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Review

Can Nanofertilizers Mitigate Multiple Environmental Stresses for Higher Crop Productivity?

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Abstract: The global food production for the worldwide population mainly depends on the huge contributions of the agricultural sector. The cultivated crops of foods need various elements or nutrients to complete their growth, and these are indirectly consumed by humans. During this production, several environmental constraints or stresses may cause losses in the global agricultural production. These obstacles may include abiotic and biotic stresses, which have already been studied in both individual and combined cases. However, there are very few studies on multiple stresses. On the basis of the myriad benefits of nanotechnology in agriculture, nanofertilizers (or nanonutrients) have become promising tools for agricultural sustainability. Nanofertilizers are also the proper solution to overcoming the environmental and health problems that can result from conventional fertilizers. The role of nanofertilizers has increased, especially under different environmental stresses, which can include individual, combined, and multiple stresses. The stresses are most commonly the result of nature; however, studies are still needed on the different stress levels. Nanofertilizers can play a crucial role in supporting cultivated plants under stress and in improving the plant yield, both quantitatively and qualitatively. Similar to other biological issues, many open-ended questions still require further investigation: Is the right time and era for nanofertilizers in agriculture? Will the nanofertilizers be the dominant source of nutrients in modern agriculture? Are nanofertilizers, and particularly biological synthesized ones, the magic solution for sustainable agriculture? What are the expected damages of multiple stresses on plants?

Keywords: salinity; drought; heat stress; nanofertilizers; combined stress

1. Introduction

Nowadays, food security faces a great challenge, which is persistently represented in the rapid increase in the global population and the drastic changes in the climate [1]. This food security mainly depends on the agricultural sector, and particularly on crop production, which supplies the human diet with the major sources of the bioactive compounds for human nutrition [2,3]. This productivity faces different stresses, which may produce losses of up to 50–70% in the case of abiotic stresses, and of up to 40–60% in the case of biotic stresses [4]. The most common abiotic stresses include salinity, drought, flooding, and heat stress, whereas bacteria, viruses, and fungi are the key biotic stresses. These stresses can be mitigated in cultivated plants through the application of a variety of antistressors, such as nitric oxide [5]; pyraclostrobin [6]; rhizobia, or plant-growth-promoting rhizobacteria (PGPR) [7,8]; melatonin [4]; strigolactones [9]; phytohormones [10]; and nutrients such as silicon [11,12] and selenium [13], as well as their nanoforms [9,14]. Several studies have already been published on the individual stresses [6,9,15], but there are only a few publications on combined stress (e.g., [1,14,16–18]), and very few articles on multiple stresses [19].

Nanofertilizers are considered to be promising candidates for the fertilizer industry, and they have the considerable potential to improve the retention of different nutrients for optimal crop production [20]. Nanofertilizers may be crucial for plant nutrition and human health [2], particularly the current nanofertilizers, which are highly efficient (50–70%) compared to traditional fertilizers (40–50%) in terms of the controlled release of the nutrients [21]. These nanofertilizers can solve the main problem of traditional fertilizers (i.e., the high nutrient losses in the soil) by allowing the slow and sustained release of nutrients over an extended period. They also have high reactivities because of their small sizes, high surface areas, and increased productivity [22]. Several nutrients have been used through soil and/or foliar application in cultivated plants (e.g., Cu, Mn, and Zn, which support crop productivity [20]), as has been reported for the following studied crops: wheat [23], maize [24], tomato [25], sweet basil [26], lettuce [27], cabbage [28], and strawberry [29].

Therefore, this review attempts to highlight nanofertilizers and their impacts on crop production. The effects of the application of nanofertilizers on plants under stressful conditions (i.e., individual, combined, and multiple stresses) are also investigated.

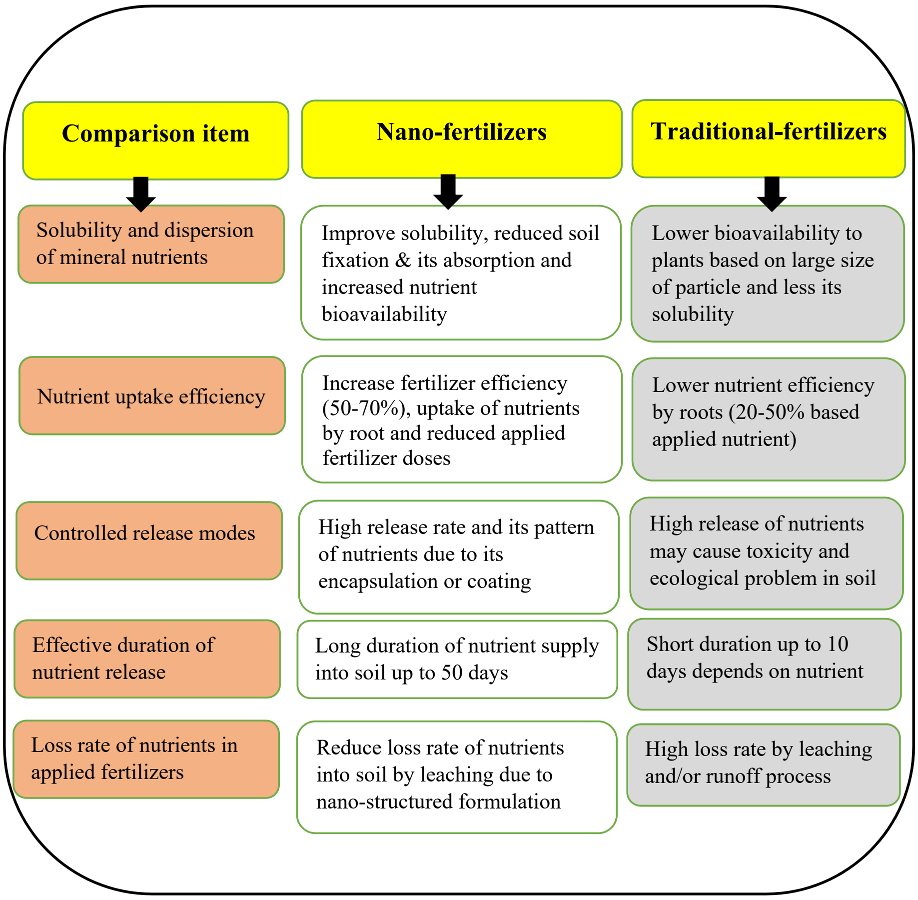
2. Nanofertilizers and Agriculture

2.1. Nanofertilizers for Crop Production

Nanotechnology can be defined as the science of the production of nanoparticles through the modification and/or self-assembly of individual atoms, molecules, or molecular clusters, which are endowed with new or drastically different properties [30]. Nanotechnology has several applications in all sectors, including agriculture, industry, medicine, pharmacology, etc. In the agriculture sector, nanotechnology applications can be broadly classified into the following main sectors: (1) Crop production through the use of nanoherbicides/nanopesticides and nanomaterials to control the viral and fungal diseases of plants; (2) Precision farming; and (3) Crop improvement using nanofertilizers and nanobiosensors for soil/plant systems, and for the nanoremediation of soils, water, and the food sector [31–33]. Although agro-nanotechnology has several benefits, nanomaterials may also be associated with many risks, which include: (1) Safety issues that are due to the penetration of the cells, which are small sizes; (2) The degradation of the nanomaterials and/or nanocomposites under environmental conditions, with the release of the inserted nanomaterials into the environment; (3) A significant amount of leaching of the nanoparticles into the agro-environment, which may cause nanotoxicity; and (4) The integration of many nanoparticles into the human body via inhalation, ingestion, or cutaneous contact [33].

