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Review

Fertilizers Based on Nanoparticles as Sources of Macro- and Microelements for Plant Crop Growth: A Review

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Abstract: The necessity for efficacious, sophisticated methodologies to facilitate agricultural intensification in the context of global population growth is widely accepted. One of the principal methods for enhancing the yield of plant agricultural products is the application of fertilizers. In light of the rapid advancement of nanotechnology over recent decades, the potential of utilizing fertilizing systems based on nanoparticles and nanomaterials—termed "nanofertilizers"—as an alternative to classical mineral fertilizers is increasingly being explored. Due to their unique properties, nanofertilizers demonstrate a number of qualities useful for agriculture. These include high activity, more accurate dosing, targeted delivery of fertilizers to plants, reduced accumulation in soils and groundwater, high durability, and so forth. This review presents a synthesis of data on the efficacy of nanofertilizers over the last decade, focusing on macro-based (N, P, K, Ca, Mg, S) and micro-based (Fe, Zn, Mn, B, Cu, Mo) nanoformulations for agricultural crops. We analyzed over 200 publications, published mainly over the last decade, on the topic of "nanofertilizers". An analysis of published data on the effectiveness of using nanoparticles as applied fertilizers was carried out, and the effectiveness of using nanofertilizers was compared with traditional chemical fertilizers for a number of elements.

Keywords: nanofertilizers; nanoparticles; nanomaterials; macronutrients; micronutrients; plant nutrition; sustainable agriculture

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1. Introduction

The rapid growth of the global population, the reduction of cultivable land due to environmental problems resulting from the improper exploitation of agricultural areas and introduction of excess fertilizer, climate change, environmental degradation, the irrational use of nonrenewable resources, and high urbanization rates have collectively led to food shortages [1]. A significant increase in the total population of the Earth, which is projected to reach 9.7 billion by 2050 [2], will lead to an increase in food demand [3], with the need to increase global grain production by at least 70% [4]. Ways to solve the problems of food shortages for agricultural products can be either extensive (through the expansion of arable land), typical for developing countries, or intensive (through the introduction of modern technologies). Thus, for the global sustainable development of the agro-industrial complex, it is necessary to develop an effective system of nutrition and plant protection with minimal damage to the environment.

Advances in science and technology could be a potential solution for increasing added value in current production systems [5]. A significant increase in agricultural production is possible through the use of modern knowledge in the field of nanotechnology to create effective nutrition and plant protection systems; apply innovative phenotyping methods; implement water management and nanopurification systems and systems for the efficient use of solar energy by plants, which can be used in precision farming systems; and much more [6–14].

Until recently, it was believed that applying more fertilizer could increase crop yields around the world. However, this approach to agriculture can cause serious threats to

the environment in the form of eutrophication and the pollution of fresh water sources, which, in turn, can negatively affect aquatic flora and fauna and can also be dangerous for the local population [15]. Moreover, the intensive application of fertilizers increases the concentration of nitrates in groundwater to toxic levels [16]. It is known that most of the bulk fertilizers applied directly to the soil and irrigation system enter the atmosphere and are washed away by wastewater, adversely affecting ecosystems [17]. In addition, the low efficiency of traditional fertilizers (20–50%) and the costly increase in their application rates have prompted researchers around the world to develop and promote the use of nanofertilizers [12,18], which can reduce nutrient deficiencies due to their conversion into biologically inaccessible forms [19].

Nanomaterials differ from their bulk counterparts in a number of physical and chemical properties that give them unique properties and high reactivity due to their high surface area-to-volume ratio [20]. Nanofertilizers are nanoparticles (1–100 nm in size) or emulsions containing one or more macro- and/or microelements [21]. However, this definition is not entirely accurate. Nanofertilizers also include materials larger than 100 nm, modified with nanosized particles, also called nanostructured bulk fertilizers [22]. Nanofertilizers can reduce the loss of nutrients and reduce the load on ecosystems. Depending on the chemical composition, nanofertilizers can be monocomponent [23,24] or multicomponent (multinutrient) [25–27]. Chemical composition determines the basic optical, magnetic, electrical, and catalytic properties of nanoparticles [28]. The size and shape of nanoparticles also influences the physical and chemical properties and determines their unique action [29–31].

Nanofertilizers have shown their effectiveness on many crops, including grains [32–34], vegetables [31,35,36], and industrial crops [37–40], helping to increase growth rates, the concentration of photosynthetic pigments, and productivity. Some nanofertilizers allow the dosed release of nutritional components into the substrate, providing a prolonged effect [41–43].

Nanotechnologies are effective as stress protectors, allowing the mitigation of harmful effects of negative factors (salinization, heavy metal pollution) [25,33,44]. For example, under salinity conditions, nanoparticles accelerate the metabolism of sugars by increasing α-amylase activity, restore redox imbalance and the content of reactive oxygen species (ROS) by reducing lipoxygenase activity, influence the ion profile of plants, improve nutrient uptake and nitric oxide production, limit Na accumulation; optimize the K to Na ratio, and increase plant resistance to stress [45–47]. These beneficial effects may be explained by changes in the relevant genes [45]. The reduction of the toxic effects of heavy metals by the use of nanoparticles has similar mechanisms: the reduction of oxidative stress (reduction of ROS synthesis); improvements in nutrient absorption, the expression of relevant genes, chlorophyll synthesis, and photosynthetic efficiency; and increases in membrane stability [48,49]. In addition, nanoparticles of essential minerals help enhance the development of beneficial microflora by stimulating enzyme activity and the synthesis of exopolysaccharides and secondary metabolites [50]. Beneficial microorganisms, in turn, participate in the transformation of nanoparticles in the rhizosphere, reducing toxic effects [51]. However, it should be noted that the simultaneous development of pathogenic microflora also occurs. NPs can also exhibit a negative, inhibitory effect on beneficial microflora and other factors affecting cell metabolism and the stability of cell membranes due to their chemical nature or high concentrations [52]. The use of biodegradable nanomaterials with a polymer coating can prevent the negative consequences of using NPs.

Nanotechnology has already revolutionized agriculture. According to forecasts, by 2030, the average annual growth of the nanotechnology market will be 15% [3]. Many new studies are devoted to the development of nanoparticles and nanomaterials that can be used to increase the rate of seed germination [53,54], as a source of nutrients [55], for the biofortification of plants [11,56], and to control growth, yield, and other physiological parameters [57]. However, there are conflicting data on the effect of nanofertilizers on crop yields. Thus, some studies confirm the effectiveness of using nanofertilizers, which allow

one to obtain a 30% increase in yield compared to bulk analogs [58]. Others, on the contrary, show the absence of clear advantages of their use [59].

The use of nano-sized fertilizers, despite the obvious positive effects obtained on many types of plants, can also have negative consequences for the environment, including the toxicity of some types of nano-fertilizers for soil microflora, nano-pollution in the soil, danger to beneficial insects, etc. [23,60], which must be taken into account when developing timing, methods, and application rates.

The main purpose of this review is to summarize and analyze recent developments in the field of using nanoparticles as fertilizers to increase the productivity of agricultural crops. Particular attention is paid to quantitative effects that increase the growth and productivity of cultivated plants, taking into account side effects; factors influencing their effectiveness are also considered. Possible directions for further research and prospects for the successful implementation of nanofertilizers in sustainable agriculture are identified.

A comprehensive literature search was conducted using the following scientific search engines: Google Scholar, PubMed, and Scopus. This review is primarily based on a critical analysis of scientific publications since 2012. The primary search terms employed in the literature review were "nanofertilizers", "use of nanoparticles as fertilizers", "nanoparticles", "nanoparticles as sources of micronutrients", "nanoparticles as sources of macronutrients", and so forth, as well as various combinations thereof. In total, the analysis encompassed more than 200 sources. It should be noted that the selection of specific publications was not a criterion for analysis; only those works that were suggested by the search engines were included.

2. Nanoparticles in Agriculture

Nanoparticles (NPs) are an innovative tool to solve many emerging global problems, including in the agricultural industry. A nanoparticle is any particle whose one characteristic size is in the range of 1–100 nm [61]. The small size of nanoparticles makes it possible to more effectively exhibit properties such as ion exchange, diffusion, ion adsorption, and complexation [62]. This is primarily a consequence of the high proportion of atoms present on the surface with an increased proportion of centers and operating with higher reactivity towards adsorption and electrochemical interactions [24]. Due to their small size, nanoparticles can easily pass through cellular barriers directly (5–20 nm). However, research does not exclude the absorption of dissolved nanoparticles from the soil solution in the form of ions. Like the ions of conventional bulk fertilizers, they are not absorbed selectively, but their dissolution rate and quantity per unit volume are much higher [57].

Nanoparticles, as well as nanomaterials (NMs), are potential candidates for implementation in agriculture. Nanomaterials perform the functions of delivering forms of ions available to plants in the required volume and order, ensure the expression of plant genes on nanomatrices, and provide targeted delivery of molecules and genes to living cells [63]; these features of nanomaterials open up wide possibilities for their use in point farming and preventing the accumulation of excess nutrients in soils to reduce environmental load [64].

The main modern direction of development of nanotechnology in the agricultural sector is the development of environmentally friendly application technologies of nanofertilizers that can provide effective delivery of ions (for soluble NPs) and nutrients to plant cells, as well as for genome transformation and the stimulation of temporary or stable gene expression to produce plants with the desired properties both in vitro and in vivo (resistance to drought, phytopathogens, accelerated growth cycles, etc.) [62,65,66].

3. Nanofertilizers

Nanofertilizers (NFs) are nanomaterials that contain macro- and/or micronutrients essential to plants or are used as nanocarriers for conventional chemical fertilizers, thereby facilitating the effective delivery of nutrients.

Nanofertilizers have been demonstrated to be more effective than conventional chemical fertilizers due to their unique mechanisms of action, which enhance their efficacy,

reduce nutrient losses, and minimize environmental degradation (Figure 1) [67,68]. For example, on sandy soils, nanocomposite fertilizers release 78% more nitrogen than bulk fertilizers [69].

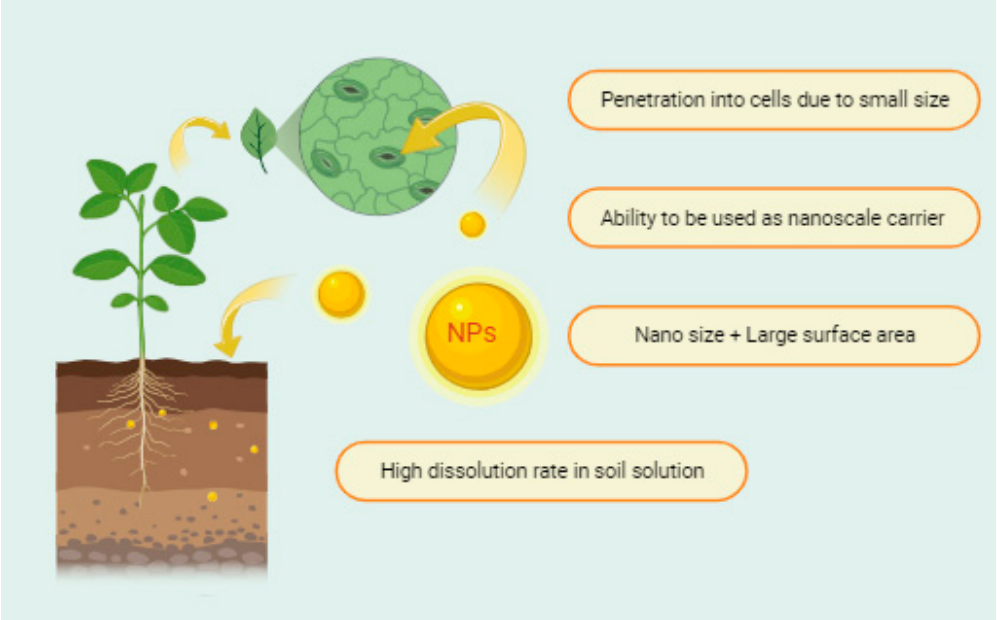


Figure 1. Advantages of NPs allowing them to penetrate plants more easily. The figure was created using BioRender web application https://app.biorender.com/ (accessed on 5 February 2024).

Regarding the mechanisms of penetration of nanofertilizers into plant cells, small particle sizes and significant increases in their surface area contribute to more efficient absorption [70]. Moreover, nanofertilizers are able to penetrate directly into cells, which makes it possible to reduce energy costs for their absorption and delivery, or even avoid them completely [71,72].

Like conventional fertilizers, nanofertilizers are dissolved in the soil solution for direct absorption by plants. However, due to their small particle size, their solubility is usually higher than that of traditional fertilizer counterparts. Nanofertilizers are more effective compared to conventional ones; they can reduce nitrogen losses due to processes such as leaching, emissions, and long-term uptake by soil microorganisms [66,73]. Moreover, controlled-release nanofertilizers can improve fertilizer use efficiency and reduce soil degradation by reducing the toxic effects that are associated with the overuse of traditional chemical fertilizers [74]. Some studies have looked at the use of time-release nanoencapsulated fertilizers. For example, biodegradable polymeric chitosan nanoparticles (~78 nm) have been used for the controlled release of NPK fertilizer sources such as urea, calcium phosphate, and potassium chloride [75]. Other nanomaterials such as kaolin and polymeric biocompatible nanoparticles can also be used for this purpose [72].

According to the classification of Liu and Lal, 2015, depending on the composition, nanofertilizers are divided into four categories: macronutrient nanofertilizers, micronutrient nanofertilizers, nutrient-loaded nanofertilizers, and plant growth-enhancing nanomaterials [57]. We consider the first two categories, the mechanism of action of which can be comparable to the use of bulk analogs.

