Nanomaterials for managing abiotic and biotic stress in the soil-plant system for sustainable agriculture

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Environmental Significance statement

The human population is continuously increasing together with the demand for food; to satisfy the necessary criteria, the production of plants will have to reach double their actual production in less than 30 years. Plants face many challenges, in which are included biotic and abiotic stressors. This is a worldwide problem, and this review focuses on the recent investigations that involve nanotechnology to ameliorate abiotic and biotic stress in plants, thus becoming a pathway to increase productivity. We are confident that this review is suitable for since it converges biotic and abiotic stresses affecting plants worldwide and the recent investigations related to nanotechnology to mitigate them. Thus, involving environmental impacts, agriculture, and nanomaterials.

Nanomaterials for managing abiotic and biotic stress in the soil-plant system for sustainable agriculture

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Abstract

As the global population steadily increases, the need to increase agricultural productivity has become more pressing. It is estimated that agricultural production needs to double in less than 30 years to meet the projected food demand. However, crop species are being cultivated under a range of increasingly challenging environmental stressors, including the effects of climate change and factors. To address these issues, nanotechnology has emerged as an enabling strategy to bolster plant resistance to the adverse effects of stressors and improve their overall performance. In this review, we evaluate recent research in this field, examining the strategies by which nanomaterials (NMs) and nanoparticles (NPs) have been used to facilitate enhanced tolerance to pests, excessive salinity in soil, pathogenic fungi, and other stressors. The intent is to focus on the mechanisms by which plants cope with environmental stressors at the physiological and molecular levels. We also examine how plants interact with and acquire NMs, with a specific focus on the mechanisms behind their beneficial effects regarding stress response. Our review also evaluates key knowledge gaps and offers suggestions on how to address them. Additionally, we discuss the potential of NMs to enhance agricultural production systems and highlight essential considerations for mitigating crop stress and promoting sustainable agriculture at a global scale. While the use of nanotechnology in the agricultural sector is growing and shows tremendous promise, more mechanistic studies and field-scale demonstrations are needed to fully understand and optimize the use of nanomaterials on plants stress tolerance in a changing climate. In addition, few studies conducted life cycle field experiments to verify the effects of nano-agrichemicals on yield and nutritional quality, and importantly, there is a lack of multiple-year and multiple-location experiments. Only by doing

this can the technology-readiness-level of nano-enabled agro-technologies be improved and forwarded to commercial application.

1- Nanomaterial applications in agriculture production systems

The global population is projected to increase to 9.7 billion by 2050, and 11 billion by 2100, meaning that an increase of at least 50% in agricultural production is needed to achieve food security.[1–4] The food gap, as described in the world resources institute report[5], refers to the difference between the quantity of food that will be required in 2050 and the quantity produced in 2010. This food gap will likely increase as a function of climate change. Importantly, worldwide there is approximately 20-40% crop loss due to pests and plant diseases[6], and these losses are also predicted to increase with the changing climate.

Furthermore, crops are exposed to a variety of environmental biotic and abiotic stresses, which restrains agricultural production.[7–10] Biotic stress refers to damage from pests and pathogens such as nematodes, fungi, bacteria, viruses, insects, and weed species, as well as from herbivores. Abiotic stress refers to environmental factors such as drought, salinity, harsh temperatures, metal toxicity, and nutrient deficiency.[7,9–13] Collectively, these factors affect crop growth and decrease yields. Therefore, increasing agricultural production using current methods will be exceptionally resource-intensive and unlikely to achieve the production levels necessary to ensure food security. Thus, there is a critical need to investigate and develop novel technologies that effectively reduce stress and deliver agrochemicals to crops in an environmentally sustainable fashion to guarantee food security for the growing population.

Consequently, research has intensified in recent years to mitigate these various stresses. The mitigation of abiotic and biotic stresses has been observed upon applying stress tolerant and plant growth promoting rhizobacteria (PGPRs)[14-17], elemental nutrients[18-21], phytohormones, chemical modulators[22], and nanoparticles (NPs) and nanomaterials (NMs), among other strategies.

NPs as defined by Rajput et al.[23] are materials known to have at least one dimension around 1-100 nm. However, NMs are materials that have an internal structure or external dimension in the nanoscale size.[24] The use of NPs and NMs is increasing in the management of abiotic and biotic stresses.[23] Importantly, both abiotic and biotic stresses negatively affect crop growth and yield, and although often investigated separately, in the field they most often act in concert. There is growing certainty that nanotechnology can be a critical tool to increase agricultural productivity in this effort.[4,7] Many conventional agricultural systems are highly inefficient, with the efficiency of agrochemical delivery at 10-75%.[4] The goal is to use nanotechnology as a sustainable alternative to the resource-inefficient and environmentally damaging practices of conventional agriculture.

A very wide range of NMs may have utility in sustainable agriculture. Zero-dimensional or 0D nanomaterials are defined by Singhal *et al.*[24] as solid core spherical and hollow spheres, including nanoparticles, nanoclusters, graphene quantum dots, polymer dots among others.[25–27] For example, sulfur 0D NMs have many applications, such as antifungal and antibacterial agents, photoelectric conversion materials, and plant growth regulators.[28] One-dimensional 1D NMs include nanowires, nanotubes, nanofilaments, and nanorods; these only have one dimension of less than 100 nm, and are known to be suitable for their elevated porosity, catalysis, and filtration, as well as being highly absorbent.[24,25] Some uses include carbon nanotubes as biosensors, nanowires as nanosensors, and nanorod-based fibers as immunosensors.[29,30] Two-dimensional 2D NMs have select dimensions outside the nanometric size range; these include graphene oxide and derivatives, transition metal dichalcogenides and derivatives, and MXene composites. The agricultural application of 2D NMs can improve plant growth and development, plant nutrition, and help against pests and diseases.[24,25] Lastly, there are three-dimensional or 3D NMs. These include materials with three dimensions that are less than 100 nm and can include bulk solids, nanocomposites, nano-balls, nano-coils, nano-cones, nanocrystalline materials, basil seed gum nanoparticles (BSG), nanostructured films, and nano-pillars.[25,31] Some of the applications of 3D NMs in agriculture include 3D graphene for electrochemical detection of cadmium in rice[32] and 3D hydrogels can be used as soil conditioners and as carriers of nutrients[33]. More current literature on the use of nanomaterials is described in the following sections.

2- Abiotic stresses

The present era is one of significant environmental change, with several abiotic stresses becoming increasingly problematic. The causal agents for abiotic stresses can be natural factors; however, some of the most intense abiotic stresses are directly linked to anthropogenic activities.[34] Abiotic stresses refer to adverse impacts from factors such as temperature, ultraviolet light, salinity, drought, heavy metals, persistent organic pollutants, nutrient deficiency, greenhouse gases, inadequate soils, and poor-quality water irrigation. These factors can negatively impact crop plants, with the magnitude of impact depending on the type and intensity of stress, plant species, soil type, combinations of stresses, plant life stage, and pH, among others. For example, reactive oxygen species (ROS) are crucial signaling molecules that are involved in metabolic processes that assist plants with their defense responses. These can increase in plants under stressful conditions, causing a disruption of the cellular redox homeostasis, leading to disruptions in cell membranes, DNA, lipids and proteins, reducing growth and production. Zhao *et al*.[35] mentions that NPs such as CuO, Ag, CeO_2 and Mn_3O_4 have been shown to act as ROS-scavenging NPs in plants under abiotic and biotic stresses, protecting plants by facilitating the alleviation of detrimental ROS effects. A schematic diagram of plant responses to abiotic stress is shown in **Figure 1**.

2.1- Application of nanomaterials for mitigation of temperature stress

Temperature stress refers to either high (heat) or low temperatures (chilling/cold/freeze) that deviate from the ideal range. These conditions affect the productivity of crops by causing negative impacts by a range of factors.[36,37] These can include, photosynthesis, osmotic regulation, yield, transpiration, water potential and content, growth, development, cell membrane thermostability, cell damage, oxidative damage, increase in superoxide radical (O_2•−), hydrogen peroxide (H_2O_2), genetic damage, dehydration, cytosol outflow, increase of sugar content, and tissue chlorosis/necrosis, among others.[36,37] Many options have been developed to help plants mitigate such adverse conditions. These include different types of shelters, shade, nutrient supplements, development of new cultivars, phytohormones, polyamines, soluble sugars, and proline. Notably, the application of nanomaterials has been shown to be particularly effective. For example, a soil application of AgNPs (50 and 75 mg/L) have helped to mitigate heat stress (35-40 °C) in wheat (*Triticum aestivum* L.) when compared to controls as measured by plant yield, weight and morphological growth in general.[38] Djanaguiraman et al.[39] reported foliar spray of SeNPs at @ 10 mg/L to sorghum (*Sorghum bicolor* L. Moench) at the booting stage against the heat stress (38/28°C) showed an improvement in antioxidant defense system, increased unsaturated phospholipids, pollen germination (6%) and seed yield (11%). Mahmoud and Abdelhameed[40] reported that foliar sprayed a solution of 15% TiO_2 NPs and multi-walled carbon nanotubes (TiO_2@MWCNTs) in reddish yellow and white sesame seedlings (*Sesamum indicum* L.) alleviated heat (45 °C) stress by improving peroxidase enzyme activity, which is an antioxidant, and reduced malondialdehyde (MDA) content.