2.2. Nanofertilizers vs. Traditional Fertilizers

There are many problems that result from the intensive use of traditional or chemical fertilizers that have led to many negative impacts on the agroecosystem, such as the low efficiency of the nutrient use by crops, and the high losses of nutrients to groundwater, especially NPK (by 40–70%, 80–90%, and 50–90%, respectively [34,35]). Thus, nanotechnology has become an emerging approach in the revolution of agricultural systems through its controlled-release manner of delivering nutrients to cultivated plants [36]. Nanofertilizers are a type of fertilizer, and they are synthesized using physical, chemical, or biological methods that are based on nanotechnology. The physical methods induce rapid synthesis, but they produce many impurities; the chemical methods are precise in terms of the size of the nanoparticles, but they may produce toxicity; and the biological methods are eco-friendly and low toxic, but they induce slow synthesis [34]. These nanofertilizers can enhance crop production by supplying one or more nutrients to the cultivated plants via smart delivery, which results in sustained nutrient release, improved plant growth, high nutrient uptake efficiency, and improved soil quality [37,38]. Compared to conventional fertilizers, nanofertilizers have many distinguished attributes, such as high nutrient uptake efficiency, controlled-release modes, effective durations of the nutrient release, and a reduced loss rate of the fertilizer nutrients (Figure 1) [30]. These benefits of nanofertilizers may support their role in the production of higher crop yields of high quality. The benefits also include the lower-cost production and eco-friendly synthesis of nanofertilizers, which may reduce the use of traditional fertilizers [39–41]. In addition, the management of crop nutrition could be achieved by using nanofertilizers, which can improve the crop productivity, and enhance the tolerance of these crops to biotic/abiotic stresses [42].



Comparison item	Nano-fertilizers	Traditional-fertilizers
Solubility and dispersion of mineral nutrients	Improve solubility, reduced soil fixation & its absorption and increased nutrient bioavailability	Lower bioavailability to plants based on large size of particle and less its solubility
Nutrient uptake efficiency	Increase fertilizer efficiency (50-70%), uptake of nutrients by root and reduced applied fertilizer doses	Lower nutrient efficiency by roots (20-50% based applied nutrient)
Controlled release modes	High release rate and its pattern of nutrients due to its encapsulation or coating	High release of nutrients may cause toxicity and ecological problem in soil
Effective duration of nutrient release	Long duration of nutrient supply into soil up to 50 days	Short duration up to 10 days depends on nutrient
Loss rate of nutrients in applied fertilizers	Reduce loss rate of nutrients into soil by leaching due to nano-structured formulation	High loss rate by leaching and/or runoff process

Figure 1. A comparison between traditional fertilizers and nanofertilizers. Sources: from Seleiman et al. [22], Kalwani et al. [42], Belal and El-Ramady [43], and Rizwan et al. [44].

2.3. The Nanofertilizer Industry and Its Obstacles

However, the nanofertilizer industry faces many challenges, which represent important and real obstacles. These risks include the release and reactivity of nanofertilizers, which depend on the environmental factors and that can cause phytotoxicity effects, depending on their doses and the durations of long-term exposure. This may lead to chronic effects on health of consumers [30]. The physical and chemical methods of nanofertilizer synthesis have recorded higher toxicities compared to the biological methods, which are still under intensive investigations [39]. The studies that have recently been published on nanofertilizers include different points of view, such as: the crucial impacts on the soil, the crop yield, and the entire environment [45]; the risks and benefits on the soil rhizospheric and plant-associated microbial communities [42]; and the use of nanofertilizers for sustainable agriculture, in addition to crop production enhancement under abiotic/biotic stresses [34–36,38,41].

2.4. Nanofertilizers for the Mitigation of Stress on Plants

Nanofertilizers have a great ability to mitigate the abiotic/biotic stresses on cultivated plants through many mechanisms because of their vast surface areas and their nanoscale size. Nanofertilizers can improve the morphological, biochemical, and physiological indices of cultivated plants, such as the photosynthetic rate and its efficiency, the nutrient uptake efficiency, the regulation of phytohormones, and the enhancement of the plant defense system (Figure 2) [41]. Therefore, the mechanisms of nanofertilizers on the crop productivity under stress may include: a reduction in the oxidative stress, which leads to an increase in the stress tolerance of the plants; the enhancement of several biochemical activities in stressed plants (e.g., by increasing the contents of the proline, chlorophyll, and relative water); the regulation of the salt toxicity; a reduction in the accumulation of malondialdehyde and H_2O_2; and the maintenance of the ionic equilibrium, depending on the type of stress [46]. The mechanisms of nanofertilizers mainly depend on the nanoactive ingredients (the large specific surface areas), which could result in an acceptable reactivity, which could increase the effective uptake of nutrient elements for the growth of cultivated plants and their metabolisms. Nanofertilizers allow for the encapsulation of the nutrients by nanomaterials, for the delivery of them as nanoparticles or emulsions, or for the release of the nutrients in a controlled manner, as "smart" nanofertilizers [47].

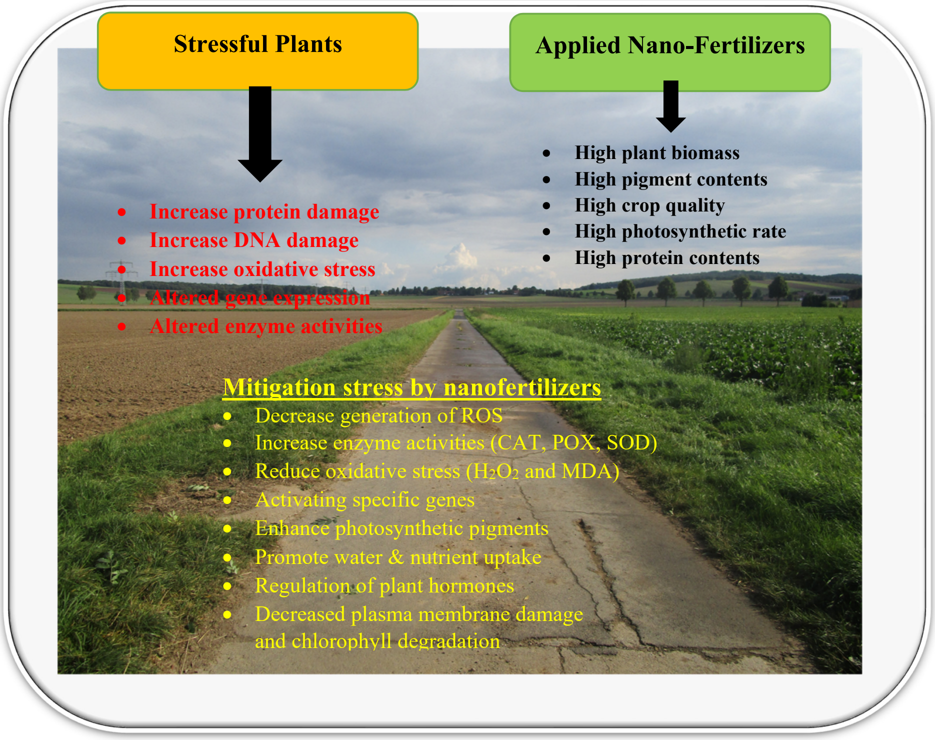


Figure 2. The main problems that result from stresses on plants, the expected roles of applied nanofertilizers, and the different mechanisms of the mitigation of stress on cultivated plants by nanofertilizers. ROS: reactive oxygen species; CAT: catalase; POX: peroxidase; SOD: superoxide dismutase; MDA: malondialdehyde.