3.1. Nanofertilizers: Sources of Macronutrients

Nanofertilizers aimed at delivering macroelements chemically consist of one or more nano-sized macroelements necessary for crops for various metabolic processes of growth and development, as well as for mitigating stress reactions [76]. Traditionally, plant macronutrients include nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and sulfur (S) [77]. The most common agrochemical chemical forms for re-

plenishing the listed elements are NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, NH_4NO_3, $Ca(NO_3)_2$, and KNO_3 (nitrogen); $Ca(H_2PO_4)_2 \cdot H_2O$, $Ca(H_2PO_4)_2 \cdot H_2O$, $(NH_4)_2HPO_4$, and KH_2PO_4 (phosphorus); KCl, KNO_3, K_2SO_4, KH_2PO_4, and K-$MgSO_4$ (potassium); $CaCO_3$, $Ca(NO_3)_2$, $Ca(H_2PO_4)_2 \cdot H_2O$, and $CaSO_4 \cdot 2H_2O$ (calcium); $MgSO_4$, MgO, $MgCl_2$, $Mg(NO_3)_2$, and $CaMg(CO_3)_2$ (magnesium); and $MgSO_4$, $NH_4)_2SO_4$, $(NH_4)_2SO_4$, $FeSO_4$, and K_2SO_4 (sulfur).

Scientific interest in the possibility of using nanoparticles as fertilizers to deliver macroelements to plants has grown several times over the past 10 years (Figure 2). An analysis of published research results showed that the bulk of the work is devoted to nanofertilizers containing nitrogen, which is a key element necessary for plant growth. Table 1 shows shortened results of a number of modern works demonstrating the production and effectiveness of using nanofertilizers as sources of macroelements. A more detailed description of the effectiveness of using nanofertilizers for the delivery of each of the main macroelements (N, P, K, Ca, Mg, S) is presented below in the corresponding subsections.

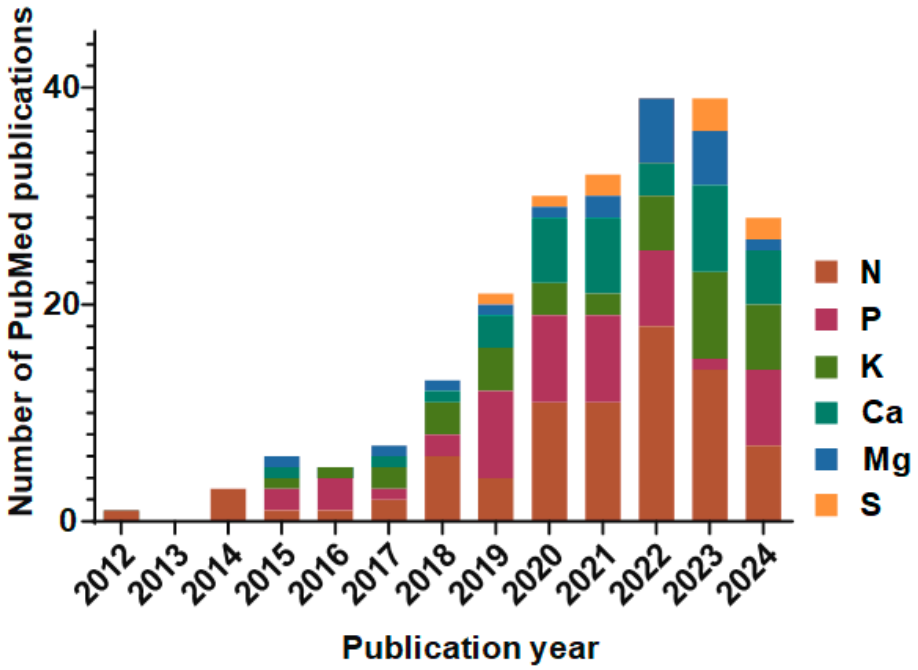


Figure 2. The dynamics of the number of publications containing the keywords "Nitrogen/phosphorus/potassium/calcium/magnesium/sulfur" and "nanoparticles plant fertilizers". Data taken from PubMed database https://pubmed.ncbi.nlm.nih.gov/ (accessed on 29 April 2024).

Table 1. The application of nanoparticles as sources of macronutrients and their effect on the growth, photosynthesis, and yield of crops.

Fertilizer Composition	Method	Particle Size, nm	Object/Plant Culture	Experimental Conditions	Optimal Concentration	Experiment Results	Refs.
U-modified HA NPs	Wet chemical method with encapsulation of urea-modified HA nanoparticles into micro/nanoporous cavities of *Glyricidia sepium* (Jacg.) Kunth Walp. under pressure	100 × 150	Nitrogen release	Three types of soils with different pH (4.2, 5.2, and 7.0)	-	The nanoparticles showed slow release of nitrogen even at day 60 compared to the control. The control released nitrogen earlier and in large quantities until about day 30, but this was followed by the release of nitrogen in low and patchy quantities.	[41]
Chitosan NPs	Biosynthesis from shrimp waste by *Penicillium oxalicum* Currie and Thom	10–20	*Triticum aestivum* L. var. Misr-1 and Gemaiza-11	Foliar spraying in a field experiment	14 L·ha^{-1}	↑ chlorophyll content (+13–19% depending on the variety) ↑ number of shoots (+5–11%) ↑ spike length (+8–28%) ↑ number of spikelets (+7–8%) ↑ spike weight (+5–13%) ↑ 1000-grain weight (+7–16%) ↑ grain yield (+27–31%) Plant height did not change	[32]
U-doped amorphous $Ca_3(PO_4)_2$-NPs	Batch method	13.5	*Triticum durum* Desf.	Cultivation in a growth chamber in a substrate consisting of a 1:1 mixture of soil and sand under simulated sunlight	15 kg·ha^{-1}	↑ number of shoots per plant (+11%) ↑ FW (+30%) ↑ number of spikelets (+30%) ↑ spike weight (+36%) ↑ 1000-grain weight (+23%) ↑ Grain quantity (+27%) ↑ protein content (+13%)	[33]
			Cucumis sativus L.	Cultivation in an aerated hydroponic solution followed by provocation of nitrogen starvation for 7 days	3.7 mM	↑ total root length (2.5 times), number (2.4 times), and surface area (2.3 times) ↑ Ca, P, and S ↑ N uptake (1.7 times) ↑ gene expression *CsDUR3* (5 times) SPAD level did not change	[25]
			Vitis vinifera L.	Field experiment	0.4 kg·ha^{-1}	↑ N content in berries (+28.6%) ↑ amino acid concentrations in plants ↑ arginine concentrations in the musts (+21%) ↓ proline concentration compared to commercial urea treatment (6 kg·ha^{-1})	[44]

Table 1. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Object/Plant Culture	Experimental Conditions	Optimal Concentration	Experiment Results	Refs.
Nitrogen-doped CDs	Hydrothermal method	2.6	*Lactuca sativa* L.	Hydroponic culture	100 $mg \cdot L^{-1}$	↑ FW (+42%) ↑ nutrient content ↑ chlorophyll content (+12.7%) ↑ ETR (+39%) ↑ light energy conversion efficiency (Y (II)) (+31%) ↑ photosynthesis rates—Rubisco activity (+61%)	[36]
HA-U-NPs	Chemical method with centrifugation	38.7	*Triticum aestivum* L. Pusa HD 3086	Cultivation in pots under controlled conditions	75 $kg \cdot ha^{-1}$	↑ plant height (+13%) ↑ spike length (+24%) ↑ spike weight (+79%) ↑ number of spikelets (3.6 times) ↑ Grain quantity (+2.8) ↑ Mg (2.4 times), N (2.4 times), P (2.6 times), K (1.8 times), Ca (5.5 times), and Fe (3 times) in grains ↑ protein content (2 times) ↑ phospholipid concentration (+51%) ↑ proline concentration (+12%)	[26]
Mg-doped HA-U-NPs	Chemical method with centrifugation	28.3	*Triticum aestivum* L. Pusa HD 3086	Cultivation in pots under controlled conditions	75 $kg \cdot ha^{-1}$	↑ plant height (+13%) ↑ spike length (+24%) ↑ spike weight (+79%) ↑ stem weight (+56%) ↑ number of spikelets (3.2 times) ↑ Grain quantity (+2.5) ↑ Mg (3 times), N (2.7 times), P (3.8 times), K (1.9 times), Ca (5.4 times), and Fe (3.7 times) in grains ↑ protein content (2 times) ↑ phospholipid concentration (+28%) ↑ proline concentration (+20%)	[26]

Table 1. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Object/Plant Culture	Experimental Conditions	Optimal Concentration	Experiment Results	Refs.
Zn-doped HA-U-NPs	Chemical method with centrifugation	20.8	*Triticum aestivum* L. Pusa HD 3086	Cultivation in pots under controlled conditions	37.5 kg·ha^{-1}	↑ plant height (+10%) ↑ spike length (+18%) ↑ spike weight (+61.5%) ↑ stem weight (+40%) ↑ number of spikelets (2.8 times) ↑ Grain quantity (+2.5) ↑ N (2.2 times), P (2.3 times), Mg (2.1 times), K (1.8 times), Fe (2.8 times), and Ca (4.2 times) in grains ↑ protein content (+50%)	[26]
HA-NPs	One-step wet chemical method	8–22	*Glycine max* L.	Greenhouse conditions	21.8 mg·L^{-1} P	↑ growth rate (+32.6%) ↑ seed yield (+20.4%) ↑ shoot DW (+18.2%) ↑ root DW (+41.2%)	[37]
HA-NPs	Chemical method with centrifugation	100	*Zea mays* L. yellow cultivar	Foliar application in field conditions	50 mg·L^{-1}	↑ height (+12.6%) ↑ leaf surface area (+27.7%) ↑ FW (+53%) ↑ green cob yield, t/ha (+29.4%) ↑ chlorophyll concentration (+52%) ↑ protein content (+22.1%) ↑ TPC (+12.9%) ↑ total flavonoids (+33.3%) ↑ total indoles (+32.4%)	[38,78]
			Zea mays L. white cultivar		100 mg·L^{-1}	↑ height (+17.0%) ↑ leaf surface area (+18.6%) ↑ FW (+58.8%) ↑ green cob yield, t/ha (+45.2%) ↑ chlorophyll concentration (+53%) ↑ TPC (+28.0%) ↑ total flavonoids (+10.0%) ↑ total indoles (+25.5%)	
HA-NPs with different surface charges	Wet chemical deposition and subsequent surface functionalization with glycine or dibasic ammonium citrate to obtain positively or negatively surface charged-nano-apatite	25.7	*Helianthus annuus* L.	Cultivation in pots for 35 days using two phosphorus-deficient soils (Ultisol and Vertisol)	150 mg·kg^{-1} P	In Ultisol (pH 4.7): ↑ FW (6.4–11.6 times) ↑ P in shoots (1.5 times) and Ca (2 times) ↓ Fe (8 times) and Zn (2 times) In Vertisol (pH 8.2): NP_S did not significantly affect biomass ↓ Ca (3 times)	[79,80]

Table 1. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Object/Plant Culture	Experimental Conditions	Optimal Concentration	Experiment Results	Refs.
K-NPs	Green synthesis using *Morus alba* L. extract	21–30	*Triticum aestivum* L. (var. HD2967)	Field conditions, sandy loam soil, and foliar treatment	20, 40, and 60 $mg \cdot L^{-1}$	All K-NP concentrations ↑ number of spikes (1.5–2 times) ↑ yield per hectare (2–3 times) ↑ protein content (30–50%) ↑ photosynthetic pigments (+50–60%) compared to the bulk analog (K_2SO_4) and control (without added potassium)	[81]
DAP with $KFeO_2$-NP nano-coating	Chemical (sol–gel) method	7–18	Clayey and clayey-loamy soils; assessment of the dynamics of the release of N, P, K, and Fe	Incubation studies on clay and loamy soils	10% nano-coating	Provides controlled release of P and N over a longer period compared to traditional DAP. ↑ release pattern of K (+8–12.5%), P (7–10 times), N (3 times), and Fe (2.5–3 times) in 60 days depending on soil type	[42]
$CaCO_3$-NPs	Heterogeneous phase precipitation of $Ca(OH)_2$ after hydration of CaO and subsequent calcination	20–80	*Arachis hypogaea* L. var. Luhua No. 4	Greenhouse study, sand substrate, 80 days of cultivation	160 $mg \cdot L^{-1}$ Ca	↑ Ca (+0.4%), N (+0.9%), P (+0.04%), and K (0.5%) ↑ total branches (+10%) ↑ leaf surface area (+21%) ↑ DW (+19%) ↑ soluble sugar content (+33%) ↑ protein content (+90%) compared to negative control and results are equivalent to $Ca(NO_3)_2$ treatments	[82]
			Arachis hypogaea L.	Two-year experiment in field conditions, foliar spraying	200 $mg \cdot L^{-1}$	↑ plant height (+10%) ↑ branching number (+9.5%) ↑ growth rate (+16%) ↑ seed yield (1.6 times) ↑ 100-seed weight (1.6 times) ↑ protein content (+10.5%) ↑ oil (+6%) ↑ P (+12%) and K (2.5 times)	[39]

Table 1. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Object/Plant Culture	Experimental Conditions	Optimal Concentration	Experiment Results	Refs.
Khazra nano-chelated calcium (Khazra Sodour Ahrar Shargh Co., Tehran, Iran)	-	-	*Malus domestica* Borkh. *cv. Red Delicious*	Spraying 70 days after full flowering, a month before harvest, and during storage	25 $mg \cdot L^{-1}$	↑ fruit firmness, TA, TSS, TPC, TAA, and fiber content in fruits ↓ internal browning ↓ FW, total soluble solids compared to control ↓ polygalacturonase activity, pectin methylesterase, and β-galactosidase in fruits that were treated with both $CaCO_3$-NPs and $CaCl_2$ With increasing shelf life, the quality of fruits treated with $CaCO_3$-NPs was higher than that of fruits treated with $CaCl_2$	[83]
$Sr_{0.96}Mg_{0.02}Ca_{0.02}Fe_{12}O_{19}$, SrMgCa nano-HF	Sol–gel autoignition method	42.4	*Hordeum vulgare* L.	Cultivation in the field, treatment at the stages of germination and growth separately	125–250 $mg \cdot L^{-1}$	↑ germination rate (+20%) ↑ plant height (+38%) ↑ FW (+20%) ↑ protein soluble content (+41%) ↑ chlorophyll concentration (+33–42%) compared to untreated control Higher doses ↓ growth parameters	[27]
					500 $mg \cdot L^{-1}$	↑ Fe (20 times), Ca (18 times), Mg (3 times), and Sr (60 times) in leaves	
Mg-NPs+ $FeSO_4$	Chemical method with centrifugation	20	*Vigna unguiculata* ssp. *unguiculata*	85 days of cultivation in field, application of Mg and/or Fe 56 and 72 days after sowing	0.5 + 0.5 $g \cdot L^{-1}$	↑ yield (+14%) ↑ Fe (+27%) and Mg (+7%) in leaves ↑ plasma membrane stability	[84]
Mg-NPs	Chemical method with centrifugation	100			0.5 $g \cdot L^{-1}$	↑ Fe (+17%) and Mg (+9%) in leaves ↑ SPAD (+5%) ↓ yield (2.7 times)	
Mg-NPs	-	-	Green bean *Phaseolus vulgaris* L. cv. 'Stike'	60 days of cultivation after planting in a greenhouse; foliar plant treatments every 10 days (5 in total); a mixture of vermiculite and perlite in a 2:1 ratio was used as a substrate	0.05–0.1 $g \cdot L^{-1}$	↑ stem FW (+23%) ↑ root FW (+20%) ↑ pod production (+18%) ↑ total polyphenols (+21%) ↑ flavonoid content (970–1703 mg catechin/100 g FW, not determined without treatment) ↑ DPPH (+35%) when using 50 $mg \cdot L^{-1}$ Mg-NPs compared to $MgSO_4$ at the same concentration	[85]