Conversely, Amini *et al.*[41] investigated the growth of chickpea plants (*Cicer arietinum* L.) exposed to cold temperatures (4 °C for 6 days) with foliar TiO_2 NPs treatment (5 mg/L). A cDNA amplified fragment length polymorphism analysis showed a reduction of oxidative stress and the electrolyte leakage index, along with increased productivity, upon TiO_2 NPs application. The use of TiO_2 NPs was reported to alleviate cold stress on licorice (*Glycyrrhiza glabra* L.); the authors demonstrated that TiO_2 NPs (0, 2 and 5 ppm) with spermine applied during growth in Murashige and Skook medium decreased oxidative damage as measured by MDA and H_2O_2 content when compared to controls.[42] Sugarcane (*Saccharum officinarum* L.) was exposed to low temperatures (day/night 16.6/6 °C for 6 days) by Elsheery *et al.*[43]; the authors reported that a foliar application of NPs of SiO_2 (300 ppm), ZnO (50 ppm), Se (15 ppm), and graphene (50 ppm) improved photosynthesis (5.04, 4.54, 3.19, and 4.23 %) and carotenoid content (4.2, 10.3, 19.7, and 11.8%), subsequently ameliorating the cold weather effects when compared to controls. SiO_2 NPs showed a higher improvement in photosynthesis compared to the rest of the NPs, primarily due to its ability to aid in the regulation of genes related to stress-related physiological and biochemical activities. Chen *et al.*[44] reported that under cold stress exposure (15 °C), priming maize (*Zea mays* L.) seeds with AgNPs (40 mg/L) increased the germination rate, vigor index (28.8%), and growth in shoot and root compared to hydro-primed seeds. **Table 1 (supplementary information)** provides a list of additional studies on this topic. We believe future studies should include longer duration stress exposures; multiple temperature treatments; initial stage vs. full life cycle evaluation; different type, size and concentrations of NPs; and a more thorough comparison with ionic and/or bulk forms of corresponding NPs.

2.2- Application of nanomaterials for mitigation of salinity stress

Salinity refers to the salt concentration in the water, soil, or atmosphere, which can negatively impact crop plants. Although Na^+ and Cl^- are essential minerals for plants, an excess can induce detrimental effects such as reduction of growth, productivity, ion homeostasis dysregulation, osmotic stress, oxidative stress, decreased photosynthetic rates, and altered nutrient uptake. Freshwater ecosystems can experience increased salinity due to discharges from dryland, irrigation, rainfall, and weathering, subsequently causing a decline in the quality and quantity of crops. Razzaq *et al.*[45] report that annually, global losses approach $30 billion due to salinity stress in crops. Importantly, different nanomaterial treatment strategies have shown efficacy against salinity stress.

The use of ZnO NPs (10 mg/L) as a foliar spray was reported by Alabdallah and Alzahrani[46] on okra (*Abelmoschus esculentus* L.) under salt stress (diluted seawater at 0, 10, 25, 50, and 100%). The authors reported an increase of carotenoids (0.4%), total chlorophyll (2.74%), and antioxidant enzyme activity even in 100% seawater treatment when compared to control. Also, the proline and total soluble sugar accumulation were lower in ZnO NPs when compared to control with 100% seawater. Proline is a nonpolar amino acid that is found throughout the plant and can accumulate at high levels due to stress factors such as salinity because, as an osmoregulatory agent, it mediates water uptake by cells. In fact, exogenous proline can help reduce stress.[47] ZnO NPs functionalized with proline (0, 50 and 100 mg/L) has been shown to alleviate salt stress at 50 mM NaCl in coriander (*Coriandrum sativum*) by decreasing the antioxidant activities of superoxide dismutase (SOD) by 23% and peroxidase (POD) by 38%, therefore preserving a homeostasis level[48], resulting in increased biomass. Similarly, coriander (*Coriandrum sativum*) treated with ZnO NPs capped with glycine betaine (ZnOBt) at 100 mg/L demonstrated alleviation of salt stress (50mM NaCl) by stimulating antioxidant mechanisms by decrease in SOD (27%) and POD (33%) when compared to salt stress treatments; this resulted in improved morphological, biochemical, and physiological reaction against salinity and increased in plant fresh shoot and root biomass.[49]

Rizwan *et al.*[50] reported that the application of SiNPs (75 mg/kg) in soil ameliorated saline-sodic soil stress (Na 67 mEq/L and total soluble salts 86 mEq/L) in maize (*Zea mays* L.) plants by increasing availability of P and K, chlorophyll (52.5%), transpiration (100.2%), CO_2 concentration (61.6%) and stomatal conductance (50.5%). Ijaz *et al.*[51] reported that foliar spray of SiNPs (20 mg/L) alleviated salt stress (100 mM NaCl) in two rice (*Oryza sativa* L.) genotypes (N-22 and Super-Basby) by stimulating high-affinity potassium transporters (HKT). The authors also reported increased chlorophyll by 16 and 13%, carotenoids by 15 and 11%, protein content by 21 and 18%, and antioxidant enzymatic activity such as catalase (CAT) (28 and 25%) and SOD (31 and 27%), respectively. Similarly, Sheikhalipour *et al.*[52] reported that priming bitter melon seeds (*Momordica charantia* L.) with 20 mg/L of Se and chitosan (Se-CS) ameliorated salt stress (50 and 100 mM NaCl) by increasing photosynthesis (10.17 and 9.50%), relative water content (RWC) (5.69 and 7.85%), proline (19.78 and 9.26%) and antioxidant enzymatic activity such as POD (47.71 and 34.22%), SOD (35.43 and 41.08%) and CAT (16.10 and 16.51%). Graphene oxide (GO) and proline-functionalized graphene oxide NPs (GO-Pro NPs) at 100 mg/L enhanced the content of total chlorophyll (15.8%) and carotenoids (19.2%), and reduced electrolyte leakage (41.2%) in grape seedlings (*Vitis vinifera* L.) under salt stress (50 and 100 mM NaCl). Notably, high concentrations of graphene did cause phytotoxicity, such as decreased ascorbate peroxidase (APX) (80.3%) activity.[53]

Ye *et al.*[7]reported that the nano-priming of seeds with manganese (III) oxide NPs (MnNPs) (0.1 and 1 mg/L) reduced salinity stress (100 mM NaCl) in *Capsicum annuum* L. in the germination stage and increased the root growth (55.4 and 55.7%), respectively. Manganese sulfate is a common fertilizer because it is an essential micronutrient for over 100 enzymes with important roles in photosynthesis, respiration, and nitrogen metabolism[7,54–56], as well as acting as a Lewis acid and as an oxidation catalyst.[55,57] Shiri *et al.*[58] investigated spearmint (*Mentha spicata* L.) treated with cerium oxide and salicylic acid NPs CeO_2-SA nanocomposite (25 mg/L CeO_2 + 50 μM SA and 50 mg/L CeO_2 + 100 μM SA) under saline stress (50 and 100 mM of NaCl). The authors reported an increase in elemental content of K, Zn, Cu, Mn and Fe (1.52, 166.6, 16.5, 36.4 and 1.27%) protein content (6,14%), carbohydrate content (53.3%), phenolics (58.8%), flavonoids (82%) and essential oil percentage (244.6%) when compared to controls.[58] These and additional studies demonstrate that salinity stress in plants can be ameliorated with NPs (**Table 1, supplementary information**). However, further investigation is needed to better understand the nanoscale-specific mechanisms of NPs mediated salinity stress alleviation, as well as on optimizing benefits regarding the timing and amount of application, prolonged stress exposure, plant life stage and level of stress and plant species among others.

2.3- Application of nanomaterials for mitigation of drought and flooding stress in plants and crops

Drought refers to a period of dryness or lack of water availability. This can cause many effects in plants, including stomatal closure, cellular damage, osmotic stress, ROS accumulation, decrease in CO_2 availability, chlorophyll content, photosynthesis, enzymatic activity, nitric oxide (NO) synthesis, growth, and productivity, among others.[59–62] It has been estimated that drought stress causes yearly losses of $80 billion in agricultural yields.[45] There are a number of reports of NPs mitigating the damage from drought stress. For example, Ali *et al.*[59] reported that foliar application of chitosan (CS-NPs) (1%) in periwinkle plants (*Catharanthus roseus*) alleviated drought-induced stress (50 and 100% of field capacity) by improving proline accumulation by 3.76-fold when compared to control treatment. Zahedi *et al.*[63] investigated SiO_2 NPs at 50 mg/L as a foliar spray to strawberry plants (*Fragaria X ananassa* Duch.) under moderate and severe drought stress (100, 50 and 25 of FC). The authors found that in severe drought (25%FC) the NPs application increased the number of leaves (56%), petiole length (91%), chlorophyll content (56%), enzymatic activity [POD (133%), CAT (203%), SOD (46%), APX (143%) and PAL (33%)], and osmolytes when compared to the control drought treatment. Similarly, Bidabadi *et al.* reported that the application of Fe_2O_3 NPs at 10μM on grape (*Vitis vinifera* L.) under drought stress (7% PEG-6000) increased chlorophyll content and antioxidant enzymatic activity when compared to controls.[60]