2.5. Nanofertilizers and Their Research Gap

It is well known that cultivated plants need many essential and beneficial nutrients for their growth, which can be classified on the basis of their relative essentiality, their function, and their mobility in plants and soils [40]. There are three groups of essential mineral nutrients that uptake in ionic form from the soil solution. These groups include (1) Essential and beneficial nutrients (based on their relative essentiality); (2) A group of basic, accessary, regulatory, and catalyst nutrients (based on their physiological function); and (3) A group of mobile, intermediate, or immobile nutrients (based on their mobility in plants or soils). Further basic information about these essential nutrients is presented in Table 1. These nutrients may exist as nanosized and as nanonutrients (i.e., in sizes that range from 1 to 100 nm), and they can be naturally occurring or engineered. A "fertilizer" can be defined as any natural or synthetic material that is applied through the soil (root application) or the plant (foliar application) in order to supply the plant with nutrients. The application of nanofertilizers to crops has been gaining immense attention worldwide. It is worth mentioning that the sizes of the ions can be expressed from angstroms (10^{-10} m) to picometers (10^{-12} m), whereas nanonutrients can be expressed on the nanometer scale (10^{-9} m). Nanonutrients are 100 to 1000 times larger than their bulk ions, which protects them from being lost by leaching or runoff, or from becoming fixed in the spaces in clay lattices, which makes them more available to cultivated plants [40].

Table 1. List of basic information on essential nutrients, including their mobilities in soil and plants, and their hydrated and crystal ionic radii.

Nutrient Element	Symbol	Uptake Form	Nutrient Mobility		Ionic Radius (nm)	
			in Soil	in Plants	Crystal	Hydrated
Nitrogen	N	NH_4^+ and NO_3^-	Mobile	Mobile	0.132	0.279 and 0.345, resp.
Phosphorus	P	$H_2PO_4^-$; HPO_4^{2-}	Immobile	Intermediate	0.377	0.377
Potassium	K	K^+	Intermediate	Mobile	0.138	0.2798
Calcium	Ca	Ca^{2+}	Intermediate	Immobile	0.100	0.2422
Magnesium	Mg	Mg^{2+}	Immobile	Intermediate	0.072	0.2090
Sulfur	S	SO_4^{2-}	Mobile	Intermediate	0.230	0.3815
Boron	B	$H_2BO_3^-$	Mobile	Immobile	0.244	0.261
Copper	Cu	Cu^{2+}	Immobile	Immobile	0.072	0.073
Chlorine	Cl	Cl^-	Mobile	Mobile	0.180	0.181
Iron	Fe	Fe^{2+}	Immobile	Immobile	0.072	0.078
Nickel	Ni	Ni^{+2}	Intermediate	Mobile	0.067	0.069
Manganese	Mn	Mn^{2+}	Mobile	Immobile	0.080	0.083
Molybdenum	Mo	MoO_4^-	Intermediate	Immobile	0.267	0.270
Zinc	Zn	Zn^{2+}	Immobile	Immobile	0.070	0.075

Source: combined from [40].

Nanofertilizers can be classified into the following groups:

1. Nanoscale input fertilizers, or nanoscale fertilizers: this category includes the nutrients that already exist in nanofertilizers (nanoparticles, which contain nutrients), alone, or in combination with other constituents;
2. Nanoscale additive fertilizers, or nanoscale additives, which are traditional fertilizers with nanoscale additives. This category includes the application of nanoscale materials or formulations to the existing traditional macroscale fertilizers; and
3. Nanoscale host fertilizers, or nanoscale coating, which is formed from traditional fertilizers that have been coated or loaded with nanoparticles. This category includes nutrient or fertilizer supplements, which could be entrapped, adsorbed, or encapsulated into any type of nanospace of the host material [40].

2.6. Nanofertilizers and Phytotoxicity

There are research gaps that are related to nanofertilizer production, including with regard to the energy use and the technology expense, as well as with regard to their unknown interactions in the environment and their toxicities. There are several reports that are based on the phytotoxicities of nanoparticles in crops, which are common, and which result from the induction of the synthesis of reactive oxygen species (ROS) and the oxidative damage from the use of many metal-oxide nanoparticles, such as AgO, CeO_2, CuO, NiO, TiO_2, and ZnO (e.g., [41,46,48]). Most of the toxicity studies report on pesticides or many salts, which are not conventionally used as fertilizers for the production of crops [40]. In general, there are many features of the phytotoxicity and genotoxicity from the excessive use of nanoparticles on plants that could be mentioned, such as chromosome fragmentation, genetic mutation, ROS production, biomass reduction, and retarded growth (Figure 3) [48].

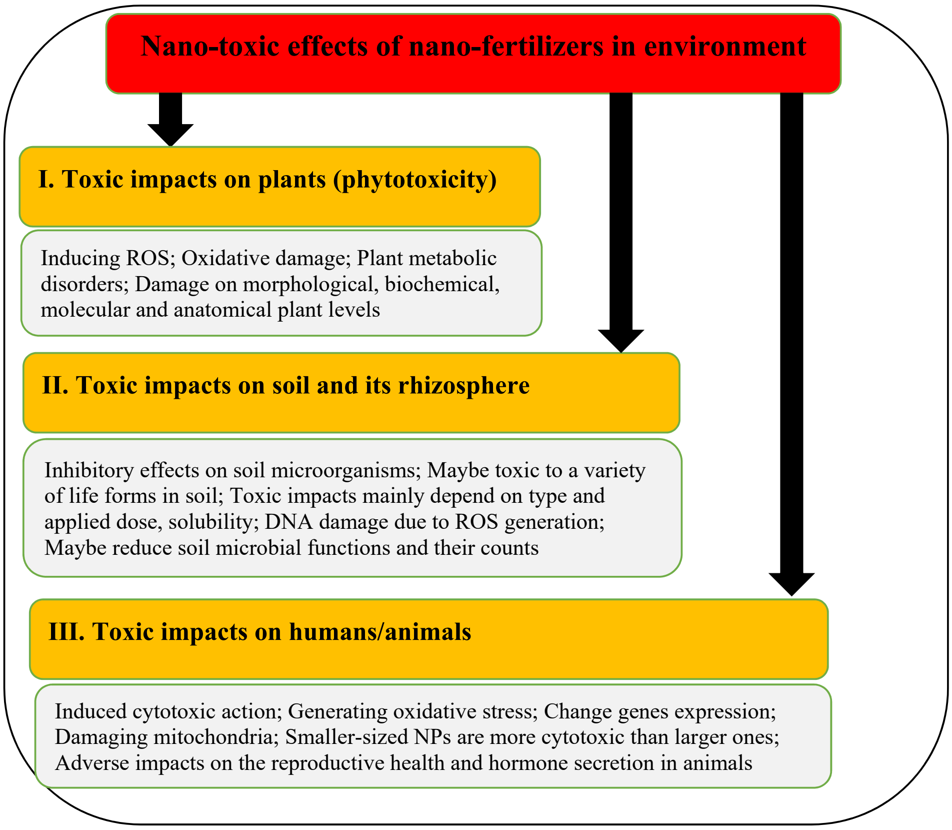


Figure 3. Different suggested mechanisms of toxic impacts of nanofertilizers/nanoparticles on plants, soil, and human or animals, which, in general, focus on the cytotoxicity and genotoxicity. ROS: reactive oxygen species. Sources for Part I: Verma et al. [41] and Zhang et al. [49]; source for Part II: Kalwani et al. [42]; and source for Part III: Bhardwaj et al. [40].

Recently, several studies have been published that report on the nano-phytotoxicities of different plants, such as *Capsicum annuum* [50], *Lycium barbarum* L. [51], *Solanum lycopersicum* L. [52], *Oryza sativa* L. [53], *Pisum sativum* L. [54], and *Hordeum vulgare* L. [55], whereas there are only a few studies that focus on this phenomenon with regard to the use of nanofertilizers, such as Bhardwaj et al. [40], Kalwani et al. [42], and Zhang et al. [49]. The ecotoxicological implications of nanofertilizers on other agro-ecosystems besides plants has been investigated in detail, such as the soil and its rhizosphere [42]. The expected toxic effects of nanofertilizers on the food chain and, subsequently, on human health, especially under higher doses, still requires more studies, which should use different crops and different kinds of nanofertilizers. However, many published works report on the accumulation of nanoparticles in soil/plant systems and their potential effects on human health, such as Rajput et al. [56], Toksha et al. [45], and Babu et al. [38].