Table 1. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Object/Plant Culture	Experimental Conditions	Optimal Concentration	Experiment Results	Refs.
S-NPs	Chemical method	20–40	*Triticum aestivum* L.	Research in the field and greenhouse, seed treatment time 15 min	3.4 g·L^{-1}	↑ seed germination (3 times) ↑ early ripeness (3 weeks) ↑ number of productive shoots ↑ Grain quantity ↑ grain weight and yield (+30–100% depending on the variety) ↑ pathogen resistance	[86]
S-NPs	Chemical method	20–40	*Solanum lycopersicum* L.	Application to soil as a multifunctional fertilizer	200 mg·L^{-1}	↑ root FW (+73%) ↑ shoot FW (+35%) ↑ linear electron flow ↑ quantum yield of photosystem II ↑ relative chlorophyll content	[87]
S-NPs modified with stearic acid (cS)	Chemical method	20–40	*Solanum lycopersicum* L.	Application to soil as a multifunctional fertilizer	200 mg·L^{-1}	↑ root FW (+81%) ↑ shoot FW (+50%) ↑ linear electron flow ↑ quantum yield of photosystem II ↑ relative chlorophyll content ↑ content of tryptophan, tomatidine, and scopoletin in leaves	[87]
S-NPs	Aqueous precipitation method	35–45	*Helianthus annuus* L. var. KBSH 42	Field experiment	40 kg·ha^{-1} S	↑ content of available S in the soil ↑ DW (+11–12%) ↑ gain yield (+15%) ↑ oil content (+14,7%), compared to plants fertilized with gypsum ↑ sulfur release (+7 days compared with gypsum)	[40]

HA—hydroxyapatite; **FW**—fresh weight; **DW**—dry weight; **U**—urea; **ETR**—electron transfer rate; **TPC**—total phenolic content; **TA**—titrable acidity; **TAA**—total antioxidant activity; **TSS**—total soluble solids; **HF**—hexaferrites; **DAP**—diammonium phosphate; **CDs**—carbon quantum dots; **DPPH**—2.2-diphenyl-1-picrylhydrazyl; **SPAD**—soil plant analysis development. ↑: indicator increase; ↓: indicator decrease.

The macronutrient requirements of crop plants are increasing as the demand for more food supplies increases for the ever-growing world population. The demand for macronutrients is expected to increase to 263 million tons by 2050 [88]. To reduce the amount of fertilizer applied that harms the environment, nanofertilizers have been proposed that have increased application efficiency compared to conventional chemical fertilizers. Developed nanofertilizers containing macronutrients are constantly being improved by scientists and technicians around the world, and their use allows for greater growth and productivity of agricultural crops. Thus, nanofertilizers with macroelements are designed to not only increase the efficiency of agricultural production but also reduce production costs and, as a result, are an economical alternative to existing traditional fertilizers. A detailed description of nanofertilizers in the context of each key plant macronutrient (N, P, K, Ca, Mg, S) is provided in the relevant sections below.

3.1.1. NFs: Nitrogen Sources

Nitrogen is a crucial nutrient involved in numerous life processes of cultivated plants. Nevertheless, the widespread use of mineral nitrogen fertilizers is associated with a significant drawback: more than half of the nitrogen applied is lost to the environment [89]. Part of the applied nitrogen enters the atmosphere in the form of nitrogen oxide, which is one of the harmful greenhouse gases that contribute to global warming [90]. In order to enhance the efficacy of nitrogen utilization, a range of strategies have been implemented, with nitrogen nanofertilizers occupying a distinctive position [41,91,92]. For example, the slow release of nitrogen was observed when urea (ammonium) was applied to zeolite chips [93]. Similarly, urea-modified hydroxyapatite nanoparticles were pressure-encapsulated in the cavity of softwood *Gliricidia sepium* (Jacq.) Steud. and tested to release nitrogen slowly and steadily into the soil. Interestingly, nitrogen supply with this strategy was found to be optimal for up to 60 days compared to conventional nitrogen fertilizers, which provided a greater nitrogen supply to the plants initially and a very low supply at a later stage, up to 30 days [41].

Replacing the traditional use of nitrogen mineral fertilizers with nanosubstitutes has recently shown effectiveness in obtaining high crop yields. For example, the use of chitosan-based nanoparticles as a replacement for mineral nitrogen fertilizers has proven its effectiveness in growing soft wheat (*Triticum aestivum* L.); the yield indicators when using these nanofertilizers at a concentration of 14 L·ha^{-1} were not inferior to the application of mineral fertilizers (240 kg·ha^{-1}). Thus, nanofertilizers make it possible, if not to completely replace mineral ones, then to reduce their application, which would reduce the environmental load on the environment and make a certain contribution to the development of sustainable agriculture [32].

Also, in studies on the effect of nanoparticles of amorphous calcium phosphate enriched with urea (U-ACP) on the growth and yield of durum wheat (*Triticum durum* Desf.), it was found that the yield and quality of plants treated with nanofertilizers (15 kg·ha^{-1} U-ACP + 60 kg·ha^{-1} diammonium hydrogen phosphate) were similar to those obtained using a conventional mineral fertilizer application protocol (diammonium hydrogen phosphate 150 kg·ha^{-1}) [33]. However, the nitrogen content was slightly reduced (by 40%), and there were more grains in a spike, but they were smaller than small grains compared to the standard growing protocol, which was due to the greater availability of nitrogen in the nanofertilizer, which affected the number of inflorescences formed and grains set [94]. The treatment of cucumber plants (*Cucumis sativus* L.) with U-ACP at a nitrogen concentration equivalent to half the concentration of urea applied in the control treatment showed better results in nitrogen assimilation, while no significant changes were observed in the accumulation of biomass and chlorophyll [95]. In experiments, an increased accumulation of calcium and phosphorus in plants was noted, since this nanofertilizer also contains Ca and P, and there is evidence of the possibility of using its base (hydroxyapatite nanoparticles) as a source of phosphorus [96]. Grapes harvested from plants treated with U-ACP provided levels of yeast-available nitrogen similar to increased doses of urea

(6 kg·ha^{-1}), despite a decrease in the dose of nitrogen applied. The concentration of amino acids was higher than in the control and when 3 kg·ha^{-1}of urea was added. Nanofertilizers provided a high concentration of arginine in the wort, but a decrease in proline compared to the application of 6 kg·ha^{-1} of urea [44].

U-ACP is essentially a multi-component fertilizer, although the majority of researchers consider it to be a nitrogen fertilizer. Based on ACP, nanoU-NPKs have also been developed to provide a slow, gradual release of macronutrients. The use of nanoU-NPK has been demonstrated to reduce the amount of nitrogen supplied to plants by 40% compared to the application of mineral fertilizers while maintaining the weight of the yield obtained [43].

The efficacy of the application of urea nanohybrids (hydroxyapatite-urea HAU, hydroxyapatite-urea with added Mg-MgHAU, hydroxyapatite-urea with added Zn-ZnHAU) in doses equal to 25 and 50% of nitrogen compared to a control (urea 150 kg·ha^{-1}) was also demonstrated. The application of such doses to wheat (*Triticum aestivum* L.) resulted in an increase in growth and yield, improved plant uptake of nutrient elements (N, P, K, Ca, Mg, Fe, etc.), and an increase in protein and phospholipid content in the grain. Consequently, the application of nanohybrids can result in a reduction of up to 75% in the requirement for nitrogen fertilizer, without affecting the growth or quality of the plants. The urea in nanohybrid fertilizers is released at a gradual pace, providing a prolonged period of action. In terms of agronomic outcomes, plants treated with suspension nanohybrids demonstrated superior performance compared to those treated with granular mineral fertilizers [26].

The incorporation of NPK fertilizer into a hydrogel nanocomposite network results in a delayed release of nutrient elements, offering a promising avenue for the optimization of fertilizer use and water conservation in sustainable agriculture [97].

A comprehensive assessment of the use of nitrogen nanofertilizers on pastures was also carried out and optimal application parameters and problems associated with their use were established [98]. It was found that the most effective way to apply nitrogen-containing nanofertilizers is foliar treatment [99]. However, the use of foliar treatments requires special conditions for their use (absence of direct sunlight, precipitation during the treatment period, strict adherence to the concentration) and, if not observed, the treatments can cause a number of undesirable consequences, such as leaf burns and growth inhibition [100]. In addition, the costs of production and multiple applications of fertilizers may not be recouped, and the mechanisms for converting nanoparticles into ionic forms are not fully understood, which poses a potential threat to ecosystems [101]. Therefore, large-scale field experiments and the standardization of nanofertilizer application methods are necessary. When assessing the impact of six different foliar treatments (50 kg·ha^{-1}) with bulk and nano-nitrogen-based fertilizers (granular and dissolved urea, ammonium nitrate solution, and nanoformulations based on nitrates, urea, and ammonium) on the dynamics of ammonia and nitrous oxide emissions from pastures, it was found that NH_3 volatilization was the main pathway of N loss (2–51% of N applied). Higher emissions were observed when using NH_4 foliar formulations and lower emissions were observed when applying nitrate fertilizers. None of the treatments had a significant effect on pasture productivity. However, in the context of reducing total emissions of nitrogen gas, the use of NO_3 foliar formulations is considered promising [102].

3.1.2. NFs: Phosphorus Sources

Phosphorus is an essential component of numerous metabolites and plays a pivotal role in numerous plant metabolic processes. Phosphorus is supplied to cultivated plants through chemical fertilizers, of which only a portion (15–30%) is assimilated by cultivated plants [103]. The remainder is fixed in the soil and/or accumulates in water leached through runoff, which, in turn, leads to eutrophication.

Moreover, phosphorus deficiency is regarded as a significant global challenge affecting environmental change and food security [104]. Nanotechnology has the potential to play a pivotal role in enhancing the efficiency of phosphorus utilization by crop plants, thereby reducing the associated environmental threats. In the last decade, calcium phosphate

(CaP) nanoparticles, especially nanocrystalline hydroxyapatite (nAp-$Ca_5(PO_4)_3OH$) and amorphous calcium phosphate (ACP-$Ca_3(PO_4)_2$-nH_2O), have attracted significant interest due to their high surface-to-volume ratio, which allows them to be enriched with urea or nitrate [105]. Hydroxyapatite nanoparticles (HA, $Ca_5(PO_4)_3OH$) synthesized using a one-step wet chemical method were compared with conventional mineral phosphorus fertilizers for their role in increasing plant growth and yield. The soybean (*Glycine max* L.) was utilized as a test crop under greenhouse conditions. A notable enhancement in the growth rate (by 33%) and yield of soybean seeds (by 20%) was observed in comparison to conventional chemical phosphorus fertilizers as a result of the simultaneous application of calcium and phosphorus [37].

In addition, the interaction of HA nanoparticles with soil components was found to be less pronounced than that of conventional chemical phosphorus fertilizers. Furthermore, the HA nanoparticles demonstrated no phytotoxic effect on the germination rate of lettuce leaves (*Lactuca sativa* L.). Another study examined the synthesis of phosphorus nanoparticles by biological means using *Aspergillus tubingensis* TFR-5 from tricalcium phosphate ($Ca_3P_2O_8$) [106]. Nevertheless, these nanoparticles have not yet been subjected to field testing. It has been demonstrated that the efficacy of HA-based nanofertilizers is contingent upon soil acidity and the surface charge of the particles [79]. Furthermore, HA nanoparticles exhibit remarkable potential for surface modification and the fabrication of multicomponent and multifunctional nanofertilizers [107].

3.1.3. NFs: Potassium Sources

Potassium is a vital element for plants, playing a pivotal role in plant growth and development, yield, enzymatic activity regulation, and stomatal control. Additionally, potassium influences plant photosynthesis and their capacity to withstand abiotic stress [108]. For instance, biosynthesized K-NPs (21–30 nM) demonstrated a notable increase in yield, total protein content, and photosynthetic pigments in wheat relative to the bulk counterpart (K_2SO_4) and control (no potassium supplementation) [81].

In a separate study conducted by Saleem et al., 2021, potassium ferrite nanoparticles ($KFeO_2$-NPs) with a size range of 7 to 18 nm were applied to diammonium phosphate (DAP) fertilizer to assess the release of N, P, K, and Fe in loamy and clay-loamy soil over a period of up to 60 days. The findings indicated that the incorporation of DAP with 10% $KFeO_2$-NPs resulted in a more sustained release of phosphorus and mineral nitrogen compared to the use of conventional DAP. Additionally, the average release of potassium and iron over 60 days was increased when DAP with 10% $KFeO_2$-NP coating was used in clay loam soil compared to the control, with increases of 19.7 $\mu g \cdot g^{-1}$ and 7.3 $\mu g \cdot g^{-1}$, respectively [42].