Flooding stress in plants refers to waterlogged or submerged soils either for short or prolonged periods due to overwatering, prolonged rainfalls, irregular rainfall, or overflow in water bodies. These circumstances can lead to a state of prolonged lack of oxygen in plants which can negatively affect production, protein metabolism, fresh and dry weight, photosynthesis, chlorophyll production, ethylene and starch content.[64–66] Waterlogging also causes a lack of O_2 to beneficial microorganisms and reduces gaseous diffusion which can affect cellular respiration and damage plants at a biochemical and physiological level.[67] An estimated yearly loss of $88 billion globally is thought to occur due to flooding stress in crops.[45] Mustafa *et al.*[65] evaluated the response of soybean (*Glycine max* L. cv. Enrei) under flooding stress with a gel-free proteomic technique upon application of different size AgNPs (2, 15 and 50-80 nm). The authors reported that the application of AgNPs (15 nm) improved the root length, ribosomal proteins, protein metabolism, cell division and organization, and amino acid metabolism. This induced a number of phenotypic changes, including increased formation of waxes, that reduced the adverse impact of flooding stress, since these cuticular waxes aid in nonstomatal water depletion and work as an exterior covering for plants.[65] Hashimoto et al[68] investigated soybean seedlings (*Glycine max* L.) under flooding stress (4 cm of water in 2-day old plants), and demonstrated that AgNPs (5 ppm) in combination with nicotinic acid (8 μM) and potassium nitrate (0.1 mM) enhanced the length and mass of the root and hypocotyl, and also induced changes in protein degradation, decreasing six proteins and increasing 14 proteins in a manner which reduced flooding stress.[68] Hussain *et al.*[64] reported that the foliar and root application of 250 mg/L of SiO_2 NPs helped Rubidoux (*Poncirus trifoliata* L.), Carrizo citrange (*Poncirus trifoliata* L.) and Rich-16-6 citrus rootstocks that were exposed to flooding stress (plants 4 cm below the root scion/rootstock). This resulted in biomass increase, enhanced free polyamine content, and decreased in leaf and root content of O_2^-, H_2O_2 and lipid peroxidation, in all three different plants when compared to flooding treatments with or without aeration.[64] Additional studies can be found in **Table 1 (supplementary information)**. Understanding the dynamics of flooding cycles on the plant and associated soil microbiome, full cycle studies should also be taken into consideration.

2.4- Application of nanomaterials for mitigation of ultraviolet stress

Ultraviolet light has wavelengths ranging from 100 to 400 nm.[69,70] There are three classifications of UV radiation (UV-A, UV-B and UV-C); in this review, we will focus on UV-B. This abiotic stress refers to the radiation of wavelengths that reach from 280-315 nm and can cause damage to plants such as altered leaf morphology, reduced mass and height, DNA damage, accumulation of ROS and decreased photosynthesis.[69–71] However, UV light is also pivotal for plants and plays a role in protecting against pathogens and herbivores.[72] The increase in anthropogenic activities has created harmful emissions that contribute to the destruction of the atmospheric ozone layer, which allows a greater part of UV-B radiation to reach the earth's surface. Tripathi *et al.*[73] reported an *in-vitro* study where silicon NPs (SiNPs) at 10 μM in a hydroponic application mitigated UV-B stress in wheat seedlings (*Triticum aestivum*). The authors demonstrated that the SiNPs enhanced photosynthesis, modulated total soluble protein content, increased antioxidant content, and reduced electrolyte leakage from 26 to 36% when compared to controls. Moradi Rikabad *et al.*[74] reported that foliar application of TiO_2 NPs at 25 and 50 mg/L has mitigated UV-B stress (1 month of daily exposure for 30 and 45 min with lamp irradiance rate of 18.3 kJ/m²) in saffron (*Crocus sativus* L.) by increasing the content of phenolics (26 and 25%) and flavonoids, and by promoting antioxidant activity in saffron stigmas by 11%. Azadi *et al.*[69] applied AgNPs (0, 50 and 100 mg/L) to thyme (*Thymus vulgaris* L.) exposed to UV-B stress induced by exposure of plants to 312 nm wavelength bulb for 0, 30 and 60 mins. The authors showed that applying AgNPs at 100 mg/L alleviated some of the damage caused by UV-B, resulting in increased plant growth, yield, and some biochemical compounds such as dissolved carbohydrates and photosynthetic pigments. UV-B stress in plants can affect many mechanisms, though it depends on the intensity level and duration of exposure to these factors; thus, more studies with different UV-B periods of exposure, higher intensity of UV-B exposure, and at different life stages of plants are needed.

2.5- Application of nanomaterials for mitigation of heavy metal (metalloid) stress

Although some elements, including heavy metals and metalloids, are essential and beneficial to plants, most exert significant phytotoxicity at moderate to high concentrations. Relevant essential micronutrients for plants include B, Cl, Mn, Fe, Zn, Cu, Mo, Ni.[75–77] From these essential micronutrients Mn, Fe, Zn, Cu, Ni, and Mo are heavy metals. Micronutrients are required in small quantities for many functions in plants, including as coenzymes and components of photosynthesis, respiration, nitrogen fixation, and redox reactions.[77–81] Heavy metal stress in plants refers to the toxicity caused by the levels surpassing specific threshold concentrations. Heavy metal uptake in plants is more common through the roots since these have a greater binding capacity in its cell walls than leaves, as well as the fact the soil burdens of these contaminants frequently exceed atmospheric content.[82] There are some plants that can tolerate high amounts of heavy metals and have developed sophisticated mechanisms to manage exposure. Hyperaccumulator plants can accumulate high concentrations of certain elements, amounting to some percent of the dry mass of the aerial parts.[83] Plants have two mechanisms in which they respond to metal and metalloid exposure. The first is direct complexation, which reduces bioavailability by reducing the adsorption of heavy metal ions. Secondly, compartmentalization can isolate the toxic element while simultaneously stimulating defense and tolerance pathways that aid with stress after the metal uptake. Excess heavy metal exposure can negatively affect germination, seedling development, plant growth and biomass, membrane structure and permeability, cell formation, endodermal cell structure and function, water and nutrient homeostasis, and photosynthesis/respiration.[82] Significantly, the phytotoxicity of heavy metals in plants is largely affected by soil-related parameters, including pH, redox state, temperature, microbiome activity, and organic matter content, among others. Also, toxic element bioavailability can decrease or increase dynamically due to a range of environmental factors.[76,82] Some of the most phytotoxic heavy metals include Cd, As, Pb, Al, and Cr.[77,81, 84-90] In summary, plant heavy metals toxicity has often two mechanisms. There is ex planta direct complexation with the heavy metal that reduces bioavailability but there is also in planta stimulation of defense and tolerance pathways that help with stress after metal uptake.

Hussain *et al*.[87] reported that wheat plants (*Triticum aestivum*) grown for 125 days in Cd-contaminated soil were positively impacted by FeNPs at 5, 10, 15, and 20 ppm via both foliar and soil applications. In both application routes, the higher concentration of FeNPs caused a reduced Cd concentration in plant tissue, suggesting Cd complexation by FeNPs that reduced *ex planta* and *in planta* bioavailable metal.[87] Zou *et al.*[90] investigated the use of α-Fe_2O_3 NPs at 50 mg/kg in muskmelon seedlings (*Curcumis melo* L.) to mitigate Cd toxicity (400 mg/kg). The authors reported that α-Fe_2O_3 NPs reduced Cd content by 52.25% in fruits when compared to treatments with only Cd; decreases in SOD (24.98%), CAT (29.54%), and 369 genes were also reported with treatment. In addition, the activation of auxin-responsive and ROS related genes was noted, which enhanced Cd-toxicity tolerance.[90] Khan *et al.*[88] reported that silicon nanoparticles (SiNPs) synthesized by *Trichoderma* (10 mL at 2% and 3%) alleviated Cd-toxicity (100 mg/kg in soil) symptoms in tomato (*Solanum lycopersicum* L.) when applied to the soil; the authors reported enhanced photosynthesis (45.83) and antioxidant enzyme activity, as well as increases in the transcriptional level of genes related to enzymes that mediate stress reduction. Chandra *et al.*[91] synthesized silica NPs (SiNPs) that ameliorated Al toxicity in *Cicer arientinum;* exogenous application in germination paper, resulted in a reduction of ROS by up-regulating the expression of genes responsible for antioxidant production. Ogunkunle *et al.*[92] reported that CeO_2 NPs reduced Cd phytotoxicity in okra plants (*Abelmoschus esculentus* L. Moench) upon foliar application at 200, 400, and 600 mg/L. The authors reported increased chlorophyll and carotenoid content, as well as antioxidant enzymes and bioactive compounds, and significant decreases in Cd content in plant tissues when compared to plants grown only with Cd stress (Cd 10 mg/kg in soil). Panahirad *et al.*[93] demonstrated that foliar putrescine-functionalized carbon quantum dot (put-CQD) NPs at 25 and 50 mg/L alleviated Cd stress (Cd 10 mg/kg) in grape (*Vitis vinifera* cv. Sultana) by increasing the content of chlorophyll (86.42%) and polyamines such as putrescine, spermine and, spermidine; the result was an increase in fresh mass by up to 30%.[93] Yuan *et al.*[94] reported that SNPs (300 mg/L) mitigated mercury (Hg) toxicity at (10 mg/L) in *Brassica napus* L. grown in agar media by reducing the elements accumulation by 6-10 fold. The authors reported increases in the dry weight of shoots and roots (42.4 and 37.8% respectively) and the uptake of micro- (Mn, Zn and Fe) and macro-nutrients (Ca, K, P and Mg) when compared to treatments with Hg alone.[94] Importantly, additional studies are needed to understand the impact in soil properties such as humic acid, organic matter content, and pH, as well as the role of the soil microbiome. In addition, additional future research is needed on the role of plant life stage, comparisons to conventional and non-nanoscale controls, NPs size and type, and field scale evaluation.