2.7. Nanofertilizers and Climate Change

It is well known that nutrients can be lost from agricultural fields through the leaching process and/or through gaseous emissions, which may lead to environmental pollution and climate change. These environmental issues may be mitigated by applying nanofertilizers, even under stress [57]. There are a few studies that have been published on the impact of applied nanofertilizers on reducing gas emissions to the atmosphere (such as [58,59]). Nanoparticles are the most important adsorbents in soil, and they can affect the nutrient transportation, the organic matter fixation, and the precipitation of the new mineral phase. In the future, the presence of nanoparticles in intact soil formations will be crucial. Furthermore, nanoparticles have direct effects on plants, which include increased enzyme activity, better seed germination, increased plant tolerance to adverse conditions, increased carbon sequestration and nitrogen fixation, and increased photosynthetic and respiratory activities [60]. Therefore, the role of nanofertilizers in mitigating climate change is an urgent global concern. Further studies are needed to answer many questions with regard to the role of nanofertilizers in the promotion of crop production under stress and climate change, such as: What is the role of nanofertilizers in increasing the plant's ability to tolerant climate change? What is the expected scenario of increasing the temperature, which leads to heat stress, on this role of nanofertilizers? Is there a certain scenario that belongs to each kind of nanofertilizer for each climatic zone?

3. Application of Nanofertilizers

The intensive global production of foods requires the correct and proper amount of applied nutrients. However, the primary sources of nutrients were, for a long time, the chemical forms of the nutrients, which caused an environmental crisis. Nowadays, the organic, bio-, and nanoforms of these nutrients are applied at an ascent rate to replace the chemical forms of the nutrients [61]. Nanofertilizers may achieve sustainability in agriculture through their high use efficiency and by minimizing the pollution of the environment [62]. These nanofertilizers, as nanofertilizers, may also improve the crop productivity by increasing the bioavailability of these nutrients in the soil, as well as their uptake by cultivated plants. The advantage is the self-regulated, time-controlled, and spatially targeted delivery of the active ingredients [63]. Nanofertilizers can be defined as a type of fertilizer that contains nutrients in the nanoscale form, and/or nutrients in encapsulation, which can systematically release different nutrients to targeted plants [27]. Nanofertilizers represent any applied nanomaterials for which the nutrients are converted into the nanoscale, and that act as plant nutritional mediators that mainly provide nutrients to the plant in order to support its growth [63,64]. These nanofertilizers can be encapsulated through nanocoating nanoporous polymeric materials, which are supplied in the nanoforms of emulsions, or as slow-release fertilizer particles [63]. Recently, many studies have focused on nanofertilizers from different perspectives, such as: nanofertilizers and their role as plant-growth-promoters in agriculture [62]; plant nanonutrients and their transport in soils [65]; the application of nanomaterials as fertilizers [66]; reducing the dispersion rate of nano-ZnO fertilizer in the environment by entrapping it in the biodegradable polymer beads of alginate and polyvinyl alcohol [67]; coating potassium ferrite nanoparticles on di-ammonium phosphate fertilizer to improve the nutrient use efficiency of this fertilizer [68]; and using zero-valent iron (Fe_3O_4) and Fe_2O_3 nanoparticles as Fe fertilizers on rice [69]. These studies confirm the potential for using these nanofertilizers for different cases of crop production under various environmental stresses, as is presented in Table 2.

Table 2. A survey on the recently published studies on some nanofertilizers for crop production.

Nanofertilizer	Crop (Scientific Name)	Main Findings	Reference
CeO_2 NPs and nanofertilizers (N, P, K, Zn, Fe)	Cabbage (*Brassica oleracea* var. capitata L.)	CeO_2 NPs enhanced the uptake of NPK nanofertilizer; increased head weight by three times, compared to control plants.	[28]
Nano-vermicompost	Tomato (*Solanum lycopersicon* L.)	Improved tomato growth and photosynthetic performance under drought stress.	[25]
Nanoboron, nanosilica, and nanozinc	Wheat (*Triticum aestivum* L.)	Nano-Zn increased the protein (%) in wheat grains; nanosilica reduced the damage caused by drought;	[23]
Nano-urea-amorphous calcium phosphate (NUACP)	Cucumber (*Cucumis sativus* L.)	NUACP has NUE of 69%, compared to urea (49%); NUACP + 50% reduced N content of urea, resulted in the same biomass.	[70]
Nano-liposome-containing Fe^{2+}	Sweet basil (*Ocimum basilicum* L.)	Increased total leaf area, and chlorophyll, ferrous, and essential oil contents of plants, compared to the $FeSO_4$ fertilizer.	[26]
Nanoscale zero-valent iron (nZVI)	Rice (*Oryza sativa* L. cv. Gobindobhog)	Priming rice with nZVI (10–80 mg L^{-1}) enhances yield; promoted the distribution of nutrients in grains and their contents.	[71]
Hydroxyapatite nanoparticles	Maize (*Zea mays* L.)	This nanophosphate fertilizer improved growth and physiological properties of maize.	[24]
Nano-Zn fertilizer	Strawberry (*Fragaria* × *ananassa* Duch.)	Nano-Zn improved crop yield and its quality compared to conventional Zn sources (i.e., $ZnSO_4$, Zn EDTA, ZnO).	[29]
NPK nanofertilizers	Potato (*Solanum tuberosum* L.)	NPK nanofertilizers significantly improved potato yield and its parameters compared to NPK chemical fertilizers.	[72]
$Cu(OH)_2$ nanofertilizer	Alfalfa (*Medicago sativa* L.)	$Cu(OH)_2$ nanowire was considered as a potential nanofertilizer at 80 and 280 mg kg^{-1} because it prompted growth.	[73]
Nano-NPK + nanochelated-Fe	Dragon's Head (*Lallemantia iberica* (Fischer and Meyer)	Nanofertilizers improved yield components and antioxidant traits during winter cultivation compared to control.	[74]
ZnO nanoparticles (18 nm)	Wheat (*Triticum aestivum* L.)	Nano-ZnO modulated drought effects; increased growth and content of Zn, S, and Mg in grains.	[75]
ZnO NPs (67 nm and 250 mg L^{-1})	Cucumber (*Cucumis sativus* L.)	Applied *Bacillus subtilis* combined with ZnO NPs controlled powdery mildew disease as an alternative to fungicide.	[76]
Nanochelated fertilizer (N, P, K, Fe, Zn, Mn)	Peppermint (*Mentha* x *piperita* L.)	This nanofertilizer is reported to be an alternative and eco-friendly strategy in peppermint oil production.	[77]
Boron nanofertilizer	Lettuce (*Lactuca sativa*); zucchini (*Cucurbita pepo*)	Foliar spray of B-nano fertilizer increased the biomass by 58 and 66%, compared to control (B for lettuce and zucchini).	[78]
(A) nano-Ca and Mg; (B) nano-Zn-Fe-Mn	Chili pepper (*Capsicum annuum*)	Nanofertilizers promoted uptake of nutrients; improved photosynthetic pigments and cell membrane stability under salinity stress.	[79]
$FePO_4$ nanoparticles	Cucumber (*Cucumis sativus* L.) and maize (*Zea mays* L.)	$FePO_4$ NPs are an efficient source of P and Fe compared to their bulk forms and are a new and promising class of fertilizers.	[80]
Mn–Zn ferrite nanoparticles ($Mn_{0.5}Zn_{0.5}Fe_2O_4$)	Squash (*Cucurbita pepo* L.)	Nanoferrite produced the highest increase (of about 50%) as an appropriate fertilizer at 30 ppm, and was synthesized at 180 °C.	[81]
CuO nanoparticles	Green onion (*Allium fistulosum*)	Nano-CuO (150 mg kg^{-1}) increased root Ca, Fe (86 and 71%), and bulb Ca, Mg (74 and 108%), compared with control and enhanced allicin content in scallion.	[82]
ZnO NPs (zinc oxide nanoparticles)	Soybean (*Glycine max* L.)	ZnO NPs promoted seed yield up to 160 mg kg^{-1}; may consider nanofertilizer for enriching Zn-deficient soil with Zn.	[83]