3.1.4. NFs: Calcium Sources

Calcium is involved in numerous metabolic processes in plants, including cell elongation, the strengthening of cell wall structure by calcium pectate formation, the improvement of stomata function, the induction of heat shock proteins, and protection against various fungal and bacterial diseases [109,110]. Furthermore, calcium plays a pivotal role in the transmission of intercellular signals and the regulation of systemic responses throughout the plant [111].

In their study, Liu et al. [82] employed calcium carbonate nanoparticles ($CaCO_3$-NPs) with a size range of 20–80 nm and a Ca content of 160 $mg \cdot L^{-1}$ as fertilizers. The nanoparticles were subjected to an evaluation of their impact on crop yield and growth by means of their incorporation into Hoagland's solution. Comparisons were made between the control (no calcium addition) and a soluble calcium source in the form of $Ca(NO_3)_2$ [Ca] = 200 $mg \cdot L^{-1}$. The results demonstrated a notable enhancement in the quality of fresh groundnut biomass in comparison to the control. However, this improvement was comparable on a dry weight basis to that observed with $Ca(NO_3)_2$ application. The uptake of calcium by plant stems and roots was found to be increased compared to the control, which makes it reasonable

to conclude that Ca-NPs enhance calcium uptake and transport from root to shoot. This is due to their high surface area for uptake by the plant root surface in the rhizosphere. Moreover, in the same experiment, when Ca-NPs and humic acid (1 $g \cdot L^{-1}$) were co-applied, the maximum increase in seedling dry weight was observed (by 30% and 14% compared to the control and $Ca(NO_3)_2$ treatment, respectively).

In addition, the efficacy of nanocalcium application for enhancing the quality of apple fruits has been substantiated [83]. In comparison to the treatment of apple trees with a $CaCl_2$ solution, the use of nanocalcium resulted in an improvement in apple fruit storage, as evidenced by a reduction in fruit weight loss, both in comparison to control fruit and following the treatment of apple trees with calcium mineral fertilizer. Furthermore, the application of nanocalcium to apple trees resulted in a reduction in the activity of cell wall enzymes, including PG, PME, and β-Gal. The demonstrated efficacy of nanocalcium in comparison to $CaCl_2$ may be attributed to its small particle size, which facilitates penetration into plant cells, enhanced uptake, and high reactivity towards plant cells.

3.1.5. NFs: Magnesium Sources

The role of magnesium in the process of photosynthesis cannot be overstated; in fact, it is arguably the most important mineral involved. As an essential component of chlorophyll, the green pigment responsible for absorbing light, its presence is vital for the accumulation of biomass. Magnesium also plays a key role in regulating the synthesis of amino acids and cellular proteins. Furthermore, it affects phosphorus uptake and migration and enhances plant resistance to biotic and abiotic stress by stimulating the production of protective substances and strengthening cell walls. These findings are supported by numerous studies [100,112].

Delfani et al. examined the impact of a combined foliar application of magnesium and iron nanoparticles (Mg-NPs and Fe-NPs, 0.5 $g \cdot L^{-1}$) on the photosynthetic efficiency of black-eyed peas (*Vigna unguiculata* (L.) Walp.) under field conditions [84]. The co-application of magnesium and iron nanoparticles was found to significantly enhance photosynthesis efficiency, which, in turn, led to improvements in growth parameters, including plant height and dry and fresh biomass. Notably, the application of nanofertilizers alone resulted in a statistically significant decrease in plant yield, with a reduction of approximately 8%. Nevertheless, the authors observed an increase in magnesium uptake in different plant tissues compared to the control and conventional magnesium fertilizer, indicating that magnesium uptake is enhanced by the application of Mg-NPs [84]. It has been demonstrated that the chemical synthesis of nanomaterials and their subsequent application often result in an increased environmental load. Conversely, the green synthesis of nanomaterials offers a potential avenue for the development of more effective nano-fertilizers and nano-pesticides [113].

A recent study by Dubua et al. demonstrated the efficacy of magnesium nano-fertilizer in the treatment of green bean plants (*Phaseolus vulgaris* L. cv. 'Stike'). The nanofertilizer treatment was most effective when the concentration was 50 $mg \cdot L^{-1}$. A notable enhancement in biomass was observed in comparison to the nanofertilizer treatment at other concentrations, as well as when $MgSO_4$ was employed. The application of nonmagnesium at a concentration of 50 $mg \cdot L^{-1}$ also contributed to an effective increase in bioactive compounds and antioxidant capacity in plants compared to the application of $MgSO_4$ [85].

3.1.6. NFs: Sulfur Sources

Sulfur is a constituent of numerous essential compounds, including proteins, vitamins, and amino acids such as cysteine, methionine, and glutathione. It also plays a crucial role in the formation of chlorophyll [114]. In plants, sulfur can be found in the form of the thiol group of proteins or non-protein molecules, as well as in the form of sulfur-containing small biomolecules, including iron–sulfur clusters, molybdenum cofactors, and sulfur-modified nucleotides [115]. It has been demonstrated that sulfur is involved in nitrogen and iron metabolism [114,116]. Active forms of sulfur (hydrogen sulfide, persulfides, and

polysulfides) are synthesized in all living organisms, primarily from cysteine. These play an important role in redox regulation and stress response [117]. In addition, due to its insecticidal and antibacterial properties, sulfur is part of widely used pesticides [118].

The primary indications of sulfur deficiency in plants include the chlorosis of young leaves. In addition, excess sulfur can also result in chlorosis, although this is typically observed on the margins of leaves, which then become necrotic. The impact of sulfur on the yield and quality of grain crops has been empirically demonstrated in multiple studies [119,120].

There are many different sulfur-containing bulk fertilizers, but sulfates have the best digestibility [121]; however, even with their use, the efficiency of sulfur use remains low (18% for grain crops) and depends on many factors (soil composition and acidity, soil microbiome, etc.) [122]. Unlike bulk fertilizers, nano-sulfur has more possible absorption paths (in addition to penetration in the form of sulfates through the root system, endocytosis and diffusion are also possible, which do not require additional energy costs from plants) and rapid transportation (through phloem vessels along with the evaporation flow, intracellular transport) [123,124], contributing to increasing the efficiency of its use. In addition, unlike bulk fertilizers, the direct absorption of nano-sulfur by plants can significantly reduce the formation of cytotoxic ions [125,126].

In agricultural practice, S—containing nanoparticles are mainly used in the form of elemental sulfur, sulfide (ZnS, CuS) and materials, modificated via coating or loading [124]. The use of powdered and dissolved sulfur-containing nanofertilizers (20–40 nm) has been demonstrated to promote early maturation, the increased productivity of wheat, and increased resistance to pathogens [86].

The application of stearic acid-modified sulfur nanoparticles to soil during tomato (*Solanum lycopersicum* L.) cultivation was found to increase shoot–root mass, while bulk sulfur and ionic sulfate had no stimulatory effect. Modified and unmodified sulfur nanoparticles demonstrated a significant improvement in leaf photosynthesis, as evidenced by their promotion of linear electron flow, the quantum yield of FSII, and the increase in relative chlorophyll content. Furthermore, the application of modified sulfur NPs resulted in an increase in the content of tryptophan, tomatidine, and scopoletin in plant leaves compared to other treatments [87].

Furthermore, in a number of studies, it was described that the sulfur release into the soil from S-NPs was more prolonged [40,127]. In particular, after the application of S-NP, the release was observed for 42 days, which is 7 days longer than using conventional sulfur fertilizer (gypsum). The application of S-NPs to the soil resulted in a significant increase in dry matter production, seed yield, and oil content in sunflower plants (*Helianthus annuus* L. var. KBSH 42) when compared to those fertilized with gypsum [40]. It is also noteworthy that S-NPs demonstrated the capacity to reduce the accumulation of mercury in *Brassica napus* L. plants, while simultaneously increasing the accumulation of macro- and micronutrients [128]. The reduced absorption of toxic metals, thanks to the introduction of nano-sized sulfur, improves food safety [128–130].

Nano-sulfur has great potential for use in agriculture due to its growth-stimulating and immunomodulatory properties, but, currently, there is still insufficient information about the mechanisms of its effect on plants and the impact on the environment, including soil microorganisms. This direction of research is potentially promising, given the already existing positive research results.

3.2. Nanofertilizers: Sources of Micronutrients

Micronutrients play an essential role in numerous physiological processes of plants. They are required in minute quantities ($\leq$100 parts per million or $\leq$100 mg·L^{-1}) and act as catalysts of various metabolic processes [131]. Approximately 20 trace elements have been identified, with iron (Fe), zinc (Zn), manganese (Mn), boron (B), copper (Cu), and molybdenum (Mo) representing the most crucial for plant growth. These elements are included in Hoagland's solution [132]. Micronutrients may be included in complex

fertilizers or applied separately, with the latter occurring more frequently in the form of foliar feeding or soil application. The availability of micronutrients is significantly influenced by the pH of the soil solution, the granulometric composition, and the soil organic matter content [133]. In light of the aforementioned considerations, it can be posited that the optimal availability of micronutrients can be achieved through their application in the form of nanofertilizers.

A review of the literature on the impact of nanofertilizers as a source of trace elements revealed that the majority of studies focus on nanofertilizers that provide iron and zinc. The lowest number of studies are devoted to manganese and molybdenum nanoparticles (Figure 3).

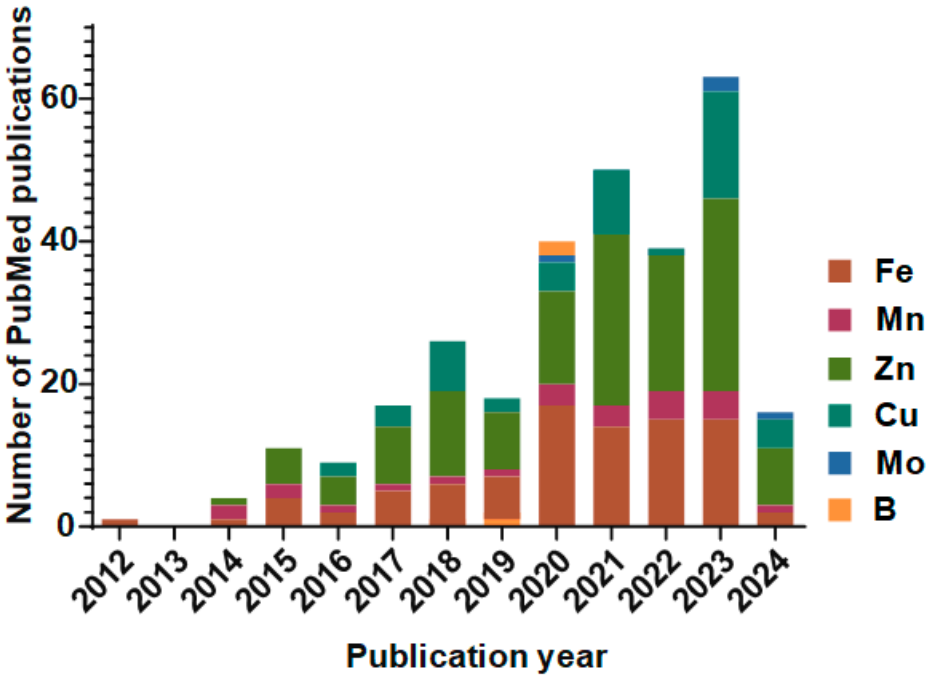


Figure 3. The dynamics of the number of publications containing the keywords "Iron/manganese/zinc/copper/molybdenum" and "nanoparticles plant fertilizers". Data taken from PubMed database https://pubmed.ncbi.nlm.nih.gov/ (accessed on 29 April 2024).

Table 2 provides a detailed description of nanofertilizers containing micronutrients, including their characteristics and effects on plants.

Table 2. The application of nanoparticles as sources of micronutrients and their effect on the growth, photosynthesis, and yield of crops.

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
Fe_3O_4-NPs	Chemical method	20	0.5 g·L^{-1}	*Vigna unguiculata* ssp. *Unguiculata*	Foliar treatment 56 and 72 days after sowing, testing a week after the last treatment	↑ yield (+7%) ↑ chlorophyll content (+9%) ↑ Fe in leaves (+25%)	[84]
Fe_3O_4 + Mg-NPs	Chemical method	20 + 100	0.5 + 0.5 g·L^{-1}			↑ yield (+9%) ↑ Fe in leaves (+25%) ↑ chlorophyll content (+10%)	
SPION	Chemical method	18.9–20.3	45 mg·L^{-1}	*Glycine max* (L.) Merr.	Adding nanoparticles to a nutrient solution with aeration at the stage of 2 paired leaves in a greenhouse	↑ chlorophyll content	[134]
Humic acid-coated Fe_3O_4-NPs	Chemical co-precipitation method	60–72	40 mg·L^{-1}	*Sorghum bicolor* L. Moench	Foliar treatment in the field a week after inoculation with *Acremonium striticum*	↑ plant height (+2–5% depending on the variety) ↑ yield (+5%) ↑ gibberellic acid (2 times), ↓ fungal infection	[34]
Fe_3O_4-NPs	Synthesis by simple photochemical polymerization in situ	6.3–6.6	100 mg·g^{-1}	*Vicia faba* L. var. *major Harz*	Field experiment; spraying was carried out 60, 90, and 120 days after sowing and harvest took place after 98 days	↑ plant height (+54%) ↑ FW (+27%) ↑ DW (+22%) ↑ leaf surface area (+63%) ↑ number of branches (2 times) ↑ number of pods (2 times) ↑ number of seeds (+50%) ↑ harvest index (2 times) ↑ 100-seed mass (+26%) ↑ total chlorophyll (+17%) ↑ carotenoids (+22%) ↑ photosynthesis rate (2.4 times) ↑ stomatal conductance (+67%) ↑ water use efficiency (2 times) ↑ gibberellic acid (+29%) ↑ indole-3-acetic acid (+37%) ↑ N (2 times), P (4 times), K (+35%), Ca (4 times), Fe (2.5 times), Zn (2 times), and Mn (+30%) ↑ total carbohydrate (+26%) ↑ crude protein (+34%) ↑ fat content (+29%) ↑ arginine (+33%) and leucine (+20%) ↓ abscisic acid (−44%) ↓ alanine (−5%)	[135]