2.6- Application of nanomaterials for mitigation of nutrient deficiency

The loss of availability of micronutrients in soil can be caused by erosion, liming of acid soils, weathering, and leaching.[77] These low levels in soil can lead to nutrient deficiency in crops. Nutrient deficiency in plants can be phenotypically evident as leaves having an over pigmentation or discoloration; spots on edges or the whole leaf; dark green veins; falling, wilt or folded tips of leaves; chlorosis, and necrosis. Although conventional fertilizers have been used extensively, the use efficiency of most elements is quite low.[31,95] More specifically, fertilizers are commonly used to provide nutrients, enhance water retention, and promote aeration in soil; these may include N, P, K, S, Ca and Mg as well additional micronutrients noted above. These nutrients are key components of proteins, nucleic acids, chlorophyll, plant regulators, and participate in important cellular processes such as cell division, enzyme activity, seed germination ion absorption, respiration, sugar transport and nutrient transport.[96-100] Importantly, nanofertilizers have demonstrated significant advantages over conventional formulations, including more effective, gradual, and controlled release; increased nutrient uptake efficiency; enhanced crop productivity; higher reactivity and surface area, and reduced loss from the system.[31,95,100–103] Sharma *et al.*[104] reported that Zn and Mg doped hydroxyapatite NPs modified with urea (MgHAU and ZnHAU) at

(0, 50, 75 and 100%) provided multiple nutrients more effectively to wheat plants (*Triticum aestivum* L.), reducing nitrogen inputs by 50% and increasing yield by 24%. Li *et al.*[105] investigated rice (*Oryza sativa* L.) grown under Fe deficiency in Kimura nutrient solution upon treatment with NPs of zero valent iron (ZVI), Fe_3O_4 and Fe_2O_3 (50, 250 and 500 mg/L). The authors reported that ZVI and Fe_3O_4 at 50 mg/L increased chlorophyll, ameliorated the Fe deficiency, reduced oxidative stress as measured by MDA, and increased gibberellin (13.9% and 10.9%), indole-3-acetic acid (47.4% and 41.9%), and growth (7.7 and 6.3 cm).[101] Kusiak *et al.*[106] reported that barley (*Hordeum vulgare* L.) grown in Hoagland's solution with Cu deficiency treated with a foliar application of CuNPs at 0, 100 and 1000 mg/L demonstrated improved chlorophyll *a* and *b* (13.99 and 3.21 μg/g of fresh weight), and increased GSH (102%) at 100 mg/L when compared to $CuSO_4$. Understanding how application rates can be reduced due to the precise and efficient delivery and utilization of NPs should be deeply analyzed.

3- Biotic stress

Pests and pathogens cause severe crop damage, yield reduction and post-harvest product losses in agriculture,[107] with amounts totaling billions of dollars annually. Locusts, potato late blight, wheat rust, and rice blast are some common examples.[108] Biotic stresses can lead to abiotic stresses and vice versa, and multiple stresses or a mixture can also strike at the same time, also this can happen at different growth stages of the plant and post-harvest. A schematic diagram of plant responses to biotic stress is shown in **Figure 2**. Specifically, biotic stress refers to competitive or hostile interactions where biota such as fungi, viruses, bacteria, parasitic nematodes, insects, herbivores, and weeds cause damage to the plant of interest.[109,110] Plants can become infected, attacked, or damaged by biotic stresses, thus negatively influencing their cell metabolism, growth, yield, productivity, nutrient absorption, gene expression, and plant vigor in ways that compromise health and in extreme cases, cause mortality. Since plants cannot physically move, species have evolved a wide array of response strategies. To cope with biotic stress, plants can adjust their metabolism by activating stress response pathways at the molecular, biochemical, morphological, and physiological levels. Importantly, anthropogenic activities can increase CO_2 concentrations which increase stress in plants, this suggests that abiotic stress can induce biotic stresses (pathogens and infections) and vice versa.[67]

When plants get infected/invaded by pathogens and pests, a range of strategies can be employed for protection, including physical and chemical responses, as well as enlisting support from surrounding beneficial or symbiotic species. Physical barriers include thick cuticles, waxes, and specialized trichomes. Prickles, spines, and thorns can also help plants physically avoid or deter pest/insect attacks. Plants can also utilize chemical substances to biochemically deter herbivores and phytopathogens.[111] There are also reports of plants accumulating high amounts of metals such as Ni for protection against pests.[112] Physiologically, the plant's stress-induced defense system is regulated by the interplay of a number of phytohormones, transcription factors, receptors, kinases, and microRNAs.

Induced systemic resistance (ISR) and systemic acquired resistance (SAR) are two modes of resistance that are operational in plants for protection against pathogens. The two processes involve different signaling molecules.[113] Some non-pathogenic rhizobacteria trigger ISR and induce subsequent disease resistance in the host plant.[114,115] Further, PGPR and fungi can also enhance the production of phytohormones and other components of ISR.[116] Importantly, plants have specific pattern recognition receptors that can distinguish between pathogen-associated molecular patterns (PAMPs) and microbe-associated molecular patterns (MAMPs).[116] There are different molecules associated with different pathogens, pests, and herbivores and for these molecules, variable pattern recognition receptors (PRRs) are present in plants, allowing them to detect that infection or attack has begun.[117] PAMP-triggered immunity (PTI) is the first line of defense and hypersensitive response (HR) can occur to mediate and regulate cell death at the infection site.[118] If the pathogen escapes PTI, the second line of defense, called effector-triggered immunity (ETI) is activated by effector molecules produced by the pathogens.[117] Further, ETI advances the transmission of signals to downstream genes.[102] In addition, Salicylic acid (SA), jasmonic acid (JA), and ethylene (ET) are major phytohormones involved in induced defense responses.[119]

3.1- Application of nanomaterials for mitigation of insect stress

Notably, there are beneficial insects as well as insects that can detrimentally impact plants. Some beneficial insects for crops are pollinators, predators of pest insects, and parasites of pest insects. These include honeybees, butterflies, moths, ladybugs, ground beetles, green lacewings, and many other species. Conversely, pest insects can include locusts, armyworms, aphids, wheat midge, mites, stink bugs, pink borer, termites, khapra beetle, rice water weevil, rice thrips, sugar cane beetles, corn earworm, cutworms, and wireworms, among many others. Insect stress or insect pest stress refers to crop or plant exposure to harmful insects that can result in direct damage or increase susceptibility to one or more diseases. Pests and insects can attack plants in large numbers and damage whole crops by feeding, this stops plant growth as a particular tissue such as leaf is removed or damaged. Further, egg laying and larval growth on plants damage them, these can also transfer bacterial and/or viral diseases to plants.[120].

Conventional pesticides have been reported to have an inefficient delivery, often resulting in overapplication that can promote pest resistance, as well as contaminate the environment.[121,122] Nanopesticides are described by Shang *et al.*[101] as products that are used for effective crop protection and are formulated with some component of nanotechnology that is designed to offer increased precision of delivery and efficacy. Wang *et al.,* [121] reports that nanopesticides have shown an increase of effectiveness of 31.5% against targeted organism, as well as a decrease of 43.1% of its negative impact in non-targeted organisms and the environment. Many examples exist in the literature; **Figure 3** depicts a schematic diagram of nanopesticide effects on crop and pest dynamics. For example, Khoshraftar *et al.*[123] reported on the use of nanocapsules with a cargo of *Eucalyptus globulus* extract that help in the mitigation of green peach aphids (*Myzus persicae*). Applied as a fumigant at 60, 80 and, 100 mg/ml, 100% mortality against this pest was evident at 48 hours.[123] Similarly, Gao *et al.*[124] reported on an adhesive nanopesticide containing cyantraniliprole (CNAP-HMS-PDAAM) applied as foliar spray to rice plants (*Oryza sativa* L.) and showed efficacy in the field against *Cnaphalocrocis medinalis* at 30.0, 34.5, 39.0 and 69.0 g a.i./ha; importantly, the level of control was statistically equivalent to commercial pesticide Benevia® (cyantraniliprole 10% EOD). In addition, CNAP-HMS-PDAAM at 34.5, 39.0, and 69.0 g a.i./ha was more effective than Benevia® against *Chilo suppressalis.* [124] Encapsulated NMs often show improved penetration and slower release than conventional pesticides.[125] Gao *et al*.[126] developed THI@HMS@P(NIPAM-MAA as a temperature-responsive release formulation prepared with thiamethoxam by seeded precipitation polymerization and a silica core (0, 4, 8, 16 and 32 mg/L); the authors reported increased adhesion to rice (*Oryza sativa* L.) leaves as a foliar spray, as well as improved temperature-responsive release and effectivity against *Nilaparvata lugens*, when compared to the conventional insecticide. Huang *et al.*[127] investigated the mixing of thiamethoxam (TMX)-loaded UIO-66-NH_2/SL (metal-organic framework) with a mass ratio 1/200 for use on rice seeds for protection against planthoppers over a period of 42 days. Whereas, showing pest affecting seeds with uncoated TMX after 6 days.[127] Feng *et al.,*[128] reported that dinotefuran® with carboxymethyl chitosan (DNF@MIL-101@CMCS) prolonged the insecticidal effects due to the outer layer of carboxymethyl chitosan being destroyed and releasing the insecticide in a more controlled fashion. Improving its efficiency by 3.4 times when compared to the uncoated dinotefuran®.[128] Importantly, NPs can also be utilized as insecticides to protect crops and grains during storage to decelerate quality loss.[129] Laisney *et al.*[130] reported that the use of CeO_2 NPs (4nm) coated with diethylamioethyl dextran (250 ng/µl) for orally delivering short hairpin RNA (shRNA on CeO_2 dextran-DEAE NPs) against *Euschistus hero* increased mortality in both ratios (3.5:1 and 0.7:1) when compared to controls. **Table 2 (supplementary information)** lists additional studies of NPs with insecticidal properties. Future research is needed for further understanding the underlying mechanisms of NPs interactions with insecticidal and pesticidal properties and their potential damage to beneficial insects. Also considering the use of life cycle analyses will allow a broader understanding to reduce detrimental effects to non-targeted organisms.