Notes: (A) Lithovit®: a nanofertilizer made from limestone, which is rich in Ca and Mg, found in carbonate form; (B) a nano-chelated ZFM, which is rich in micronutrients, such as zinc (Zn), Mn, Fe, Mg, Ca, nitrogen (N) source (amino-acids), and ascorbic acid; NUE: nutrient use efficiency; nanochelated fertilizer: N (total N, 20%); P (P_2O_5, 25%); K (K_2O, 23%); Fe (FeO, 10%); Zn (ZnO, 20%), and Mn (MnO, 25%).

Recently, several products that are based on nanotechnology have been developed for utilization in the agricultural sector. These agro-nanotechnological products may include: nanofertilizers; biofertilizers; nano-biofertilizers; nano-pesticides; agricultural nano-sensors; nanomaterials for storage grains; harvested agricultural product protection; and food packaging [84]. There are several applications of nanotechnology in the fertilizer sector, which may include slow-release [20,85] or controlled-release fertilizers [86] (e.g., polymer-coated fertilizers [87] and hydroxyapatite nanoparticle-coated urea [24]), and the coating technology in fertilizers that use biopolymers [88] (e.g., chitosan and thermoplastic starch [84]). Nanofertilizers can be classified into different types, such as nutrient-based nanofertilizers (i.e., macro- and micro-nanofertilizers, nutrient-loaded nanofertilizers, and plant growth stimulators [34]); action-based nanofertilizers (e.g., controlled-release fertilizers and magnetic or nanocomposite fertilizers); and nanofertilizers that are based on the quantity that is applied (e.g., nanoscale fertilizers, nanoscale coating fertilizers, and nanocarriers) [84]. Many methods can be used for the delivery of nanofertilizers to plants, which include: in vitro methods, which include in vitro culture media [89]; aeroponics and hydroponics [90]; and in vivo methods, which include soil and foliar applications [19,61]. There is a promising race in the production of different nanofertilizers globally that includes many nutrients, such as phosphate [24], copper [91], magnesium [92], iron [26], zinc [23], silicon [23], selenium [14,93], and sulfur [94].

4. Crop Response to Applied Nanofertilizers under Individual Stress

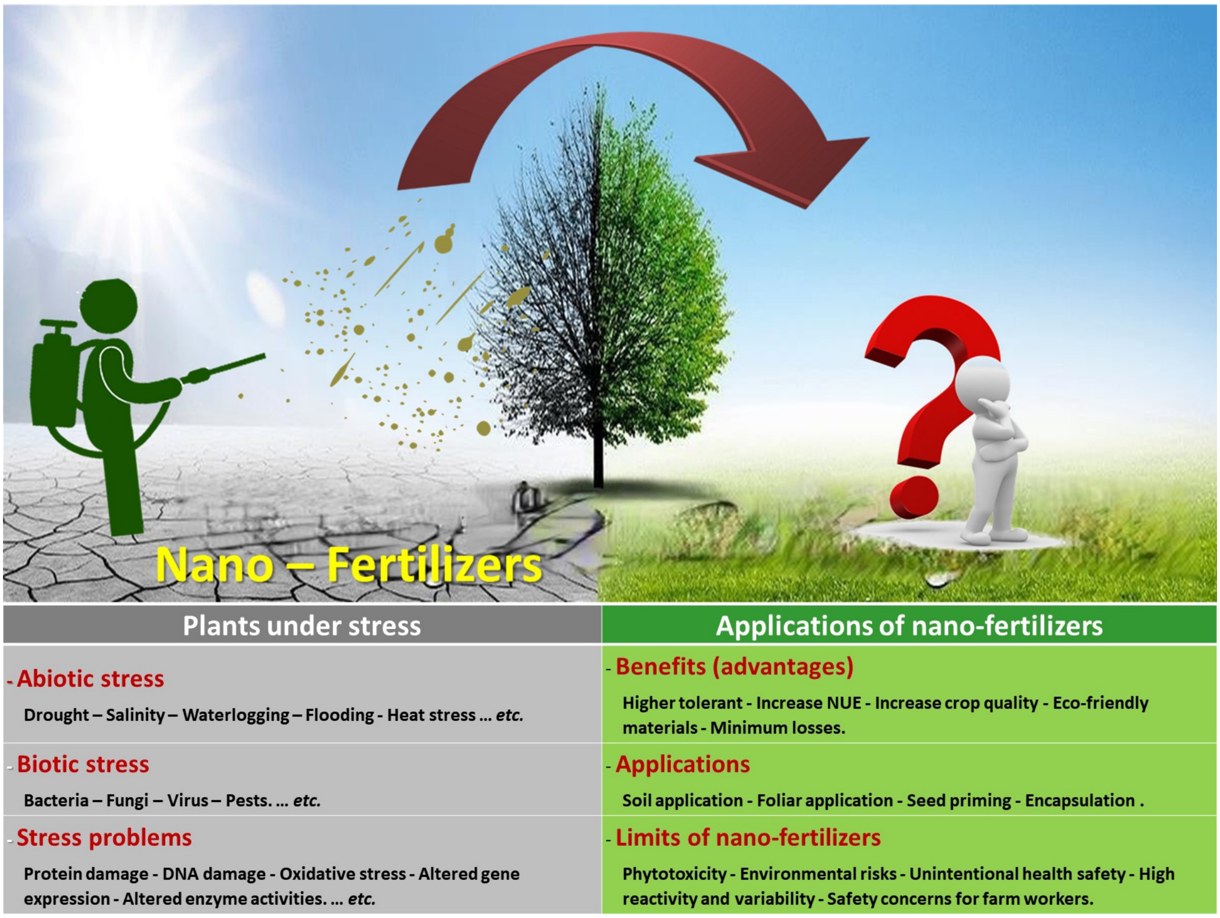
In nature, plants may be exposed to one or more stresses (i.e., biotic and abiotic stresses), either individually or in combination, which ultimately cause losses in the crop yields. These stresses include abiotic stresses, such as drought, salinity, flooding, water deficits, and low and high temperatures (cold and heat stress), as well as biotic stresses, such as diseases or the pathogens of viruses, bacteria, and fungi [95]. These plants can face individual or multiple stresses during their lifecycles, as is reported by several studies [96]. Many antistressors, such as nanofertilizers, have been applied in order to support plant growth under stress, particularly nanoselenium for salinity stress [97], nano-silicon for drought [98], and nano-copper for salinity stress [99], which can increase the plant tolerance against abiotic and biotic stresses (Figure 4; [22]). Plant nutrients have a prominent role in ameliorating several stresses, as is cited by many researchers, such as Ahmed et al. [100]. Several reports confirm the significant role of plant nutrients under different stress conditions, such as salinity stress [33], heat stress [101], heat and drought [102], and drought [103]. Several studies have been published on the individual stresses on cultivated plants and their different applied antistressors, as drought and heat stress are prevalent nowadays in different parts of our globe. Because of climate change, heat stress has become a very important stress nowadays, and it is becoming an increasing concern worldwide [104]. Table 3 compares the role of nanofertilizers in mitigating plant growth under some of the individual stresses, such as water deficits, drought, and heat stress. The main biological activities of plants generally depend on the temperature that surrounds them, which affects the germination of the seeds, the growth and development, as well as photosynthesis and the reproduction process [105]. In terms of the individual stresses on plants, the following recommended recent reviews investigate heat stress [104]; salinity stress [105]; drought stress [103]; the interplay between plants and nanoparticles [106]; nanoparticle-induced stress and toxicity in plants [107]; and the role of miRNA in the regulation and adaptation of the stress in plants [108].