Table 2. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
SPION	Chemical method	20	100 mg·L^{-1}	*Cucumis melo* L.	Growing in pots for 5 weeks, NPs added to 1/2 Hoagland solution	↑ FW (+9%) ↑ plant height (+17%) ↑ chlorophyll content at 3 weeks (+35%) ↑ vitamin C (+47%)	[136]
Fe_2O_3-NPs	Chemical co-precipitation method	9	20 mg·L^{-1}	*Citrullus lanatus* (Thunb.) Matsum. and Nakai	Germinating seeds in Petri dishes, spraying with 1/2 Hoagland's solution	↑ root activity (+23%) ↑ CAT (+24%) ↑ POD (2.3 times) ↑ SOD (+8%) ↑ MDA (11%) compared to Fe^{2+} treatment ↑ Fe content in root crop apoplasts	[29]
		18	20 mg·L^{-1}			↑ root activity (+31%) ↑ CAT (+23%) ↑ POD (+87%) ↑ SOD (+7%) ↑ MDA (9%) ↑ iron reductase activity (2.5 times) compared to Fe^{2+} treatment ↓ chlorophyll content (−8%)	
Fe_2O_3-NPs	Chemical method	80–110	500 mg·L^{-1}	*Triticum aestivum* L.	Seed treatment followed by growing in pots	↑ FW (+17%) ↑ photosynthesis and transpiration ↑ content of photosynthetic pigments in leaves (+20–30%) ↑ Fe (+25%), P (+27%), and K (+7%) ↑ ascorbate peroxidase activity ↓ MDA (−20%)	[30]
		20–40	500 mg·L^{-1}		Treatment of seedlings in a hydroponic installation with Hoagland's solution in greenhouse conditions	↑ root length (+30%) ↑ plant height ↑ FW (4 times) ↑ DW (3 times) ↑ chlorophyll content (+50%) ↑ carotenoids (+42%)	[137]
Yttrium doping-stabilized γ-Fe_2O_3 NPs	Sol–gel method	1–10	2000 mg·L^{-1} (200 mL per 1 plant)	*Brassica napus* L.	Cultivation in pots in a climate chamber after treatment drought conditions were created (4 days), after which, measurements were taken	↑ leaf growth rate (+52%) ↑ FW (+67%) ↑ chlorophyll content (+11%) ↓ H_2O_2 (−45%) ↓ MDA (−28%)	[138]

Table 2. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
γ-Fe_2O_3 NPs	Chemical method	17–23	50 mg·L^{-1}	*Citrus maxima* (Burm.) Merr.	The experiment was carried out in a climate chamber (30 days) equipped with a hydroponic system (1/2 Hoagland's nutrient solution without iron); plants were sprayed with a solution of nanoparticles	↑ Fe (2 times) ↓ FW (−18%), compared with Fe(II)-EDTA Chlorophyll content did not change	[139]
		17–23				NPs penetrated into plant roots but did not move from roots to shoots (root barrier) ↑ chlorophyll content (+23%) ↑ root activity (+24%) ↑ soluble protein (+78%) compared to control (without Fe) ↑ Fe absorption ↑ gene expression level *FRO2* ↓ gene expression level *NRAMP3*	[140]
		17–23		*Citrullus lanatus* (Thunb.) Matsum. and Nakai	Nanoparticles were added to the nutrient solution	↑ soluble sugar content (+74%) ↑ protein content (+18%) ↑ chlorophyll content (+5%) ↑ SOD (+36%) ↑ POD (+17%)	[141]
		20	200 mg·L^{-1}	*Cucumis melo* L.	Growing in pots for 5 weeks, nanoparticles added to 1/2 Hoagland solution	↑ FW (+9%) ↑ plant height (+13%) ↑ chlorophyll content at 3 weeks (+37%) ↑ soluble protein content (+35%) ↑ vitamin C (+35%) ↓ Fe in leaves (−15%) ↓ Fe in fruits (−35%)	[136]
Citrate-coated Fe_2O_3-NPs		6	1000 mg·L^{-1}	*Glycine max* (L.) Merr.	Cultivation in Petri dishes; root and foliar treatments of plants in a greenhouse (in pots)	↑ root length on day 5 (+34.5%)	[142]
			500 mg·L^{-1}	*Glycine max* (L.) Merr.		↑ photosynthetic parameters during foliar spraying at the eight-membered leaf stage SPAD index (+7%)	

Table 2. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
ZVI-NPs	Chemical method	53–55	500 mg·kg^{-1} of soil	*Arabidopsis thaliana* (L.) Heynh.	Cultivation of plants in a climate chamber for plant growth; a suspension of nanoparticles was added to the soil	↑ DW (+38%) ↑ leaf surface area (+53%) ↑ CO_2 assimilation rate (+27%) ↑ stomatal conductance (+40%) ↑ transpiration rate (+48%) ↑ plasma membrane H^+-ATPase activity ↑ stomatal aperture ↑ P (+73%) ↑ Fe uptake by plant roots (+25%) ↑ accumulation of carbohydrates: glucose (+44%), sucrose (+27%), and starch (+52%) ↓ Mn (−25%) ↓ Zn (−25%)	[143,144]
			250 mg·kg^{-1} of soil	*Cucumis sativus* L.	Growth chamber in Petri dishes/hydroponics/soil using 1/4 Hoagland solution	↑ Fe in roots (5 times) after 3 weeks of growing ↓ Fe in shoots (5 times) after 3 weeks of growing compared to Fe-EDTA treatment	[145]
		20	50 mg·L^{-1}	*Oryza sativa* L.	Cultivation in ½ Kimura solution in 2 variants: without Fe and with 0.05 mM Fe(II)-EDTA; measurements were carried out on day 14 after treatment	↑ chlorophyll content (+31%) ↑ Fe in roots (7 times) ↑ Fe in leaves (7.5 times) compared to negative control ↓ oxidative stress and concentrations of stress-related phytohormones: gibberellins (−42%) and indole-3-acetic acid (−42%)	[146]
Fe_3O_4-NPs	Chemical method	20	50 mg·L^{-1}			↑ chlorophyll content (+27%) ↑ Fe in roots (5 times) ↑ Fe in leaves (6 times) compared to negative control ↓ oxidative stress and concentrations of stress-related phytohormones: gibberellins (−46%) and indole-3-acetic acid (−39%)	
Mn-NPs	Chemical method	20	0.05 mg·L^{-1}	*Vigna radiata* (L.) R. Wilczek	Growing plants in perlite medium for 15 days in a phito chamber	↑ root length (+2%) ↑ stem length (+11%) ↑ number of nodules (+28%) ↑ DW (+50%) ↑ FW (+35%) ↑ absorption of nitrate nitrogen by roots (+48%) ↑ absorption of nitrate nitrogen by leaves (+22%) compared to $MnSO_4$ treatment	[147,148]

Table 2. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
MnO-NPs	Commercial product US Research Nanomaterials (Houston, TX)	40	0.1 mg·L^{-1}	*Solanum melongena* L.	Plants were grown in a greenhouse on a soilless medium infected with Fusarium wilt fungus for up to 6 weeks, then processed and planted in open ground a week later	↑ yield (+31%) ↓ area under the disease progression curve (AUDPC) (−28%)	[35]
$Mn_{0.5}Zn_{0.5}Fe_2O_4$-NPs	Green microwave-assisted hydrothermal method using microwaves at 160 °C	5–8	10 mg·L^{-1}	*Cucurbita pepo* L.	Foliar treatment 20 days after sowing in the field	↑ yield (+49–53%) compared to untreated plants	[31]
			20 mg·L^{-1}			↑ organic matter content (+76–77%) ↑ total energy (250–253 kcal·g^{-1}) in fruits	
	Green microwave-assisted hydrothermal method using microwaves at 180 °C	10–11	30 mg·L^{-1}			↑ organic matter content (+73%) ↑ total energy (260 and 258 kcal·g^{-1}) in leaves	
Fe–Mn nanocomposites	Green technology using *Azadirachta indica* leaf extract as a reducing and ethylene glycol as a stabilizing agent	10–12	200 mg·L^{-1}	*Triticum aestivum* L.	Seedlings were grown on nutrient-free sand and treatment solutions were applied by solid matrix priming and foliar treatment Plants were exposed to NaCl salinity	↑ percentage of germination (2 times) ↑ shoot length (+41%) ↑ shoot FW (+13%) ↑ root length (+12%) ↑ shoot DW (+30%) ↑ root DW (+21%) ↑ MDA (+54%) ↑ proline content (2.2 times)	[149]
Fe–Mn nanocomposite-doped GQDs	Synthesis of graphene quantum dots from natural polymer starch	17	200 mg·L^{-1}			↑ shoot FW (2 times) ↑ root FW (+21%) ↑ root DW (+47.6%) ↑ shoot DW (+17%) ↑ MDA (+72%) ↑ proline content (2.1 times)	
			500 mg·L^{-1}			↑ shoot length (+27%) ↑ CAT (+40.5%) ↑ POD (+103%) ↑ glutathione reductase (+130%) ↑ NADPH- oxidase (+141%) ↑ MDA (+43%) ↑ proline content (2.3 times) ↓ stress ↓ root length (−7%) ↓ number of roots (−9%)	

Table 2. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
ZnO-NPs	Biosynthesis from soil fungus *Aspergillus fumigatus* TFR-8	20–24	10 mg·L^{-1}	*Vigna radiata* (L.) R.Wilczek	Plants were grown in pots in greenhouse conditions; NPs were sprayed after 2 weeks of cultivation and samples were taken 2 weeks after treatment	↑ stem length (+32%) ↑ root length (3 times) ↑ root volume (+61%) ↑ number of nodules (+13%) ↑ enzyme activity: acid phosphatases (2 times), alkaline phosphatases (+53%), phytase (+83%), and dehydrogenase (2 times) ↑ P uptake (5.5 times) ↑ Zn content in leaves (+63%) ↑ Zn content in seeds (2 times) ↑ soil microbial population: bacteria (6 times) and fungi (3 times), incl. actinomycetes (up to 16%) ↑ biochemical parameters: total soluble protein (2 times) and chlorophyll content (4.4 times) compared to the bulk ZnO	[150]
ZnO-NPs	Chemical method	20	20 mg·L^{-1}	*Vigna radiata* (L.) R.Wilczek	Incubation in plant agar medium, 60 h	↑ root length (+42%) ↑ shoot DW (+41%) ↑ shoot length (+98%) ↑ root DW (+76%)	[151]
			1 mg·L^{-1}	*Cicer arietinum* L.		↑ root length (+53%) ↑ root DW (+37%) ↑ shoot length (+6%) ↑ shoot DW (+27%)	
ZnO-NPs	Precipitation method (Meliorum Technologies, New York, USA)	9–11	400 mg·kg^{-1}	*Cucumis sativus* L.	Growing plants in pots in loamy-sandy soil for 53 days; NPs were applied to the soil	↑ starch content (+57%) ↑ Mg (+18%) and Zn (+70%) in fruits ↑ root DW (+10%) ↓ Mo (−40%) and Cu (−25%)	[152,153]
			800 mg·kg^{-1}			↑ glutelin content (2 times) ↑ Mg (+7%) and Zn (2.5 times) ↑ root DW (+60%) ↑ fruit DW (+6%) ↓ Mo (−53%) and Cu (−19%)	

Table 2. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
ZnO-NPs	Nanostructured and Amorphous Materials Inc. (Houston, TX, USA)	12–24	1 g·L^{-1}	*Capsicum chinense* Jacq.	Growing in greenhouse conditions; foliar treatments were sprayed to cover the foliage twice at each of the following stages: vegetative growth (VG 45–89 days), flowering (FL 90–140 days), fruit development (FG 141–170 days), and maturity (M 171–205 days) to obtain total Zn amounts of 0.8 and 1.6 mg per plant	↑ plant height (101%, 9%, and 13% during treatments at stages FL, FG, and M, respectively) ↑ stem diameter (2%, 7%, and 19%) ↑ chlorophyll content (+19%, 23%, and 16%) ↑ number of fruits (+9%) ↑ fruit weight (+3.6%) ↑ yield (+12%) ↑ FW (+2.2%) ↑ DW (+4.3%) compared to $ZnSO_4$ treatments	[154]
			2 g·L^{-1}			↑ capsaicin content (+19%) ↑ dihydrocapsaicin content (+11%) ↑ maintenance of Scoville thermal units (+16%) ↑ content of total phenols (+14%) ↑ content of total flavonoids in fruits: soluble (+50%) and bound (+27%) ↑ antioxidant capacity (+15%): DPPH (+32%) and FRAP (antioxidant capacity restored by iron) (+20.5%) ↓ plant height (−10.5% and 11.6% in FG and M treatments) ↓ chlorophyll content (−8.5%, 4.3%, and 6.2% during treatments at stages FL, FG, and M) ↓ number of fruits (−7.3%) ↓ fruit weight (−3.8%) ↓ fruit yield (−11%) ↓ FW (−3%) ↓ DW (−10%)	
ZnO-NPs	Chemical method	20	2 g·L^{-1}	*Brassica napus* L. *Raphanus raphanistrum* subsp. *Sativus Lolium perenne* L. *Lactuca sativa* L. *Zea mays* L. *Cucumis sativus* L.	Germination in Petri dishes for 5 days in dark conditions	↑ radish root length (+56%) ↑ rapeseed root length (+38%) ↓ germination of corn seeds (−30%)	[155]
Zn-NPs		35	2 g·L^{-1}			↓ seed germination of L. *perenne* (−41%)	