3.2- Application of nanomaterials for mitigation of fungal damage

Fungal pathogens account for some of the most damaging approximately 85% of plant diseases.[131] Fungal diseases attack seedlings and other plant tissues at different growth stages; the result is significantly reduced yields, leaving the agricultural sector with significant losses that can reach a 10-23% pre-harvest and a 10-20% at post-harvest.[132] Some parasitic fungi known as necrotrophs release toxins to kill individual plant cells and tissues, subsequently extracting the released nutrients. Alternatively, biotrophs need living plant tissue for nutrients and successful colonization;[116] others use a combination of strategies and are considered hemibiotrophic pathogens. *Magnaporthe oryzae* is a biotroph and causes rice blast disease. Qiu *et al.*[133] reported that infected rice (*Oryza sativa* L.) seedlings treated with ZnO NPs (0, 50 and 200 mg/L) showed pathogen inhibition by reducing abscisic acid (ABA) levels, increasing both ROS accumulation and expression of genes that are related to plants defense (*OsNAC4, OsKSL4, OsPR10* and *OsPR1b*) when compared to controls. Alotaibi *et al.*[134] synthesized nanoscale CeO_2 using quinoa leaf extract and applied as foliar spray (0, 50, 75 and 100 mg/L) to treat *Ustilago tritici* in wheat (*Triticum aestivum* L.); the authors showed that 100 mg/L significantly decreased the disease severity index.[134] Mondéjar-López *et al.*[135] synthesized biogenic silver (AgNP-CH) with chitosan from recycled residues of wheat (*Triticum vulgare*) leaves. The NM was applied as a seed coating to treat *Fusarium ozysporum*, *Aspergillus niger*, *A. versicolor*, and *A. brasiliensis*. The authors reported increased biomass and root length with AgNPs and increased chlorophyll *a, b* and total (2.63 μg/mL, 10.73 μg/mL, and 0.63 μg/g DW) and shoot length with AgNP-CH.[135] Adisa *et al.*[136] found that the foliar application of CeO_2 NPs (0, 50 and 250 mg/L) to tomato (*Solanum lycopersicum*) planted in pots with soil infested with *Fusarium oxysporum* f. sp. *Lycopersici* showed an increase in fruit dry weight by 67% when compared to infested untreated control. The authors also reported an increase in Ca (261%), P (26%), and S (27%) in the fruit tissue. Functionalized biodegradable layered double hydroxide (LDH) nanosheets were used as carriers of dsRNA molecules to mitigate *Fusarium oxysporum* f. sp. *Radices-lycopersici* in tomato fruits by a topical application (300 μg dsRNA in 3mL of double distilled water per plants of dsRNA) targeting genes such as lanosterol 14α-demethylase (FoCYP51), chitin synthase 1 (FoChs1), and elongation factor 2 (FoEF2), resulting in a protection for at least 60 days.[137] Anum *et al.*[138] reported that AgNPs bio-fabricated with *Amaranthus viridis* L. leaf extract as a foliar application alleviated *Botrytis cinerea* fungal infection in tomato (*Lycopersicum esculentum*) plants; the authors reported improved chlorophyll (39.69 μg/g), carotenoids (10.05 μg/g), protein (0.31 mg/g), sugar (0.68 μg/g) and, proline (0.19 μg/g) content when compared to controls. Thammachote *et al.*[139] reported the use of AgNPs against *Lasiodioplodia theobromae* in mangosteen fruit (*Garcinia mangostana* L.); AgNPs at 300 ppm showed inhibition properties similar to that of carbendazim, which is a conventional benzimidazole fungicide used to manage soilborne diseases.[140] Other nanomaterials have also shown potential to reduce fungal damage, such as amorphous SiO_2 NPs when applied to soil with maize (*Zea mays* L. TIP TOP) against *Aspergillus niger* and *Fusarium oxysporum*. The increased silica content in the cell walls promoted leaf structural integrity and helped to resist infection.[141] **Table 2 (supplementary information)** lists additional studies related to NPs use against fungal pathogens. Importantly, NPs have shown efficacy at lower doses, but fungal pathogens have demonstrated significant ability to develop resistance against conventional formulations; whether that occurs with nanoscale control strategies remains to be seen. In addition, there is the need for further investigations to understand how these materials may impact non-target species in the environment, including the soil and rhizosphere microbiome.

3.3- Application of nanomaterials for mitigation of bacterial damage

Beneficial bacteria are pivotal for healthy plant growth, being crucial for plant nutrition, biological nitrogen fixation, phytohormone production and regulation, and tolerance against biotic and abiotic stresses.[142] However, there are a large number of phytopathogenic bacteria that cause a wide range of damaging diseases that can compromise health by causing cankers, galls, knots, tumors, scabs, spots, blights, soft rots and vascular wilt diseases.[143,144] Plants can be infected either by intracellular or intercellular pathways.[145] Common pathways include contaminated irrigation water, rain, soil, wounds, stomata, lenticels, hydathodes, and insect grazing. Gogoi *et al.*[146] biosynthesized AgNPs at varying concentrations using osbeck fruit (*Citrus grandis* L.) and conducted an *in-vitro* experiment to combat *Bacillus cereus,* and *Pseudomonas syringae* pv. *syringae.* The authors reported a minimal inhibition concentration at 20 and 30 µg/mL respectively, with no cytotoxicity in murine macrophage RAW264.7, though further evaluations are needed for comparison with a conventional option.

Additional bacterial pathogens include *Pseudomonas, Ralstonia, Xanthomonas, Erwinia, Xylell*, and *Agrobacterium,* among many others. *P. syringae* pv. *Syringae* bacteria reproduce in the apoplast and can cause canker, late blight, dieback of tree branches, necrosis of leaves, phytotoxin toxicity, injury, or even death of plant; the plant will only be infected once the bacteria enter the plant.[147] *Xanthomonas campestris* can be present in seeds and plants and causes leaf spot disease. Giri *et al.*[148] demonstrated that the foliar application of chitosan fabricated biogenic silver nanoparticles (Ch@BSNP) (0, 5, 10, 15 and 20% in 60 µg/mL) reduced the *X. campestris* population on leaves (50%) and the overall stress response as measured by decreases in GoPx (36.58%), APx (41.52%), and PAL (2.10 fold); the authors also reported increased sugar (15.43%), flavonoids (104.08%), and phenolic content (49.10%) when compared to controls. *Ralstonia solanacearum* is another important bacterial pathogen that is transmitted to plants through infected soil to the roots.[88,149] This can cause wilt disease in a variety of crops of both monocot and dicot plants, which can be shown by a yellowish discoloration in the vascular tissue, and later to a brownish color once the infection is advanced. Narasimhamurthy *et al.*[150] demonstrated that this bacterial disease can be mitigated with chitosan-derived nanoparticles (CNPs) (0, 10, 50, 100, 150, 200, 250 and 500 mL/100kg seeds) when used as a seed treatment. At 200 and 250 mg/kg CNPs, greater tomato seed germination (98 and 97%) and vigor index (1715 and 1571.4) were reported, as well as upregulation of the key antioxidant enzymes PAL, POX, PPO, CAT and GLU. In an integrated approach, Khan *et al.*[88] reported that silicon nanoparticles (SiNPs) and *Trichoderma* metabolites alone or in combination alleviated *R. solanacearum* stress by damaging the pathogen's cellular structure when applied in the soil used for growing tomato (*Solanum lycopersicum* L.). **Table 2 (supplementary information)** describes additional studies related to NPs with antibacterial properties. More studies are needed to further understand the mechanisms by which NPs affect phytopathogenic bacteria, as well as the effects on endophytic bacteria and other non-target species. Also, there is a need to consider if the NPs used enhance the uptake of contaminants or their aggregation in stomatal closure. In addition, the possible mutation of bacterial defense mechanisms against NPs needs to be investigated. Finally, life cycle analyses and field studies and dose response studies are needed to fully understand the potential of these management strategies.