Table 3. Role of nanofertilizers on cultivated plants under different individual abiotic stresses.

Abiotic Stress	Crop (Scientific Name)	Experiment Details (Nanonutrient Type)	Main Findings	Reference
Drought (for 7, 14, and 21 days)	Maize (*Zea mays* L.)	Pots (zero-valent copper NPs at 69.4 µM, 30–40 nm)	Nano-Cu NPs regulated protective mechanism of maize and are associated with drought tolerance.	[91]
Drought (irrigated at 4, 8, and 12 days)	Feverfew (*Tanacetum parthenium* L.)	Greenhouse (nano-Si at 1.5 and 3.0 mM)	Foliar-applied 1.5 mM glycine nano-Si was the best mitigator of the adverse effects of drought.	[109]
Water stress (100, 75, and 50% ET_c)	Sugar beet (*Beta vulgaris* L.)	Field experiment (nano-Si applied at 1 and 2 mM)	Nano-Si protected plants during water stress by enhancing GB, antioxidants, and flavonols, such as quercetin	[110]
Water stress (‡) (irrigated after 60, 90, and 120 mm)	Coriander (*Coriandrum Sativum* L.)	Field experiment (SiO_2 NPs, 20–35 nm at 1.5 mM)	Foliar-applied SiO_2 NPs alleviated the adverse effects of water stress and essential oil yields of coriander.	[111]
Salt stress (75, 150, and 225 mM NaCl)	Rosemary (*Rosmarinus officinalis* L.)	Soilless culture system (nano-Zn, 10–30 nm; and nano-Fe, 20 nm; both at 3 mg L^{-1})	Foliar-applied nano-Fe and -Zn increased total phenolic and total flavonoid contents; growth and salt tolerance.	[112]
Salt stress (100 or 200 mM NaCl)	Wheat (*Triticum aestivum* L.)	Pot experiments (S NPs at 100 µM, 23 nm)	S NPs mediated salt tolerance by regulating metabolic activity and decreasing oxidative stress.	[113]
Drought (hold watering till soil water content is 45%)	Maize (*Zea mays* L.)	Pot experiments (nano-ZnO, at 20 nm, 100 mg L^{-1})	ZnO NPs promoted the synthesis of melatonin and activated enzymatic antioxidants, which alleviated damage in chloroplast due to drought.	[114]
Soil zinc deficiency (0.2 mg kg^{-1})	Maize (*Zea mays* L.)	Field experiment (SiO_2 NPs, 30 nm, 2 mM)	SiO_2-NP + Zn (0.4%) increased the grain yield of maize by 37%, and linoleic acid, compared to control.	[115]
Calcareous soil (22% $CaCO_3$)	Common bean (*Phaseolus vulgaris* L.)	Pot experiments (0.1 g L^{-1} nano-P, 4.92–8.62 nm)	Integrative application of soil PSB + foliar nano-P improved plant growth and antioxidative defense system.	[116]
Arsenic stress (20-µM As)	Soybean (*Glycine max* L.)	Pot experiment (ZnO NPs, at 50 and 100 mg L^{-1})	ZnO NPs alleviated As-toxicity in plants by restricting the As-uptake, modulating antioxidant enzymes and AGC.	[117]
Cadmium stress (10 mg Cd kg^{-1} soil)	Cowpea (*Vigna unguiculata* L.)	Screen house (nano-TiO_2 at 100 and 200 mg L^{-1})	Foliar-applied nano-TiO_2 promoted total chlorophyll content and protected plants from Cd toxicity.	[118]

Notes: ET_c: crop evapotranspiration (100, 75, and 50% ET_c); GB: glycine betaine; AGC: ascorbate-glutathione cycle; PSB: phosphate-solubilizing bacteria; ‡ irrigated after 60, 90, and 120 mm of evaporation from Class A pan.

Several researchers have already discussed the individual stresses on plants, which are, specifically, a high temperature (heat stress), soil salinity, and drought, and which are associated with oxidative stress. The crop loss due to abiotic stresses is about 50%, where the crop loss due to drought is 10%, the crop loss due to heat stress is 20%, and the crop loss due to other abiotic stresses is 20% [103]. The main effects of drought stress may represent damage to the soil biota and to the cultivated plants, which creates osmotic stress, which limits the mobility of the nutrients because of the soil heterogeneity, and reduces the access of the nutrients to the plant roots [103]. The main features of cultivated plants under drought may include molecular, morphological, and physiological effects, which reduce nearly all of the biological processes and the yields of the plants (for more details, kindly read [103]). The primary responses of cultivated plants under drought stress may include drought avoidance, drought escape, and drought tolerance. Drought stress could be mitigated by using PGPR and nanofertilizers. Recently, researchers have looked to next-generation sequencing for the genetic improvement of the production of crops, such as potatoes under drought conditions [119]. The production of crops under stress, such as drought, salinity, heat stress, and others, still requires more studies on the adaptive responses.



Plants under stress	Applications of nano-fertilizers
- **Abiotic stress** Drought – Salinity – Waterlogging – Flooding - Heat stress … *etc.*	- **Benefits (advantages)** Higher tolerant - Increase NUE - Increase crop quality - Eco-friendly materials - Minimum losses.
- **Biotic stress** Bacteria – Fungi – Virus – Pests. … *etc.*	- **Applications** Soil application - Foliar application - Seed priming - Encapsulation .
- **Stress problems** Protein damage - DNA damage - Oxidative stress - Altered gene expression - Altered enzyme activities. … *etc.*	- **Limits of nano-fertilizers** Phytotoxicity - Environmental risks - Unintentional health safety - High reactivity and variability - Safety concerns for farm workers.

Figure 4. The impact of applied nanofertilizers might be crucial in the mitigation of several stresses, especially salinity, drought, and heat stress, among others. The role of nanofertilizers under stress needs much effort on the part of researchers for novel approaches, especially under multiple stresses, which represent the typical environmental conditions under which we seek global food security. There are several open-ended questions with regard to nanofertilizers and their applications that still need to be answered.

5. Combined Stress and Applied Nanofertilizers

After several studies on the effects of individual stresses on cultivated plants, many studies have begun to investigate combined stress, which is more representative of the reality of nature [120,121]. This combined stress may include abiotic stress, such as drought; biotic stress, such as bacterial infection (*Pseudomonas syringae*) [122]; or two different abiotic stresses, such as salinity and heat stress [14]. The damage of this combined stress depends on the duration and the type of stress, the type of plant and its growing stages, the soil and its amendments, and the type of growth medium [123]. The most common case studies of combined stress include soil salinity and heat stress [14;18], salinity and drought [124–129]; drought and heat stress [57,130,131]; and soil salinity and heavy metal stress [132,133]. Nanofertilizers have already been applied to stressed plants, such as nano-Se to cucumber under salinity and heat stress [14,18], and SiO_2 NPs to common beans under soil salinity and heavy metal stress [133]. More applied amendments for the support of cultivated plants under combined stresses are presented in Table 4.

Table 4. Some published studies on combined stresses that have been issued during recent years.