Table 2. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
ZnO-NPs	Chemical method	25	1 g·L^{-1}	*Arachis hypogaea* L.	Field research	↑ seed germination (+16%) ↑ shoot length (3 times) ↑ root length (2.4 times) ↑ seedling viability (2.5 times) at the germination stage compared to the $ZnSO_4$ treatment ↑ plant growth (+88%) ↑ chlorophyll content (+42%) at the flowering stage ↑ number of pods per plant (+12%) ↑ yield (+29%) ↓ flowering time (−2 days)	[156]
ZnO-NPs	Chemical method	20	0.5 g·L^{-1}	*Glycine max* (L.) Merr.	Growing in laboratory conditions; 1 day of stressful conditions (drought)	↑ percentage of germination (+89.5%) ↑ germination rate (+6.9%) of seeds in drought conditions	[157]
	Sol–gel method	38	200 mg·kg^{-1}		120 days of cultivation in open ground	↑ DW (+15%) ↑ root length (+23%) ↑ root volume (+15%) ↑ root area (+19%) compared with $ZnCl_2$ treatment	[158]
ZnO-NPs	Chemical method	20–50	2 g·L^{-1}	*Triticum aestivum* L.	7 days of cultivation in cups with sand in a greenhouse	↑ chlorophyll *a* content (+12%) ↑ chlorophyll *b* content (+12.5%) ↑ protein content (23%)	[159]
ZnO-NPs	Biosynthesis from soil fungus Rhizoctonia bataticola TFR-6	15–25	First 2 weeks—10 mg·L^{-1}, then 4 weeks—16 L ·ha^{-1}	*Pennisetum glaucum* (L.) R.Br.	6 weeks of cultivation, field experiment, arid zone, foliar treatments	↑ shoot length (+15%) ↑ root length (+4%) ↑ root volume (+24%) ↑ chlorophyll content (+24%) ↑ total amount of soluble protein (+38.7%) in leaves at the critical stage of growth (6 weeks) of the crop	[160]

Table 2. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
ZnO-NPs	Sol–gel method	27–29	100 mg·L^{-1} (per 1 kg of soil)	*Solanum lycopersicum* L.	66 days of cultivation, greenhouse conditions, application of NPs on day 14, measurements on day 28 (application onto soil and aerosol spraying)	↑ leucopene content in fruits (3 times) with foliar treatment ↑ DW (+41%) when applied to the soil	[161]
			250 mg·L^{-1} (per 1 kg of soil)			↑ plant height (+25%) when applied to the soil ↑ root length (+50%) with foliar treatment	
			1000 mg·L^{-1} (per 1 kg of soil)			↑ chlorophyll content (3 times) when applied to the soil ↑ yield (+81.9% with foliar treatment and +305.4% when applied to the soil) ↑ leucopene content in fruits (2.5 times) when applied to the soil ↓ leucopene content in fruits (3 times when foliar treatment was applied) ↓ DW (−11% when applied to the soil)	
ZnO-NPs	Chemical method	20	10 mg·L^{-1}	*Allium cepa* L.	10 days, cultivation in Petri dishes	↑ FW (+11%) ↑ DW (+11%)	[162]
ZnO-NPs	Biological synthesis using extracellular secretions of *Aspergillus fumigatus* TFR-8	1–7	10 mg·L^{-1}	*Cyamopsis tetragonoloba* L.	6 weeks of cultivation, foliar treatment on day 14	↑ FW (+27%) ↑ shoot length (+32%) ↑ root length (+66%) ↑ root area (+74%) ↑ chlorophyll content (+276%) ↑ total soluble protein in leaves (+27%) ↑ rhizospheric microbial population (+11–14%) ↑ acid phosphatase (+74%) ↑ alkaline phosphatase (+49%) ↑ phytase (+72%) in clusterbean rhizosphere ↑ gum content in clusterbean seeds (+7.5%)	[163]
ZnO-NPs	Chemical method	30	500 mg·L^{-1}	*Sorghum bicolor var M-35-1*	Potted experiment under controlled conditions	↑ leaf area index (+7%) ↑ DW (+16%) ↑ grain yield (+9.5%) ↑ Zn content in grain (+5.6%) compared to bulk $ZnSO_4$	[164]

Table 2. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
ZnO-NPs	Chemical method	10	1.6 g·L^{-1}	*Medicago sativa* L.	Germination in Petri dishes	↓ germination percentage (−40%) ↓ root length (2 times)	[165]
			200 mg·L^{-1}	*Cucumis sativus* L.		↑ root length (2.7 times) ↓ FW (−13%)	
			1600 mg·L^{-1}			↑ germination percentage (+10%)	
			800 g·L^{-1}	*Solanum lycopersicum* L.		↓ root length (−43%), ↑ FW (+35%)	
			1600 mg·L^{-1}			↓ germination percentage (−20%) ↓ root length (−42%)	
ZnO-NPs	Green synthesis using leaf extract of *Moringa oleifera* Lam.	15–30	10–250 mg·L^{-1}	*Amaranthus caudatus* L.	Germination in Petri dishes	Did not have a significant effect on germination	[166]
			500 mg·L^{-1}			↓ germination percentage (−5–10%)	
			10 mg·L^{-1}		Growing in pots in greenhouse conditions, spraying with NPs was carried out in the 4-leaf phase, watering with Hoagland's solution, sampling was carried out 30 days after treatment	↑ plant height (+35%) ↑ FW (+67%) ↑ agronomic efficiency (3.7 times) ↑ physiological efficiency (3.9 times) Zn concentration in plants did not change compared to the bulk analog ($ZnSO_4$)	
ZnO-NPs	Green synthesis using leaf litter of *E. lanceolatus*	100	200 mg·L^{-1}	*Zea mays* L. var. *PG2458*	Seed primer	↑ germination percentage (+13%) ↑ seed vigor index (+50%) ↑ shoot length (+27%) ↑ root length (+71%) ↑ FW (+12%) compared to bulk analog ($ZnSO_4$)	[167]
					Foliar treatments in greenhouse conditions 40 days before ripening	↑ leaf surface area (+10%) ↑ stem diameter (+3%) ↑ number of leaves (+15%) ↑ chlorophyll *a* content (+20%) ↑ chlorophyll *b* content (+53%) ↑ carotenoid content (+14%) ↑ protein content (+23%) ↑ SOD (+20%) ↑ CAT (+50%) ↑ Zn in grains (+33%) ↑ total Zn content (+33%) compared to bulk analog ($ZnSO_4$)	

Table 2. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
Urea coated by ZnO-NPs	Chemical method	50–90	0.5%	*Triticum aestivum* L.	Growing in soil in a field	↑ plant height ↑ root length ↑ root volume ↑ grain yield ↑ DW	[168]
ZnO-NPs	Green synthesis using leaf extract of *Terminalia bellirica* (Gaertn.) Roxb.	22	200 mg·L^{-1}	*Brassica juncea* L.	Growing in the field	↑ length of roots and shoots ↑ number of seeds ↑ seed weight ↑ oil content ↓ disease damage (−70%)	[169,170]
ZnO-NPs	Chemical method	20	10, 20, 50, 100, 200, and 1000 mg·L^{-1}	*Lolium perenne* L.	12 days of growing in hydroponics	↓ FW Morphological abnormalities: root tips shriveled, epidermal and cortical root cells were severely vacuolated or destroyed	[171]
Cu-NPs	Chemical method	50	200, 400, 600, 800, and 1000 mg·L^{-1}	*Vigna radiata* (L.) R.Wilczek *Triticum aestivum subsp. Aestivum*	Growing on plant agar medium	NPs were toxic and bioavailable to both species, with mung being more sensitive to the trace element than prenica (toxicity concentrations of 335 and 570 mg·L^{-1}, respectively)	[172]
Cu-NPs			100, 500 mg·L^{-1}	*Cucurbita pepo* L.	14 days of growing in hydroponics without humic acid and with its addition (50 mg·L^{-1})	Cu-NPs and bulk Cu solution at all concentrations were found to be phytotoxic; humic acid decreased the ion content in bulk Cu solution but increased Cu^{2+} in Cu-NPs solutions	[173]
Cu-NPs	Chemical method	40–60	13 and 66 g·kg^{-1}	*Lactuca sativa* L.	15 days of cultivation in soil; assessment of microbial colonies and ecotoxicity of NPs	NPs did not have a significant effect on soil microbiota and seed germination; Cu-NPs at higher concentrations and the combination of Au-NPs + Cu-NPs significantly affected plant growth after 15 days of incubation	[174]
Au-NPs + Cu-NPs		100 + 50	13 + 13 mg·kg^{-1}			↑ ratio of shoots and roots compared to control	
70% CuO, 30% Cu_2O (Cu-NPs)	Chemical method	30	0.025, 0.25, 0.5, 1, and 5 mg·L^{-1} Cu	*Elodea densa* Planch	3 days of growing in hydroponics	↑ lipid peroxidation (up to 120 and 180%) ↑ CAT and SOD activity (1.5–2.0 times) phytotoxicity was observed at a concentration of 1.0 mg·L^{-1}	[175]

Table 2. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
		100–250	8 mg·L^{-1}	*Cicer arietinum* L.	Soil rhizosphere study "Experience options:" Control/microbiological preparation/colloidal Mo-NPs/microbiological preparation + Mo-NPs	↑ number of nodules (0.6/6.7/3.3/ 12.8 pcs per plant) ↑ mass of nodules (90/560/770/ 780 mg per plant) ↑ antioxidant enzyme activity ↑ activity of symbiotic bacteria	[176]
Mo-NPs	Chemical method	100	100 mg·L^{-1}	*Nicotiana tabacum* L.	Root and foliar treatments when grown in plastic containers in an artificial climate condition	↑ lignification of root cells ↑ the number of vascular bundles in tissues, especially when applied using root irrigation ↑ photosynthetic rate (+131%) ↑ MDA Foliar treatment: ↑ chlorophyll concentration (+67%) ↑ protein content (+61%) ↑ stomatal conductance (5 times) ↑ Mo in roots (14 times), in roots (9 times) Root treatment: ↑ Mo in roots (11 times), in roots (8 times) ↑ soluble sugar content (+67%) ↑ protein content (+73%) ↑ chlorophyll content (3.6 times) ↑ plant height (+50%) ↑ FW (+67%) ↑ DW (+75%)	[177]
MoS_2 NS	Chemical method	20 × 106	10 mg·kg^{-1}	*Glycine max* (L.) Merr.	Cultivation in a greenhouse for 115 days, watered with Hoagland's solution	↑ seed yield (+30%) compared to the application of traditional molybdenum fertilizers (Na_2MoO_4) ↑ nitrogenase activity (+122%) ↑ total nitrogen content in nodules (+27%) ↑ Mo (2 times)	[178]

Table 2. *Cont.*

Fertilizer Composition	Method	Particle Size, nm	Optimal Concentration	Object/Plant Culture	Experimental Conditions	Experiment Results	Ref.
Ca-NPs, B-NPs, and nanocomplexes	Chemical method	60	200 mg·L^{-1}	*Arachis hypogea* L.	Field experiment, foliar spraying at the vegetation stage (30 and 60 days after sowing)	↑ plant height (+13%) ↑ branching number (+10%) ↑ DW (+11.2%) ↑ growth rate (+22%) ↑ SPAD (+13%) ↑ seed yield (1.8 times) ↑ 100-seed weight (+16%) ↑ protein content (+26%) ↑ oil (+17%) ↑ N (+27%), P (+10%), and K (2.5 times)	[39]
$Ca_3(BO_3)_2$-NPs	Combination of co-precipitation and heat treatment methods	80	30 mg·L^{-1}	*Lactuca sativa* L.	Plants were grown in greenhouse conditions for 60 days on a modified Hoagland solution with and without boron; NPs were sprayed at intervals of 10 days	↑ shoot height (2.7 times) ↑ root length (1.9 times) ↑ FW (+58%) ↓ DPPH activity (−32%)	[179]
				Cucurbita pepo L.		↑ shoot height (+18%) ↑ root length (+66%) ↑ phenolic compounds (+51%) compared to control (without B)	

SPION—superparamagnetic iron oxide nanoparticles; **FW**—fresh weight; **DW**—dry weight; **CAT**– catalase; **POD**—peroxidase; **SOD**—superoxide dismutase; **MDA**—malondialdehyde; **ZVI**—zerovalent iron; **GQDs**—graphene quantum dots; **DPPH**—2,2-diphenyl-1-picrylhydrazyl; **SPAD**—soil plant analysis development. ↑: indicator increase; ↓: indicator decrease.

3.2.1. NFs: Iron Sources

Iron is an essential component of numerous plant proteins and is involved in the synthesis of chlorophyll and cellular respiration [180,181]. Iron deficiency is a significant nutritional disorder of plants, the primary symptom of which is mesic chlorosis, which typically manifests on young leaves due to the fact that iron is not a reusable element [182,183].

Hoagland and Arnon [132] found that the majority of plants typically require 1–5 mg·L^{-1} Fe in the soil solution. Initial investigations into the utilization of Fe_3O_4 magnetite nanoparticles in the cultivation of perennial ryegrass (*Lolium perenne* L.) and pumpkin (*Cucurbita mixta* cv. white cushaw) in hydroponics demonstrated their inappropriateness as a Fe-containing nanofertilizer, as the treatments resulted in increased oxidative stress and a lack of iron concentration elevation in both crops. This suggests that the nanoparticles were unable to translocate within the plants [184]. Further studies demonstrated that the application of superparamagnetic iron oxide nanoparticles (SPION) (30, 45, and 60 mg·L^{-1}) in greenhouse hydroponic production significantly enhanced the chlorophyll content of soybean (*Glycine max* L. Merr.) subapical leaves in comparison to the application of iron complexes with ethylenediaminetetetraacetic acid (Fe-EDTA) [134]. The findings indicated that Fe-NPs at a concentration of 45 mg·L^{-1} could serve as a more efficacious source of micronutrients than Fe-EDTA and were more effective in controlling iron deficiency-induced chlorosis. Furthermore, the efficiency of iron uptake in plants was enhanced, which ultimately resulted in an increase in chlorophyll content. Additionally, Zimbovskaya et al. [185] reported that wheat plants (*Triticum aestivum* L. cv. L15) exhibited greater iron accumulation when 1 and 10 mM iron oxide nanoparticles stabilized with humic substances were applied, exhibiting a 70–75% increase in iron accumulation compared to the application of ammonium iron sulfate and ethylenediaminetetraacetic acid (Fe-EDTA).