3.4- Application of nanomaterials for mitigation of viral infections

Plant viruses can deprive plants of nutrients, leading to a variety of diseases, and a reduction of vigor and often death. Interestingly, it has been reported that some plant viruses increase host plant tolerance to drought, salinity, and low temperature stress.[151] Nonetheless, viral plant pathogens account for yearly losses that surpass $30 billion worldwide.[152–154] There are over 2,100 viruses known to attack plants, though not all of them are equally detrimental.[154] Symptoms of infection include chlorosis, mottling, leaf curl, decreased size and yield. Viral classification according to the Baltimore System includes double-stranded DNA, single-stranded DNA, positive-sense RNA, negative-sense RNA, reverse-transcribing RNA, and retrovirus reverse transcriptase DNA.[155] Viruses rely on different vectors for introduction, including garden tools or insects to infect a cell and start its cycle to produce copies for systemic spread. Plants have evolved gene silencing as a defensive strategy; here, innate plant enzymes are synthesized that fragment viral RNA resulting in a reduction or suppression of the foreign proteins that proliferate during infection. NMs can be used as carriers of model RNA molecules to aid in a continuous and targeted delivery of genetic material to induce this response, triggering plants innage silencing response.[156] Also, mentioned by Koeppe *et al.,*[157] the effectivity and the endurability of exogenous RNA have been enhanced by utilizing polymeric, inorganic, and lipid-based NPs. Some studies reported that NPs can help in the early detection and amelioration of plant viruses. For example, Lin *et al*.[30] reported that Au nanorods (prepared using the seed-mediated growth approach) as sensing material combined with fiber optic particle plasmon resonance immunosensor (AuNRs FOPPR) allowed the detection of infected orchids (*Phalaenopsis* sp.), providing an estimate of overall disease pressure in only 10 minutes, sensing both *Cymbidium mosaic virus* and *Odontoglossum ringspot virus*. Both viruses are single-stranded RNA and known to move cell-to-cell generating synergistic symptoms in orchids; importantly, these are two of the most persistent viruses in orchids at a global level.[158] This sensor showed a better duplicability when compared to enzyme-linked immunosorbent assay (ELISA) and enabled rapid action for the removal of infected plants to prevent further spread. Ramesh and Viswanathan[159] reported that an AuNP (1 ng/µL to 1 ag/µL) assay showed better screening detection than PCR for *Begomoviruses* in pepper (*Capsicum annum* L.) and tomato (*Solanum lycopersicum*), which is spread by whitefly. NPs have been shown to interact with the exterior of viruses and assist in obstructing the entrance into plant cells, as well as directly increasing plant defense gene expression.[160] Rivero-Montejo *et al.*[153] reported that foliar application of ZnO NPs at 200 mM as preventive treatment in pepper plants (*Capsicum annum* L.) helped decrease *Pepper huasteco yellow vein virus* symptoms (inoculated with biolistic delivery) and also slowed the spread of virus in the plant. Three different varieties of tobacco plants (*Nicotiana glutinosa, N. bentamiana,* and *Nicotiana tabacum* cv. K326) were treated with a plant protein based self-assembling core shell nanocarrier (BQX@PP@SNPs) by foliar application against *Tobacco mosaic virus* (applied 1 mL of TMV-GFP supernatant to wounded leaves); reduced symptoms, as well as increased defense responses by SA and ABA related genes were reported. The authors noted that an improved delivery system giving slow release of the active ingredient, as well as promoted plant growth in all different varieties.[161] **Table 2 (supplementary information)** shows additional studies in this space. Importantly, additional studies are needed on application of NPs are needed for the development of virus early detection. Also, it is essential to understand the dynamics of plant/virus interactions as a function of nanoscale treatment regimens, as well as efficacy in systems experiencing multiple stressors.[156]

3.5- Application of nanomaterials for mitigation of nematode damage

Nematodes or roundworms are fundamental for a healthy soil environment for plants and are pivotal bioindicators, pest regulators and nutrient recyclers. These species form a critical part of the macrofauna and are widely present in soil; they also prey on fungi, bacteria, protozoans, and other nematodes that may damage agricultural crops. Similar to other species, there are beneficial nematodes and plant parasitic nematodes (PPNs). Parasitic nematode stress refers to nematodes that feed on plants, damaging their root system and decreasing the ability to uptake nutrients and water.[162] PPNs can attack seeds, fruits, leaves, stems, and roots, though they are more commonly impact roots due to their proximity to the soil. Common symptoms include wilting, nutrient deficiency, and growth retardation. Globally, approximately 20% of crops are significantly damaged by parasitic nematodes.[163,164] One of the most damaging PPN is the root-knot nematode (*Meloidogyne incognita*), which significantly impacts many crops, including fruits, grasses, weeds, and vegetables. After entry is through the roots, the pathogen spreads and creates galls, where female then lay eggs that continue the cycle of infection.[165] NPs of Ag embedded within microcrystalline cellulose have shown nematocidal properties against *M. incognita* extracted from black nightshade roots (*Solanum nigrum* L.). The in-vitro study showed that at 20-40 ppm, the nematode mortality rate was 40.36% at 24 hours (20 ppm) and 95.53% after 72 hours (40 ppm), presumably due to cellular mechanisms and membrane permeability, and ROS induced on cells.[163] Pan *et al.*[166] worked with tomato plants (*Solanum lycopersicum*) infected with *M. incognita*; the authors applied nano-capsules of enzyme-responsive release abamectin® (AVB1aNCs) at 1.0 mg a.i./plant, using sodium carboxymethyl cellulose as carrier. The authors found continuous delivery, improved mobility (horizontal and vertical), increased permeability to roots, and decreased harm to earthworms when compared to the AVB1a EC. Gan *et al*.[167] reported the application of a pH-responsive fluorescent nanopesticide utilizing thiamethoxam, mesoporous silica NPs and polyamidoamine (THI@PAMAM@MSN) with nematocidal properties when sprayed on pine twigs and needles at 0, 50, 100 and 200 µg/mL (based on THI content). This formulation showed greater stability than water-dispersible granules of thiamethoxam (THI@WG), with a decomposition rate as low as 28.88% after UV irradiation for 24h and wettability with an adhesion of 88.41×10^{-3} J/m².[167] ZnO NPs applied to *C. elegans* have been reported to reduce nematode reproduction.[168] Additional studies with NPs against nematodes are presented in **Table 2 (supplementary information)**. Importantly, additional research is needed to understand the impact that these nanoscale control measures have on beneficial nematodes, non-targeted organisms, concentration optimization and overall soil health impacts.

3.6- Application of nanomaterials for mitigation of weed stress

Non-desirable weed species will compete for space, nutrients, and water with crops. Herbicides are used extensively to control weed species but like other agrochemicals, their efficiency is low, and these materials can present a hazard to human health and the environment. Nanoherbicides, mainly through the use of nanocarriers, represent a sustainable alternative.[1,169] Here, controlled, tunable and even responsive release can result in much greater control with far less material and impact on the environment.[31,170-172]

A commonly used herbicide against weeds such as annual grasses in crops of corn, sorghum and sugarcane is atrazine. However, at high concentrations, it has shown mortality and histopathological consequences on soil-dwelling invertebrate species such as *Nsukkadrilus mbae.*[173] Oliveira *et al*.[174] reported that atrazine-containing poly (ε-caprolactone) nanocapsules reduce the dose needed for herbicidal efficiency against mustard (*Brassica juncea*) by a ten-fold of the suggested atrazine dosage (2000 g/ha). Metribuzin is commonly used for weed control in tomato, soybeans, potatoes, alfalfa and many other crops. This synthetic organic compound is a triazinone herbicide and its use can be a potential hazard to humans, fauna, and flora since it can accumulate in soil and water, is harmful through skin absorption, inhalation, and ingestion.[175]

Taban *et al.*[176] investigated an alternative option using Arabic gum-gelatin and apple pectin cross-linked by citric acid with essential oils NPs at 0, 1, 2 and 3 mL/L; the authors reported similar herbicidal effects against amaranth weeds (*Amaranthus retroflexus*) when compared to Metribuzin herbicide.[176]

Glyphosate is perhaps the most commonly used herbicide for weed control but has been reported to have concerning effects on non-target species. For example, in two studies done by Motta *et al.*[177] and Motta and Moran[178], the authors reported that exposure to this herbicide negatively impacted the gut microbiome of exposed honeybees and bumble bees. It has also been reported to increase ROS and apoptosis in human hepatocellular cell lines upon exposure, as well as negatively affect mitochondrial respiration efficiency in human sperm.[179,180] Chi *et al.*[181] found that the controlled release of glyphosate by a magnetic-responsive action palygorskite-based nanocomposite (0.5 mg/mL water) showed efficacy against tifdwarf bermudagrass (*Cynodon dactylon* L.) when compared to control treatment; the targeted weed species started to die within 6 days, which shows that the release can be controlled by magnetic field. Tribenuron-methyl herbicide is commonly used on cotton, canola, oats, and sunflowers. Still, agricultural run-off can lead to toxicity to non-target organisms like silver carp, common carp, and caspian roach fish.[182] Heydari *et al*.[183] used a microemulsion of tribenuron-methyl and pluronic as a transport nanocarrier for 2,4-D and showed efficacy against *Convolvus arvensis* at 50% of the conventional dose.[183] 2,4-D is an herbicide that functions as a plant hormone and damages the meristematic tissue of weed species. This herbicide is known to have a high mobility in soil, meaning that there is a greater chance of runoff contamination of groundwater and surface water.[184,185] Gao *et al.*[185] synthesized 2,4-dichlorophenoxyacetic acid (2,4-D@HTlcs) with Zn-Al HTLc nanosheets via a facile one-pot method and demonstrated effectiveness against *Amaranthus retroflexus* and reduced soil leaching when compared to conventional 2,4-D sodium salt. In another study, Cao *et al.*[184] synthesized positive-charged functionalized mesoporous silica NPs synthesized with trimethylammonium (MSN-TA) as an herbicide carrier and reported a reduction of 2,4-D leaching to the soil and showed continuous herbicidal activity against targeted plants as compared to 2,4-D sodium salt. Logran® is a sulfonylurea herbicide with the active ingredient triasulfuron and is commonly used for controlling weeds of many crops such as wheat, oats, and barley. Mejías *et al.*[186] showed that an encapsulation of herbicides of ortho-disulfides with metal organic frameworks based on zinc imidazolate (MOF@DIS-NH2 and MOF@DIS-O-acetyl) demonstrated better transport, aqueous solubility and bioavailability compared to conventional Logran®. The above studies show that the modification of some conventional herbicides with nanotechnology, largely through the use of carriers for more precise delivery, can reduce environmentally negative impacts, enabling increased crop yield without harming the environment. **Table 2 (supplementary information)** describes additional studies on this topic. However, further research is needed to fully comprehend exposure time, time release, and impact of nanoherbicides under different application scenarios, as well as the impact of factors such as soil pH and composition, microorganisms, and climate weed stress response in crops species.