Crop (Scientific Name)	Combined Stress (Details)	Main Findings	Reference
Cucumber (*Cucumis sativus* L.)	Soil salinity (4.49 dS m^{-1}) and heat stress (>35 °C).	Grafting is a powerful agronomic practice that improved productivity under this combined stress.	[18]
Cucumber (*Cucumis sativus* L.)	Soil salinity (4.49 dS m^{-1}) and heat stress (>35 °C).	Nano-Se (25 mg L^{-1}), Si (200 mg L^{-1}), and H_2O_2 (20 mmol l^{-1}) were active antistressors in mitigating these stresses.	[14]
Cucumber (*Cucumis sativus* L.) and tomato (*Solanum lycopersicum* L.)	Salinity (2.5–7.5 dS m^{-1}) and drought (irrigated at 40–100% FC).	Desert-adapted fungus mediated the plant's tolerance as an adapted endophyte in an agricultural system.	[128]
Barley (*Hordeum vulgare* L.)	Salinity (150 mM NaCl) and drought (withholding water in pots at 60% FC).	Rubisco activase A contributed to combined stress tolerance as a central node in overlapping gene network.	[134]
Sunflower (*Helianthus annuus* L.)	U and Cd stress (soil treated with 15 mg U and 15 mg Cd kg^{-1} soil for 30 d; seedlings were transferred to pots).	Applying PGRs (i.e., 6-BA, IAA, GA3, and 24-EBL) promoted plant growth and photosynthesis, and alleviated toxicity of U and Cd stress.	[135]
Pistachio (*Pistacia* spp.)	Salinity (from 7.57 to 24.63 dS m^{-1}) and drought (irrigated at 40–100% FC) for 60 d in two separated experiments.	Mycorrhizal fungi enhanced tolerance of pistachio rootstocks by increasing biomass, minerals, and chlorophyll content, and decreasing oxidant content.	[127]
Common bean (*Phaseolus vulgaris* L.)	Soil salinity (soil EC = 7.8 dS m^{-1}) and heavy metal stress (Cd, Pb and Ni).	Foliar bio-SiO_2 NPs (2.5 and 5.0 mmol L^{-1}) alleviated combined stress by better growth and yield due to enhancing the antioxidant defense systems.	[133]
Lentil (*Lens culinaris* L.)	Drought (irrigated 20% PEG 6000 for 3 d) and heat stress (40 °C for 4 h).	Regulating the response to these stresses is linked to multiple genes, which are related to the antioxidant activity.	[131]
Yellowhorn (*Xanthoceras sorbifolium* L.)	Drought (by withdrawing water †) and heat stress (35/25 °C day/night for 3, 6, 9 d from stress).	This plant mitigated combined drought and heat stress through the modulation of ROS homeostasis and stomatal closure.	[136]
Maize (*Zea mays* L.)	Drought (by withholding water supply) and Cr stress (Cr-VI, 10 mg L^{-1}) for 7 d.	Applied salicylic acid and the polyamine spermidine may boost maize tolerance to studied stresses by enhancing antioxidant enzyme activities.	[137]
Tomato (*Lycopersicon esculentum* L.)	Salinity (150 mM NaCl) and drought (irrigated at 50–100% FC).	Both stresses changed the compositions of mineral nutrients by decreasing Ca, Fe, N, P, K and Zn contents, but increased contents of B, Na, and Cl.	[129]
Mustard (*Brassica juncea*)	Salinity (120 mM NaCl) and drought (withholding water) for 6 days.	Silicon can postpone premature leaf senescence through modulation of ion homeostasis and antioxidative defense.	[125]
Barley (*Hordeum vulgare* L.)	Salinity (200 mM NaCl) and potassium deficit.	100 ppm 24-epibrassinolide alleviated the adverse effects of combined stress.	[17]
Hypericum ericoides	Salinity stress (from 50 to 350 mM NaCl) and drought (PEG 8000) for 30 d.	Seeds of *H. ericoides* could germinate well under moderate salinity (150 to 250 mM) and high drought stress.	[126]
Spearmint (*Mentha spicata* L.)	Salinity (150 mM NaCl) and copper stress (60 µM Cu).	In hydroponics, under studied stress, decreased N, K, and Zn (in leaves), and Ca, K, P, and Mg (in roots).	[132]
Lettuce (*Lactuca sativa* L.)	Salinity (2–10% NaCl) and drought (5–20% PEG-6000) stress).	Plant growth yeast strain, CAM4, as *Rhodotorula mucilaginosa* as biofertilizer promoted the growth.	[124]
Tomato (*Solanum lycopersicum* L.)	Drought (50% of field capacity for 7 d) and heat stress (42 °C for 6 h).	Arbuscular mycorrhizal (*Septoglomus constrictum*) increased tolerance of tomato to studied stress.	[130]

Abbreviations: PEG: polyethylene glycol; PGRs: plant-growth regulators; 6-BA: 6-benzylaminopurine; GA3: gibberellin-A3; IAA: indole acetic acid; 24-EBL: 24-epibrassinolide; FC: field capacity. †: by withdrawing water until the weight of the soil reached 40% of the weight of the control soil.

A distinguished shift in the molecular responses of plants could be noticed under combined stresses, compared with plants that had already been exposed to the same stresses independently. These responses to the individual and combined stressors have been identified at the gene expression level for several genes, with intersecting responses to these stressors [122]. However, several plant responses to the individual or combined stresses are still not known. Thus, the simultaneous occurrence of combined stresses (e.g., bacterial pathogen and drought stress) could reduce the plant growth to a greater degree compared to the impact of these stresses individually [16,121]. Transcriptomic and physiological studies on combating these combined stresses show increasing evidence that plants can merge both of the overlapping responses to the individual stresses, as well as the certain specific responses to the combined stresses [120,122]. In terms of the application of two or more nanofertilizers to cultivated plants, there has recently been an increase in concern about the combined application of nanofertilizers; however, this strategy still needs more investigations in order to emphasize the economic and environmental benefits of this application, such as combining nano-CuO and nano-ZnO [138], or selium and copper nanofertilizers [139,140].

6. Applied Nanofertilizers under Multiple Stresses

Recently, there has been an urgent need for studies on environmentally stressed plants that closely imitate the field conditions (i.e., combinations of stresses instead of individual stresses), as there are serious challenges facing the global crop productivity [141]. This requires the development of different strategies for making agriculture more resilient while reducing the negative impacts of the combination of drought and heat stress on crop productivity. These strategies may include many practices and superior crop varieties, and they may include the application of biofertilizers, which have the potential to improve the plant tolerance to the combined stresses [130]. The effects of multiple stresses largely depend on the plant age; on the inherent stress-resistance of the plant, or the susceptibility of its nature; as well as on the severity of the stresses. The plant responses under combined stress comprise the morphophysiological, generic, and molecular features that result from these stresses [141]. Under salinity, drought, and chilling stresses, osmo-protectants may accumulate, which is due to the induction of the osmotic effect on stressed plants. In general, ROS production may occur under almost all abiotic stress conditions. Moreover, it is well known that salt and heat stress commonly impact the transport and compartmentation of the ions in plants, whereas a physiological water deficit in plants is created because of drought and salinity stress, as well as a decrease in the CO_2 diffusion in the chloroplast because of the reduction in the stomatal opening, which leads to a reduction in the metabolism of the carbon [141]. Under drought and heat stress, tea plants have resistance to these stresses through the accumulation of metabolites, such as caffeine, catechins, and theanine [142].