In a separate experiment, the growth and yield performance of black-eyed peas were significantly enhanced when iron nanoparticles were applied as a foliar application at a dose of 500 mg·L^{-1} [84]. Moreover, the application of Fe-NPs enhanced the impact of co-applied Mg-NPs. The application of ultralow SPION on legume plants (*Vicia faba* L. var. major Harz) in the form of triple spraying at 60, 90, and 120 days after sowing demonstrated a significant advantage in growth, yield, seed quality, and the accumulation of photosynthetic pigments compared to the use of ferrous sulfate and chelated iron [135]. Additionally, increases in leaf size and thickness, total carbohydrate content, crude protein content, and the accumulation of major macro- and micronutrients were observed. Consequently, the application of SPIONs may prove to be an efficacious fertilization strategy in arid regions. Furthermore, Fe_3O_4-NPs have been demonstrated to be effective in priming wheat seeds [30]. The treatment at a concentration of 500 mg·L^{-1} was the most effective from a concentration range of 0.8 to 1000 mg·L^{-1} and did not cause toxic effects. This was evidenced by the reduced MDA content and PSII activity, which matched that of control plants treated with Fe-EDTA. The enhanced photosynthesis and increased content of P, K, and Fe resulted in a general acceleration of leaf growth.

A number of studies have demonstrated the efficacy of Fe_2O_3-NPs as nanofertilizers. In a related study, Al-Amri et al. [137] examined the efficacy of Fe_2O_3-NPs of varying sizes (8–10, 20–40, and 30–50 nm) when grown in a hydroponic system of wheat. The results demonstrated that Fe_2O_3-NPs of 20–40 nm exhibited greater efficacy, as evidenced by a more pronounced increase in root length, plant height, biomass, and photosynthetic pigment content (by 40–50%). The nanoparticles were well absorbed by the plants and transported from the roots to the leaves, resulting in an increase in the iron content of the plant tissues [137].

Liu et al. [186] demonstrated the efficacy of γ-Fe_2O_3-NPs as a source of micronutrients. In this study, an important aspect of the practical application of nanofertilizers, namely, phytotoxicity, was also investigated. Furthermore, the high efficiency of γ-Fe_2O_3-NPs and γ-Fe_2O_3-NPs coated with citrate in soybean (*Glycine max* (L.) Merr.) cultivation as a foliar fertilizer and soil application during soybean germination was also reported [142]. It is notable that phytotoxic properties were not observed in any of the plant growth stages

following the application of the utilized nanofertilizers. The application of γ-Fe_2O_3 resulted in an increase in root length compared to bulk fertilizer counterparts at concentrations greater than 500 mg·L^{-1}. The molar ratio of nanoparticles to citrate was found to be 1:3, resulting in an increase in the efficiency of insoluble Fe_2O_3 for foliar application. This ratio was found to significantly improve photosynthesis parameters when sprayed [142].

In an experiment conducted on the growth of pomelo (*Citrus maxima* (Burm.) Merr.) plants in a hydroponic unit, the addition of 50 mg·L^{-1} γ-Fe_2O_3 NPs to the nutrient solution resulted in a significant increase in the expression levels of the *FRO2* gene and higher iron reductase activity compared to both the control (without Fe) and Fe(II)-EDTA exposure. This promoted iron transformation and increased plant tolerance to iron deficiency [140]. The concentration of chlorophyll and soluble proteins was observed to increase, and the activity of the root system was found to have increased as well. The transport of nanoparticles from roots to leaves was not observed. In the case of foliar treatment of pomelo plants, it was also observed that γ-Fe_2O_3-NPs could penetrate into the leaves of the plants, while there was no transport of NPs to the roots. In general, the foliar application had no significant effect on the growth parameters of the plants [139]. In a related investigation, the efficacy of γ-Fe_2O_3-NPs at a dosage level of 50 mg·L^{-1} was validated for the growth of watermelon (*Citrullus lanatus* L.) [141]. It was observed that γ-Fe_2O_3-NPs treatment resulted in an increase in soluble sugar, protein, and chlorophyll content in plants. However, this was accompanied by an increase in oxidative stress one week after treatment, which was subsequently eliminated as the watermelon grew. Notably, the authors of the study also found that γ-Fe_2O_3-NPs may possess peroxidase-like activity [141]. Another study reported that γ-Fe_2O_3-NPs stabilized by yttrium doping, applied to soil with irrigation after drought, reduced malondialdehyde (MDA) and hydrogen peroxide levels and increased the leaf growth rate, fresh weight, and chlorophyll content of rapeseed (*Brassica napus* L.) compared to the application of chelated iron [138].

In another study by Li et al. [29], when magnetic Fe_2O_3-NPs of 9 and 18 nm in concentrations of 2 mg·L^{-1}, 20 mg·L^{-1}, and 50 mg·L^{-1} were applied to watermelon plants (*Citrullus lanatus* (Thunb.) Matsum. and Nakai), a positive effect was observed at the 20 mg·L^{-1} concentration. An increase in physiological parameters, including root activity; catalase (CAT), peroxidase (POD), and superoxide dismutase (SOD) enzyme activities; and MDA content, was observed for both particle sizes [29]. In the case of the larger nanoparticles, with those measuring 18 nm in size, iron reductase activity was found to be significantly increased in comparison to the application of Fe^{2+}. In addition, chlorophyll concentration was observed to be decreased. Furthermore, when 9 nm Fe_2O_3-NPs were used, an increase in apoplast iron content in roots was observed.

Comparative studies were also conducted to investigate the effect of γ-Fe_2O_3-NPs and Fe_3O_4-NPs on the physiology and fruit quality of musk melon grown in pots under controlled conditions [136]. The iron oxide NPs of both species did not affect the iron content in the stem, leaves, and fruits. However, they did stimulate plant growth, contribute to an increase in chlorophyll concentration at three weeks of growth, and have a positive effect on fruit weight and vitamin C content [136].

Yoon et al. [143] conducted experiments using *Arabidopsis thaliana* (L.) Heynh. plants, which demonstrated the efficacy of nanosized zero-valent iron (ZVI-NPs) at a concentration of 0.5 g·kg^{-1} soil as an iron source [143]. These results demonstrate that ZVI-NPs possess additional advantages as a nanofertilizer, including the ability to enhance stomatal opening and the activation of plasma membrane H^+-ATPase, which accelerates CO_2 uptake by plants [143,144]. However, when cucumber (*Cucumis sativus* L.) was cultivated in soil and soil-free growing systems, the application of ZVI-NPs at concentrations of 0, 250, and 1000 mg·L^{-1} had no effect on plant growth parameters. Furthermore, electron microscopy revealed that transformed iron nanoparticles were localized in the membrane of root cells and vacuoles of leaf parenchyma cells, while no evidence of the primary translocation of ZVI-NPs from roots to shoots was found [145].

A comparison of the effects of ZVI-NPs (20 nm), Fe_3O_4-NPs (20 nm), and Fe_2O_3-NPs (20–30 nm) applied to the roots of hydroponic-cultured plants at three concentrations (50, 250, and 500 mg·L^{-1}) demonstrated that low doses (50 mg·L^{-1}) of ZVI-NPs and Fe_3O_4-NPs were effective in enhancing crop growth under conditions of iron deficiency. However, in the presence of Fe(II)-EDTA in the solution, none of the NPs had a positive effect on the growth of rice plants. At concentrations of 500 mg·L^{-1}, plant growth inhibition (reduced root volume and plant biomass) and increased oxidative stress were observed [146]. Consequently, the potential of utilizing ZVI-NPs and Fe_3O_4 as an alternative to Fe-fertilizers in rice cultivation under conditions of iron deficiency was validated.

It is noteworthy that iron oxide nanoparticles also exhibit antifungal activity, as evidenced by numerous studies on colloidal iron oxide nanoparticles (20 μg·mL^{-1}), Fe_2O_3-NPs synthesized with *Bacillus subtilis* (1 μg·mL^{-1}), and humic acid-coated Fe_3O_4-NPs [34,187,188], which can be employed for simultaneous feeding and the prevention of fungal diseases.

3.2.2. NFs: Manganese Sources

Manganese (Mn) is a crucial micronutrient that plays a pivotal role in the water-splitting process during the operation of photosystem II (PSII). It is also a constituent of photosynthetic proteins and plant enzymes [189]. Elevated concentrations of this element can result in toxicity and oxidative stress [190].

In an experiment on the hydroponic cultivation of mung bean (*Vigna radiata* L.), the efficiency of manganese nanoparticle (Mn-NP) application was compared with that of manganese salt ($MnSO_4$), a classical Mn fertilizer [147]. Both fertilizers were applied at doses of 0.05, 0.1, 0.5, and 1.0 mg·L^{-1}. The results demonstrated that the application of Mn-NPs at a concentration of 0.05 mg·L^{-1} significantly enhanced growth and yield performance in comparison to the control group that did not receive Mn application. At higher concentrations, Mn-NPs demonstrated no toxicity to plants, whereas $MnSO_4$ at a dose of 1 mg·L^{-1} was toxic, resulting in leaf necrosis, brown roots, and the gradual disappearance of roots after 15 days of treatment. Furthermore, the application of Mn-NPs resulted in a greater release of oxygen and enhanced photophosphorylation within the chloroplasts compared to the control. The enhanced water-splitting observed at the oxygen release center in the chloroplast was responsible for the increased oxygen release. The authors concluded that Mn-NPs could serve as a potential modulator of photochemistry in the agricultural sector [147]. Mn-NPs did not exhibit phytotoxicity at any concentration, and when studying the effect on living organisms, did not show toxic effects on mouse brain mitochondria, except for partial inhibition of complex II-III activity in the electron transport chain (ETC) [148].

A stress-protective effect of MnO-NPs and their suppression of pathogenic fungal microflora on Solanum plants under foliar treatment were also reported [35]. In a study of the stress-protective properties of Fe-Mn nanocomposites and their ligated graphene quantum dot (GQD) derivatives on wheat (*Triticum aestivum* L.), it was observed that there was an increase in enzymatic antioxidants, including catalase, peroxidase, glutathione reductase, and NADPH-oxidase. This contributed to an increase in the fresh and dry weight of plants and other growth parameters [149].

3.2.3. NFs: Zinc Sources

Zinc (Zn) plays an integral role in photosynthesis, participating in PSII reduction; activating various enzymes, including RNA polymerase [191]; and maintaining membrane integrity and seed and generative organ development [192]. Zinc nanoparticles can be absorbed by plants through their roots and leaves, where they are subsequently transformed. Moderate application of zinc nanoparticles can stimulate growth and alleviate stress by affecting the rhizosphere. However, excessive application can have toxic effects [193].

Soils treated with ZnO-NPs exhibited a significant reduction in the number of soil microorganisms (up to 50%) and the carbon content of their biomass (application of 2.5 mg·kg^{-1} or more). Consequently, the utilization of ZnO-NPs results in an augmented

quantity of zinc available in the soil yet concurrently suppresses the metabolic activity of soil microorganisms [194]. The application of spherical ZnO NPs (average size 36.7 nm) at a dose of 5 mg·kg^{-1} when applied to soil and 100 mg·L^{-1} with foliar application contributed to the maintenance of soil microbial biomass carbon and bacterial populations, increased total chlorophyll and zinc contents in grain, and promoted the overall maintenance of wheat production in Zn-deficient soils [195].

Zinc deficiency is manifested in the form of the mesic chlorosis of young leaves, which is characterized by decreased chlorophyll concentrations, a weakening of plant growth and immunity, and a loss of leaf turgor [191]. Zinc is also involved in the conversion of inorganic phosphates into organic forms, acting as a cofactor for P-solubilizing enzymes (phosphatase and phytase). The application of ZnO-NPs has been shown to increase the activity of these enzymes by approximately twofold [150].

Prakash et al. [196] reported that the application of biosynthesized ZnO-NPs by spraying (10 mg·L^{-1}) to mung bean plants resulted in an increase in phosphorus uptake by 11%, concomitant with improvements in the plant growth, protein content, and chlorophyll content of leaves. The application of ZnO-NPs has been demonstrated to stimulate plant growth and mitigate the effects of stressors such as Cr^{6+}.

A number of studies have investigated the effect of ZnO-NPs on crop growth and productivity, both as a single component and in the context of coating macrofertilizer granules [197]. A field study conducted on wheat (*Triticum aestivum* L.) demonstrated that the application of urea granules coated with 0.5% ZnO-NPs, which slowed the release rate, resulted in enhanced growth and yield compared to urea coated with a layer of a bulk analog, namely, a zinc salt with similar concentrations (0.25%, 0.5%, and 4% elemental zinc) [168].

For instance, the optimal concentration of ZnO-NPs was found to significantly enhance the growth and yield performance of mung bean and chickpea [151]. The authors determined that the optimal concentration of ZnO-NPs for application varied depending on the nature of the crop. The application of 20 mg·L^{-1} ZnO-NPs to mung bean plants resulted in a significant increase in root length, fruit biomass, shoot length, and shoot biomass, with increases of 42%, 41%, 98%, and 76%, respectively. Nevertheless, the application of higher doses of ZnO-NPs resulted in a decline in the growth rate of both crops [151].

In a separate greenhouse experiment, the application of ZnO-NPs at rates of 400 and 800 mg·kg^{-1} resulted in a significant increase in the growth performance and yield of cucumber (*Cucumis sativus* L.) [153]. The results demonstrated a 10% and 60% increase in plant root dry weight when ZnO-NPs at 400 and 800 mg·kg^{-1} were applied, respectively, in comparison to the control (without NP application). ZnO-NPs at the same concentrations resulted in a slight increase in dry fruit weight of 0.6% and 6%, respectively, in comparison to the control. ZnO nanoparticles at a concentration of 400 mg·kg^{-1} were found to increase starch content. The application of nanoparticles was found to promote the accumulation of Mg and Zn in cucumber fruits, while simultaneously causing a decrease in Cu and Mo [152].

Similarly, Lin and Xing [155] reported that the application of ZnO-NPs at a concentration of 2 g·L^{-1} resulted in a significant increase in the root elongation of germinated radish (*Raphanus sativus* L.) and rape (*Brassica napus* L.) seeds compared to the control (deionized water). Additionally, the authors observed a decline in the germination and root growth performance of ryegrass (*Lolium perenne* L.) when 2 g·L^{-1} of metallic zinc nanoparticles (Zn-NPs) was applied.