4. Conclusions and future perspective

The use of NPs in the agricultural sector has increased dramatically in recent years and continues to proliferate. Nanopesticides, nanofertilizers, nanoherbicides, nanosensors, nanonematocides and nanofungicides are being developed as strategies to increase the efficiency and sustainability of agriculture while simultaneously increasing yield and mitigating negative environmental impacts. Sustainable agriculture aims to achieve healthy soil, high-quality seed, better yield, healthy plants, and effective pest/pathogen management. By evaluating the existing literature, one can see that there are still several important knowledge gaps that need to be addressed when considering the use of NPs in agriculture **(Figure 4),** including:

4.1 Current Research Gaps and Future Perspective

(i) Experimental designs often have significant shortcomings, such as appropriate positive and negative controls, including conventional, ionic and non-nanoscale exposures.

(ii) There is still a need for understanding how nanomaterial properties such as size, morphology, charge, coating/functionalization and concentration affect plant response and plant-pest/pathogen interactions.

(iii) There is much work that has to be performed related to nanoparticle exposure routes, and application times. These parameters should be optimized for greatest agricultural benefit.

(iv) It is very important that studies on plant assimilation, transport, fate, and potential toxicity associated with the use of NPs must be evaluated and understood under environmentally relevant conditions.

(v) Plant species vary in their response to abiotic and biotic stresses and NPs application as a function of developmental stage; thus, studies need to compare different plant life stage and cycles.

(vi) Finally, biotic stresses can lead to abiotic stress and vice versa. Often, more than one stress or a combination of stresses can impact plants/crops at the same time; thus, considering multiple stresses can help in understanding their interactions and will be more environmentally relevant.

(vii) Additional work must focus on the potential risks associated with nanoscale strategies to alleviate stress to ensure the safety and sustainability of all approaches.

(viii) Few studies conducted life cycle field experiments to verify the effects of nano-agrichemicals on yield and nutritional quality, especially there is lack of multiple-year and multiple-location experiments. Only by doing this, technology-readiness-level of nano-enabled agro-technologies can be improved and be closer to commercial application.

(ix) A broader focus on the environmental risks and safety when using NM in agriculture, accounting phytotoxicity, accumulation in soil and the impact on non-targeted organisms.

In conclusion, although significant knowledge gaps remain, the use of nanoscale materials to alleviate abiotic and biotic stress in agricultural systems has demonstrated tremendous potential. Considering the dramatic challenges we will face in feeding the global community in a changing climate, work such as this should expand dramatically, with a specific focus on developing and deploying technologies in the field that can begin to solve this wicked problem.

Author contributions

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Conflicts of interest

The presented review article has not been influenced by any financial or personal interest that could be perceived as competing from any of the authors.

Data availability

The review article relies on previously conducted studies, thus there is no new data to report. All the referenced studies have been cited properly to acknowledge the original authors' intellectual property.

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Abbreviations

Acronym	Meaning
NMs	nanomaterials
NPs	nanoparticles
PGPRs	plant growth promoting rhizobacteria
BSG	basil seed gum
ROS	reactive oxygen species
O_2•−	superoxide
H_2O_2	hydrogen peroxide
TiO_2@MWCNTs	TiO_2 NPs and multi-walled carbon nanotubes
MDA	malondialdehyde
SOD	superoxide dismutase

POD	peroxidase
HKT	high-affinity potassium transporters
RWC	relative water content
GO	graphene oxide
GO-Pro NPs	proline-functionalized graphene oxide nanoparticles
NO	nitric oxide
CS	chitosan
put-CQD	putrescine-functionalized carbon quantum dot
ZVI	zero valent iron
GSH	glutathione
ISR	induced systemic resistance
SAR	systemic acquired resistance
PAMPs	pathogen-associated molecular patterns
MAMPs	microbe-associated molecular patterns
PRRs	pattern recognition receptors
HR	hypersensitive response
ETI	effector-triggered immunity
SA	salicylic acid
JA	jasmonic acid
ET	ethylene
TMX	thiamethoxam
DNF@MIL-101@CMCS	dinotefuran with carboxylmethyl chitosan
LDH	layered double hydroxide
Ch@BSNP	chitosan fabricated biogenic silver nanoparticles
PAL	phenylalanine ammonia lyase
PPO	polyphenol oxidase
CAT	catalase
GLU	glutamine synthetase
ELISA	enzyme-linked immunosorbent assay
ABA	abscisic Acid
PPNs	plant parasitic nematodes
AVB1aNCs	nano-capsules of enzyme-responsive release abamectin
THI@PAMAM@MSN	pH-responsive fluorescent nanopesticide with thiamethoxam, mesoporous silica NPs and polyamidoamine

THI@WG	water-dispersible granules of thiamethoxam
2,4-D@HTlcs	2,4-dichlorophenoxyacetic acid
MSN-TA	positive-charged functionalized mesoporous silica NPs synthesized with trimethylammonium
MOF@DIS-NH2 and MOF@DIS-O-acetyl	encapsulated herbicides of ortho-disulfides with metal organic frameworks based on zinc imidazolate

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Data availability

The review article relies on previously conducted studies, thus there is no new data to report. All the referenced studies have been cited properly to acknowledge the original authors' intellectual property.

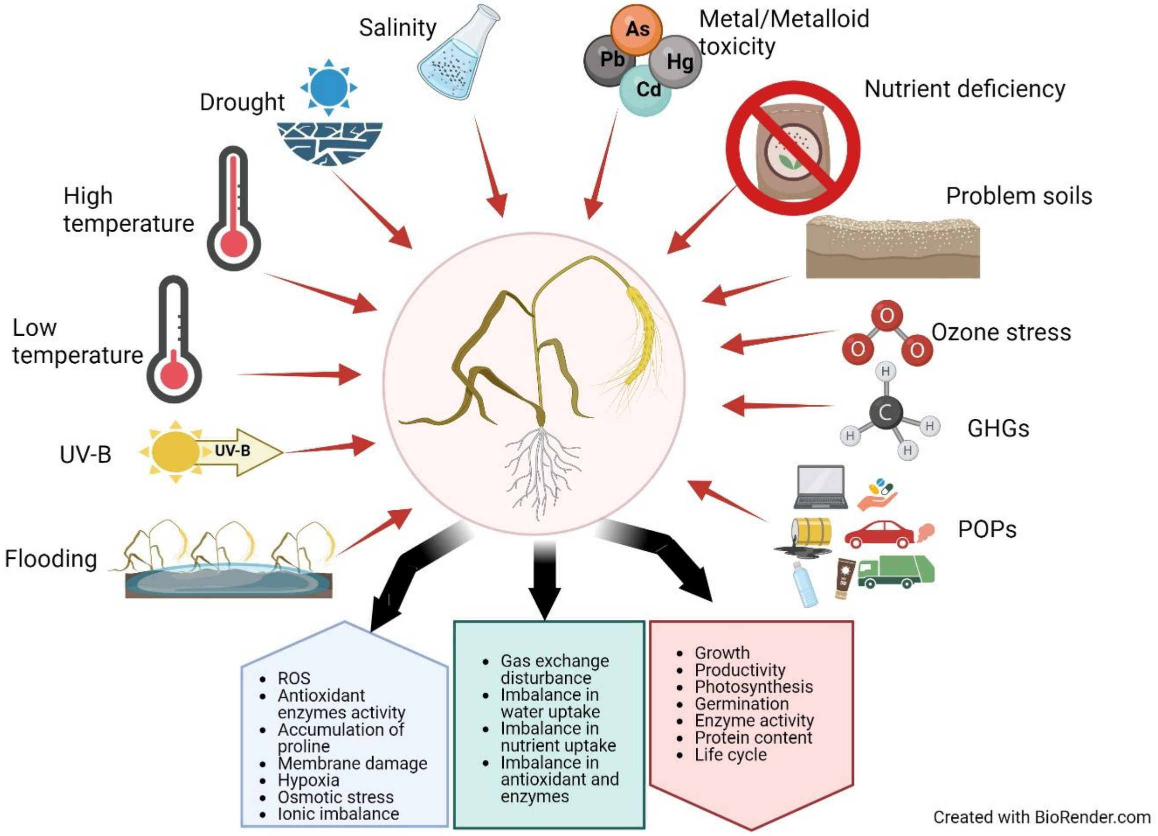

Figure 1. Schematic diagram of plant responses to abiotic stress.

Plant responses to different abiotic stresses. Symptoms can include an increase in ROS, antioxidant enzymatic activity, proline accumulation, membrane damage, hypoxia, osmotic stress, and ionic imbalance. An imbalance of gas exchange, nutrient uptake, water uptake, and antioxidant enzymatic responses is also possible, as well as a decrease in growth, productivity, biochemical activity, germination, and enzymatic activity protein content.