Day by day, there is an increase in the number of investigations into the different stresses on plants and their resilience, such as their responses to drought, submergence and flooding [143], and to chilling, freezing, and heat stress [144]. Recently, more themes have been discussed with regard to the multiple stresses on plants, such as the role of plant natriuretic peptides in maintaining the salt and water balance in the plant [145]. Multiple stresses occur during the deficiency and toxicity of boron in plants [19]: in the natural variations in the multiple abiotic stresses in a hyper-seasonal edaphic savanna [146]; and in the potential of a transcriptomic analysis under various stresses [142]. Aside from the nanofertilizers, several materials have been confirmed in their roles in mitigating the combined stresses for higher plant productivity, as is reported by many researchers, such as Lamaoui et al. [147] and Ashraf et al. [148]. The use of nanofertilizers under multiple stresses is still in the infancy period, as far as we know, and its management is very difficult in the agricultural sector because it depends on several soil and environmental factors. A comparison of the different kinds of stresses on cultivated plants under the application of nanofertilizers is briefly presented in Figure 5. In this figure, the stresses could be classified into main 3 categories: individual, combined and multiple stresses. Concerning the individual stresses, they include many stresses like salinity [112], drought [91], heavy metals [117], water stress [111], nutrient deficiency [115], which could mitigate this stress through applying following nanonutrients such as nano Cu/CuO [82], nano Se [14], nano Zn/ZnO [114], nano Si/SiO_2 [149], nano Fe_2O_3/FeO [55], and nano S [113]. Regarding the combined stresses, it may include drought and heat stress [136], drought and salinity [134], salinity and heat stress [18], salinity and heavy metals (HMs) [133], also drought and HMs [137]. The second category could be ameliorated using nanonutrients such as applied nano-Si for drought and salinity [150], nSe for salinity and heat stress [14], nSi for salinity and drought [125], nSi for salinity and HMs [133], nZn for drought and heat stress [151], nZn for drought and HMs [152]. Concerning the multiple stresses, no published materials are available on using nanofertilizers for such cases.

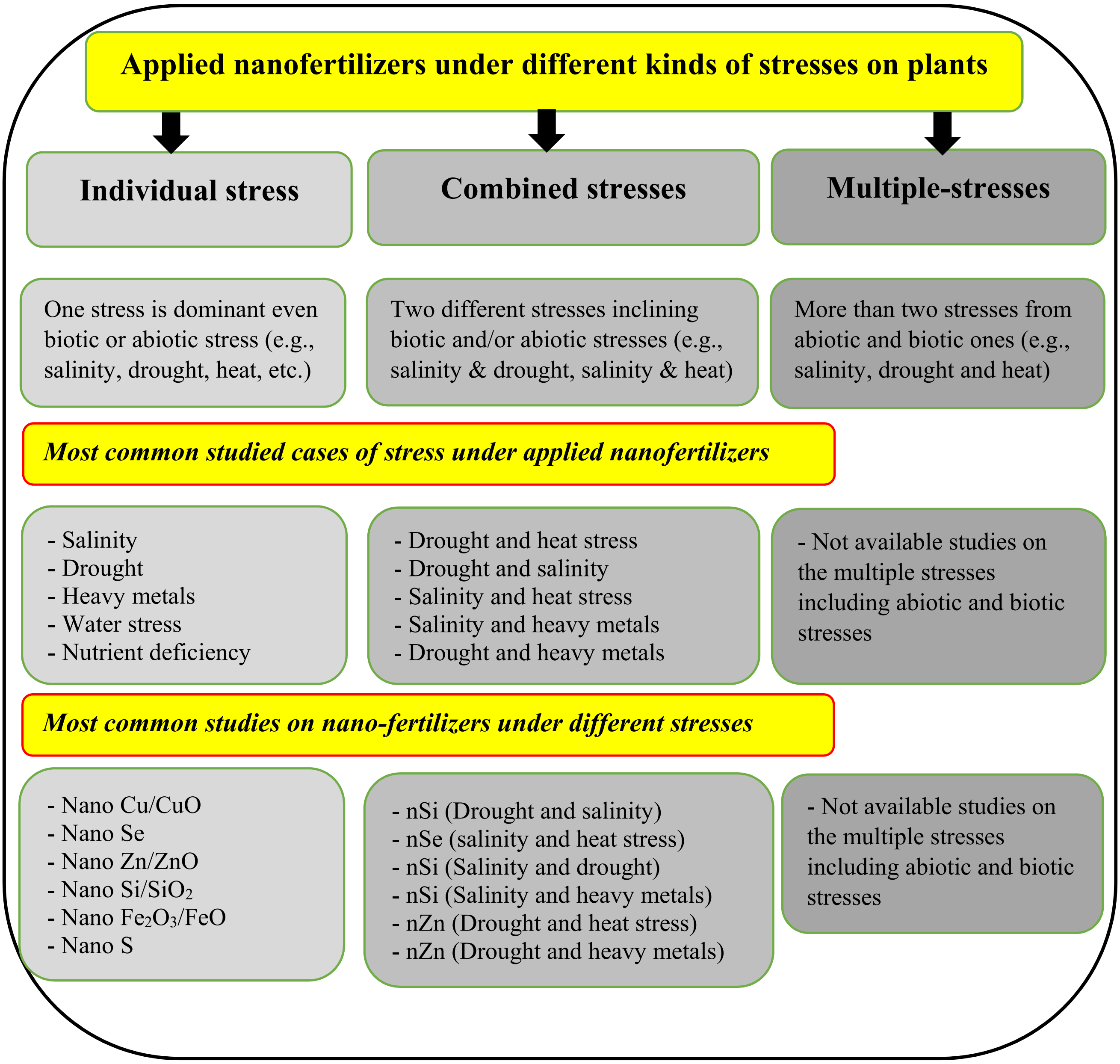


Figure 5. A comparison of the common stresses on cultivated plants, including individual, combined, and multiple stresses, and the role of applied nanofertilizers under such conditions. Numbers refer to the citations in the reference list.

The study of multiple stresses can be noticed on the model plant of *Arabidopsis thaliana*, as reported by Wang et al. [153], whereas there are few studies that have been published that remark on the higher plants, one being [19] by García-Sánchez et al. In order to study multiple stresses, it is essential to conduct experiments in the field or at commercial levels, and novel agronomic strategies are needed to manage the growth of crops under simultaneous combined stresses in order to increase their resilience to climate change, which may exacerbate the incidences of several abiotic stresses [19].

7. Conclusions

This review focuses on nanofertilizers, their potential, and their role for plants under different kinds of stresses. Nanofertilizers are an essential source of fertilizers, which can improve the crop production, compared to traditional chemical fertilizers. Nanofertilizers have many advantages, which include their slow/controlled delivery of nutrients, and their abilities to reduce the loss of nutrients in soils by adsorption or fixation, increase the bioavailability of nutrients, extend the effective duration of the nutrient release in the soil, and increase the efficient use of nutrients. On the other hand, nanofertilizers have some problems because of their high reactivity and variability, and their phytotoxicity to plants. There are also human health risks, such as safety concerns for agricultural workers and consumers. Nanofertilizers should definitely be evaluated very carefully before marketing in order to examine not only their advantages for plant growth, but also their potential limitations in terms of the environment and human health. A genuine relationship between nanofertilizers and the plant stresses, in their individual or combined states, has been reported in the published literature; however, there are only a few studies that have been published on multiple stresses. The cited studies confirm the positive role of nanofertilizers on crop production under single and/or combined stress; however, their role under multiple stresses requires more effort and investigation. These investigations may answer some of the following open-ended questions, such as when can the farmer use the nanofertilizers as a direct potential alternative strategy to traditional chemical fertilizers at the field level? What are the negative impacts of these different types of nanofertilizers on the living organisms in the soil, as well as on humans and livestock, particularly under higher applied doses? What is the fate and the accumulation of nanofertilizers under higher applied doses in the food chain under different levels of stress? What is the expected role of nanofertilizers under climate change on the basis of different scenarios, and what is the expected adaptive behavior of the cultivated crops under such stresses? All of these open-ended questions should be considered for future research.

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