of ROS. It was reported that these antioxidant enzyme that are found inside the cells are reducing agents which donates electron or hydrogen atoms and help in defending cells against hydroxyl radical which possesses the highest one-electron reduction potential which are most reactive toward protein and nucleic acid inside the cell and causes subsequent cellular damages such as lipid peroxidation, protein damage, membrane destruction and ultimately it leads premature cell death (169, 163, 170). It has been demonstrated that various abiotic stresses causes lipid peroxidation in plants (171, 172). The polyunsaturated fatty acid present in phospholipids membrane react with free radical and provoke lipid peroxidation. This process generated reactive aldehydes such as malondialdehyde (MDA) and 4-hydroxynonenal (4-HNE) which causes mutagenesis and toxicity to the plant cells. Excessive exposure of NPs in plant cells induced oxidative stress which leads to redox imbalance and causes NP-associated toxicities (173, 168).

CONCLUSION

Nanotechnology is the emerging field of technology in present century operating in all fields of science. ZnONPs become known as one of the most versatile NPs, due to its different properties, functionalities, and applications in the field of agriculture. ZnONPs have many physical, optical and antimicrobial properties against many microbes. The ZnONPs have enormous commercial importance in various aspects such as solar cells, biosensors and sun- cream etc. They have intrinsic ability to filter ultraviolet UVA as well as UVB radiations. ZnONPs are synthesised chemically as well as by biogenic method. But biogenic method is environmentally friendly and much safer to use and do not cause toxic effects as compare to chemically synthesised ZnONPs. These green synthesised NPs are through plant extract and microorganisms. As far as their usage is concerned ZnONPs play a significant role in the form of nanofertilizers in the encapsulated form. These NPs are enhancing plant growth and yield although this enhancement is dose dependent; ZnONPs also show toxicological effects on plants at high doses and causes potential health harms along with environmental risk. ZnONPs can impose serious toxicity to living organism in addition to environment when their usage is increased from their threshold limit which can threaten all living communities. Also, the intake, translocation, accumulation of NPs in the soil and plants will definitely have a serious impact on consumers. So, there is a requisite of further research and a risk assessment is necessary before we accept its applications in agriculture.

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CITATION OF THIS ARTICLE

Lalita, Priya,S Kachhwaha. Zinc Oxide Nanoparticles in Agriculture: A Critical Review.Bull. Env. Pharmacol. Life Sci., Vol 10[5] April 2021 : 289-304