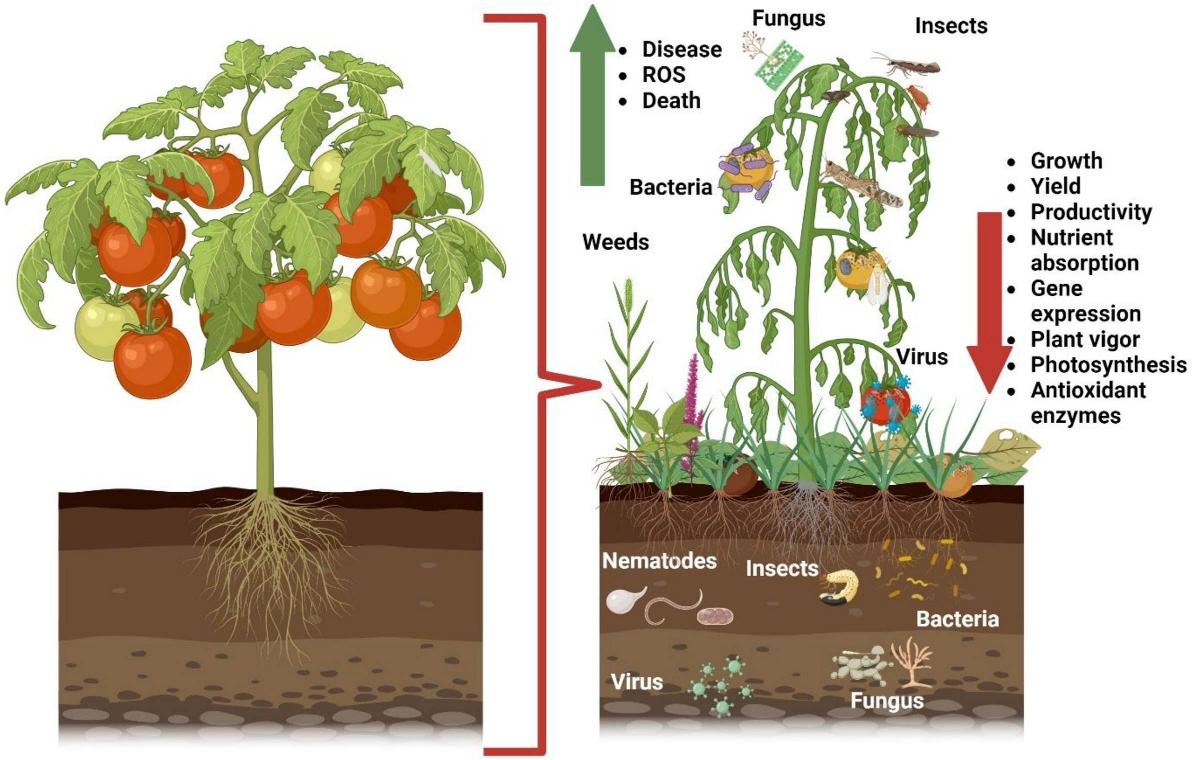

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Figure 2. Schematic diagram of plant response to biotic stress.

Plant response to biotic stresses caused by other biota such as insects, fungi, bacteria, weed nematodes, viruses, and parasites which can cause a decline in the plant's health due to associated diseases, decreasing productivity, quality, yield, nutrient absorption, gene expression, vigor, photosynthesis, antioxidant enzyme expression and life cycle perturbance.

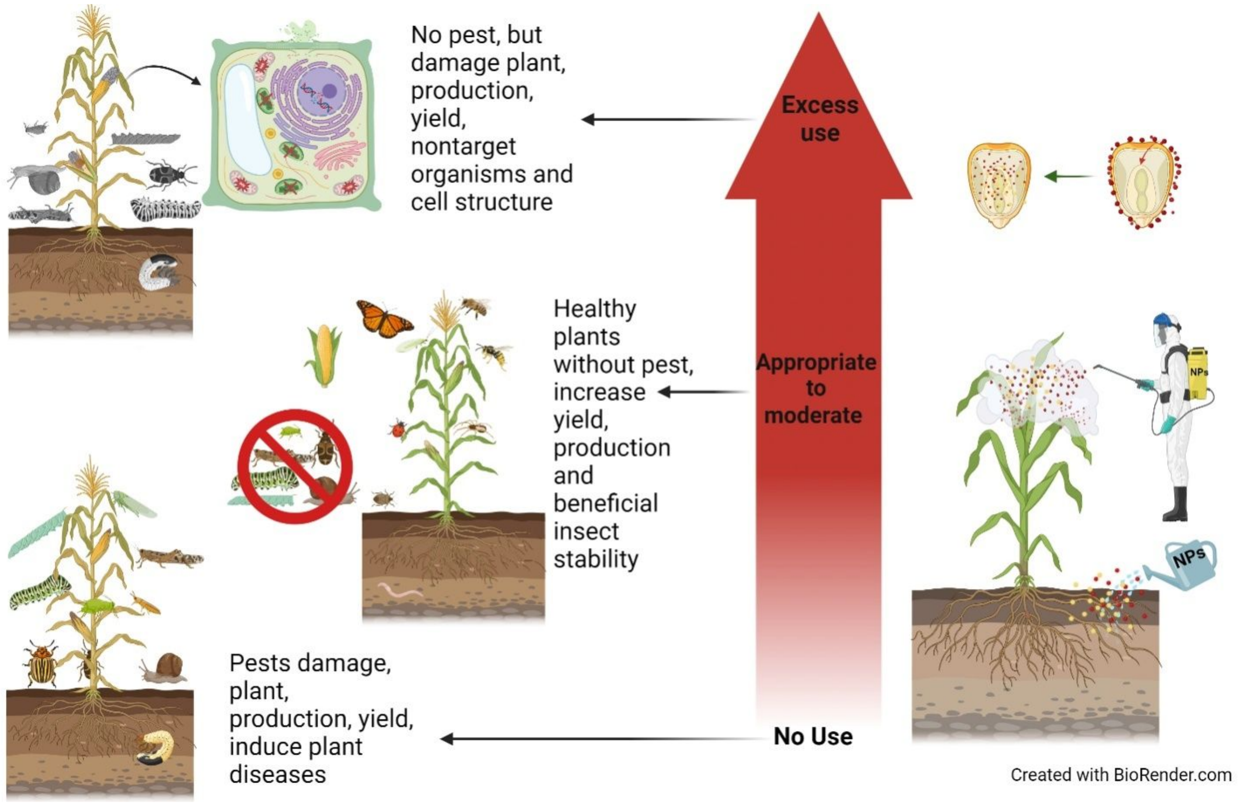

Figure 3. Schematic diagram of nanopesticide effects on crop and pest dynamics.

Potential outcomes that nanopesticides may have on plants. These are dose-dependent and show improvement from conventional pesticides such as improved adhesion, droplet formation, solubility, dispersion, mobility, bioactivity and target to specific pests if used appropriately. Benefits include increased plant yield, production and reduced environmental impact.

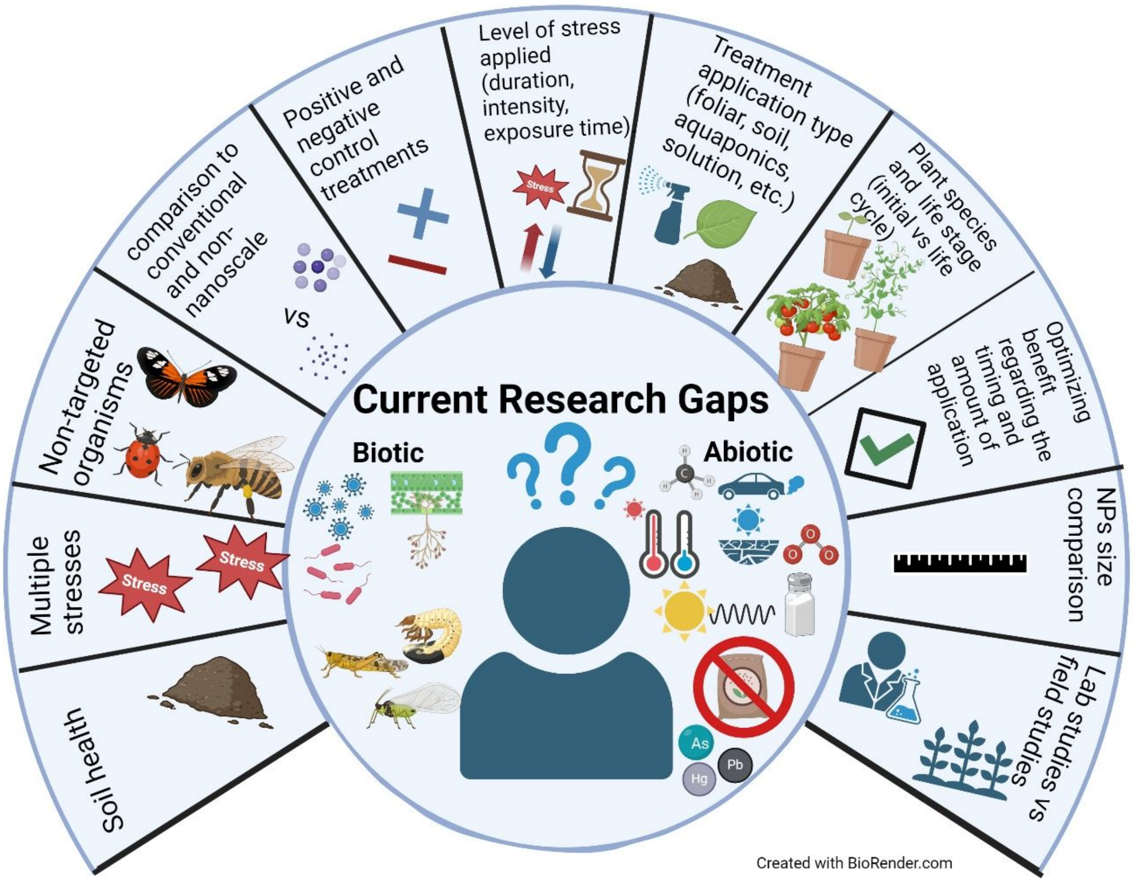

Figure 4. Current Research Gaps.

Important gaps in knowledge found in research publications related to the use of nanomaterials to reduce abiotic and biotic stress in plants and crops.