In contrast, seed germination was enhanced when lower concentrations of ZnO-NPs were applied to peanut [156], soybean [157], African millet [160], and cucumber [165]. Concomitantly, the treated peanut plants exhibited enhanced growth, elevated chlorophyll content, and an earlier flowering period (by two days) that had a favorable impact on yield (a 29% increase) [156]. ZnO-NPs at concentrations of 10, 20, 30, and 40 mg·L^{-1} demonstrated no statistically significant effect on the germination of onion seeds in Petri dishes. However, the highest subsequent growth of seedlings (in terms of both fresh and

dry weight accumulation) was observed when ZnO-NPs were applied at a concentration of 10 mg·L^{-1} [162]. A study examining the effect of different ZnO-NP concentrations (250, 500, 1000, and 2000 mg·L^{-1}) on wheat seed germination revealed no statistically significant impact. However, the study did find that the application of ZnO-NPs increased chlorophyll and protein content in the leaves of wheat seedlings during subsequent growth periods [159]. A similar experiment on tomatoes also demonstrated that ZnO nanoparticles had no effect on the germination of tomato seeds [161].

In another study conducted on the germination of cucumber, alfalfa, and tomato seeds, the application of ZnO-NPs increased the germination of cucumber seeds only [165]. Differences in plant response were observed in foliar and root applications of ZnO-NPs: for example, when ZnO-NPs were applied at 250 mg·kg^{-1} soil and 250 mg·L^{-1} as a spray, there was an increase in plant height in the former case and root length in the latter, and, when 1000 mg·kg^{-1} ZnO-NPs were applied to soil, there was a 4-fold increase in chlorophyll concentration and yield and a 2.5-fold increase in the leucopine content of fruits, while foliar treatment increased yield almost 2-fold, with a 3-fold decrease in leucopine [165].

In another experiment, a significant improvement in *Cyamopsis tetragonoloba* L. plant biomass, shoot and root growth, root area, chlorophyll and protein synthesis, rhizosphere microbial population, acid phosphatase, and alkaline phosphatase and phytase activity in the rhizosphere of common bean was recorded when foliar treatments with ZnO-NPs were applied [163].

The application of ZnO-NPs on sorghum (*Sorghum bicolor* var M-35-1) in a pot experiment consisting of twelve treatments including seed treatment (200, 500, and 1000 mg·L^{-1} ZnO-NPs and bulk $ZnSO_4$) and foliar feeding (200, 500, 1000, and 1500 mg·L^{-1} ZnO-NPs and 1000 mg·L^{-1} $ZnSO_4$) showed that the optimum application of ZnO-NPs was spraying with these NPs at a concentration of 500 mg·L^{-1}, which increased plant height, leaf area, leaf area index, dry weight, and grain yield compared to the use of $ZnSO_4$. It is noteworthy that ZnO-NPs concentrations of 1000 mg·L^{-1} or more were toxic and caused inhibitory effects [164].

The application of Zn-NPs resulted in phytotoxicity in a number of studies involving various crops [151,152,155,198,199]. Nevertheless, it was demonstrated that the degree of phytotoxicity is contingent upon the nature of the cultivated plants and that species-specific differences are responsible for the differential uptake of ZnO-NPs, which consequently influences the tolerance or toxicity of these NPs [165]. In general, most cultivated plants require 0.05 mg of soil solution per 1 L. The authors of these studies applied Zn-NPs at exceedingly high doses, ranging from 400 to 2000 mg·L^{-1}, which far exceeded the recommended concentrations. Even at a dose of 10 mg·L^{-1}, Zn-NPs were found to have a detrimental effect on the normal growth of ryegrass [171]. Additionally, the utilization of 10 mg·L^{-1} ZnO-NPs on amaranth crops was found to be the most optimal for the stimulation of growth and the accumulation of fresh mass in comparison to higher concentrations (50, 100 mg·L^{-1}), while the agronomic and physiological efficiency of Zn use exceeded that of the variant utilizing a volumetric analog ($ZnSO_4$) by a factor of four [166]. A study of ZnO NPs (100 nm) produced by green synthesis using eucalyptus lanceolens leaf fall and $ZnSO_4$ (200 and 400 mg·L^{-1}) conducted on *Zea mays* L. var. PG2458 demonstrated that seed priming with ZnO NPs resulted in enhanced germination, seed germination vigor, shoot length, root length, and fresh biomass [167]. A foliar application of 200 mg·L^{-1} resulted in an increase in stem diameter and leaf surface area, and the transfer of Zn from leaf to cob and cob to grain was more rapid for ZnO NPs compared to $ZnSO_4$. A higher concentration (400 mg·L^{-1}) of ZnO NPs and $ZnSO_4$ exhibited phytotoxic effects. Additionally, ZnO nanoparticles (22 nm) obtained by green synthesis using *Terminalia bellirica* (Gaertn.) Roxb. leaf extract at the same concentration (200 mg·L^{-1}) demonstrated a positive impact on the growth (root and shoot lengths) and yield (number and weight of seeds, oil content) parameters of mustard (*Brassica juncea* L.) [169], while concurrently reducing the percentage of Alternaria disease by 70%. The same concentration of nanoparticles (38 nm) obtained by the sol–gel method had a positive effect on the growth and development of soybean roots.

However, at higher concentrations, a toxic reaction was observed, and nanoparticles of a larger size (59 and 500 nm) showed less efficiency [158].

Nevertheless, it is worth noting that for habanero pepper (*Capsicum chinense* Jacq.) in greenhouse trials, foliar applications of ZnO-NPs at high concentrations of 1000 mg·L^{-1} at different stages demonstrated a positive effect on plant height, leaf diameter, and chlorophyll content. Additionally, ZnO-NP treatments increased fruit yield and biomass accumulation, in contrast to the $ZnSO_4$ treatments. However, treatments at a concentration of 2000 mg·L^{-1} exhibited a detrimental effect on several plant growth indices, yet significantly improved fruit quality. These improvements were observed through enhanced capsaicin and dihydrocapsaicin content, as well as an increase in the content of total phenols and total flavonoids in fruits [154].

The synthesis of manganese–zinc ferrite nanoparticles containing three trace elements simultaneously ($Mn_{0.5}Zn_{0.5}Fe_2O_4$-NPs) was achieved through a straightforward hydrothermal synthesis process, without the use of a template, using microwaves at varying temperatures (100, 120, 140, 160, and 180 °C). The results demonstrated that the particle size increased with the rise in microwave temperature [31]. The efficacy of this nanofertilizer at concentrations of 0, 10, 20, and 30 mg·L^{-1} of each of the synthesized sizes was evaluated on a zucchini (*Cucurbita pepo* L.) crop. The results indicated that the ferrite nanoparticles obtained at 160 °C (5–8 nm) and 180 °C (10–11 nm) exhibited the most optimal outcomes. The application of nanoferrites synthesized at 160 °C and sprayed on growing plants at a concentration of 10 mg·L^{-1} resulted in the highest yield increase compared to untreated pumpkins. Conversely, the maximum organic matter content in pumpkin leaves was obtained on plants treated with 30 mg·L^{-1} ferrite nanoparticles synthesized at 180 °C [31].

3.2.4. NFs: Copper Sources

Copper plays a unique role in plant biology, influencing a range of processes, including photosynthesis, the accumulation of growth inhibitors, water metabolism, and the redistribution of carbohydrates. Copper also constitutes a component of certain enzymes and has stress-protective effects [200–202].

The presence of copper in plants stimulates the synthesis of chlorophyll, thereby enhancing the plant's resistance to disease. Copper deficiency results in loss of turgor in young leaves, which causes them to curl and the plant to wilt. Copper deficiency initially manifests as an enlargement, pallor, and weakness of apical leaves, which subsequently become twisted and die off [203]. Copper deficiency is observed in the presence of excess phosphorus and is contingent upon the pH of the solution.

Copper is employed in a multitude of applications, both in livestock and plants. However, its high content has the potential to affect the resistance of soil and water sources to antibiotics and increase the risks of pathogens in the environment [204]. Additionally, high concentrations of copper are toxic to plants [205]. Consequently, it is imperative to rationalize the application of Cu fertilizers in order to prevent environmental pollution. The application of Cu-NPS and microbial Cu removal technologies can significantly reduce the risk of poisoning and environmental pollution.

It was previously determined that the concentration of Cu in Hoagland's solution at 0.02 mg·L^{-1} is optimal for the normal growth and yield of crops [132]. A significant number of researchers have identified adverse effects associated with the application of Cu-NPs at doses exceeding the required concentration [172,173]. For instance, Cu-NPs applied at concentrations of 200–1000 mg·L^{-1} were found to have toxic effects on the growth of mung bean, wheat, and yellow pumpkin seedlings. Similarly, a 90% reduction in zucchini biomass compared to the control (without Cu) was recorded after the incubation of seedlings in Hoagland's solution for 14 days when Cu-NPs were applied at a concentration of 1000 mg·L^{-1}.

Shah and Belozerova [174] observed that the growth rate of 15-day-old lettuce seedlings increased by 40% and 91%, respectively, when Cu-NPs were applied at concentrations of 130 and 600 mg·kg^{-1}. Similarly, a 35% increase in the photosynthetic rate of *Elodea densa*

Planch. was reported during a three-day incubation period when a low concentration of Cu-NPs was applied at a concentration of $\leq$0.25 mg·L^{-1} [175].

3.2.5. NFs: Molybdenum Sources

Molybdenum serves as an indispensable nutrient for the growth of leguminous plants. This is due to the fact that it plays a crucial role in biological nitrogen fixation (BNF), a process that involves the enzyme nitrogenase. Cultivated plants typically require approximately 0.01 mg·L^{-1} (0.01 mol·L^{-1}) of soil solution for normal metabolic processes.

Taran et al. [176] investigated the effect of different combinations of N-fixing bacteria and molybdenum nanoparticles (Mo-NPs, microbial inoculation with nitrogen-fixing bacteria and a combination of microbes and Mo-NPs) on the growth of *Cicer arietinum* L. under greenhouse conditions. The chickpea seeds were soaked in each of the treatments for a period of 1–2 h. The findings demonstrated that the integrated application of N-fixing bacteria and Mo-NPs markedly enhanced the microbial attributes of the rhizosphere, encompassing all categories of agriculturally significant microbes. The combination of the two treatments was found to significantly enhance the number of roots, the number of nodules per plant, and the weight of nodules per plant in comparison to the control.

In a separate study by Chen et al. [177], the effect of Mo-NPs at varying concentrations (0, 25, and 100 μg·mL^{-1}) on the growth of tobacco (*Nicotiana tabacum* L.) seedlings under foliar and root irrigation was also evaluated. The study demonstrated that root irrigation positively affects the water and sugar content of seedlings. The number of root cells decreased, while the number of vascular bundles increased in the treated tissues. The photosynthetic rate was enhanced when 100 μg·mL^{-1} Mo-NPs was applied due to an increase in chlorophyll content and stomatal conductance. An increase in MDA content and defense enzyme activities was observed in tobacco seedlings treated with Mo-NPs [177].

The application of molybdenum disulfide-based nanomaterials (nano-MoS_2) to soil during soybean cultivation resulted in the transformation of these materials within the soil and plant tissues. This process involved the release of Mo and S, which were subsequently incorporated into key enzymes involved in nitrogen metabolism and the antioxidant system. Concomitantly, enhanced biological nitrogen fixation, accelerated plant growth, and a 30% increase in yields were observed in comparison to those achieved with conventional bulk fertilizer (Na_2MoO_4). The excessive transformation of MoS_2 led to the accumulation of Mo and sulfate in plants, which, in turn, resulted in a reduction in nodule function [178].

3.2.6. NFs: Boron Sources

Boron (B) is the most important trace element involved in the formation of plant cell walls. It participates in the protein and enzymatic functioning of the cell membrane [206,207], ion fluxes (H^+, K^+, PO_4^{3-}, Rb^+, Ca^{2+}) [208], and cell division and elongation [209] and plays a key role in nitrogen metabolism [210]. Boron deficiency results in the accumulation of phenols, which can be observed in plants [211]. Boron is a vital element for plants, playing a crucial role in the normal functioning of growth points. It is also involved in the increase in the number of flowers and fruits [212]. Consequently, the symptoms of deficiency of this trace element are primarily manifested in young shoots and growth points in the form of necroses, burns, and spots.

Boron deficiency is traditionally mitigated by the addition of inorganic fertilizers that disturb soil fertility, which can lead to environmental pollution. Consequently, alternative approaches, such as the use of biostimulants (mycorrhizal fungi and rhizobacteria) and nanomaterials, are being considered as potential solutions to the issue of boron deficiency in plants. These approaches could effectively deliver boron to plants, thus allowing for the more efficient utilization of resources and reducing environmental stresses [213].

A field experiment on peanut (*Arachis hypogea* L.) cultivation was conducted to examine the effects of nanoparticles and biofertilizers on plant growth, yield, and biochemical parameters [39]. The application of Ca+B nanoparticles (200 mg·L^{-1}) to plants resulted in enhanced plant height, yield, oil content, and seed protein. In contrast, plants treated with B-

NPs exhibited the highest seed nitrogen content, number of pods per plant, and biofertilizer yield when compared to other treatments. The combined application of nanotechnology and mycorrhiza symbionts resulted in a significant increase in the growth, yield, and quality of groundnuts, thereby contributing to environmentally friendly farming practices.

A study was conducted to assess the impact of the foliar application of boron nanoparticles (B-NPs 80 nm) on the growth and physiology of lettuce (*Lactuca sativa* L.) and zucchini (*Cucurbita pepo* L.) cultivated under controlled greenhouse conditions. The findings revealed that the treatment enhanced the shoot, root, and total plant biomass growth of both crops. Furthermore, the treatment demonstrated efficacy in enhancing plant productivity in boron-deficient soil [179].

3.3. Prospects for Further Research and the Application of Nanofertilizers in Agriculture

To determine the effectiveness of nanofertilizers in comparison with bulk analogs, publications since 2012 were assessed and data regarding positive controls (bulk fertilizer) and nanofertilizers were summarized (Figure 4). For some nutrients discussed in this article (Ca, S, Mo, B), in order to conduct a full analysis, the representativeness of the samples was not enough, since the positive effect of the applied nanoparticles on germination, yield, and quality indicators of the tested crops was not sufficiently studied or is absent. Part of the research did not have a positive control, which significantly complicated the analysis of their effectiveness. In addition, the effect of nanofertilizers is species-specific, showing different effectiveness for different crops [139–141,165,179].

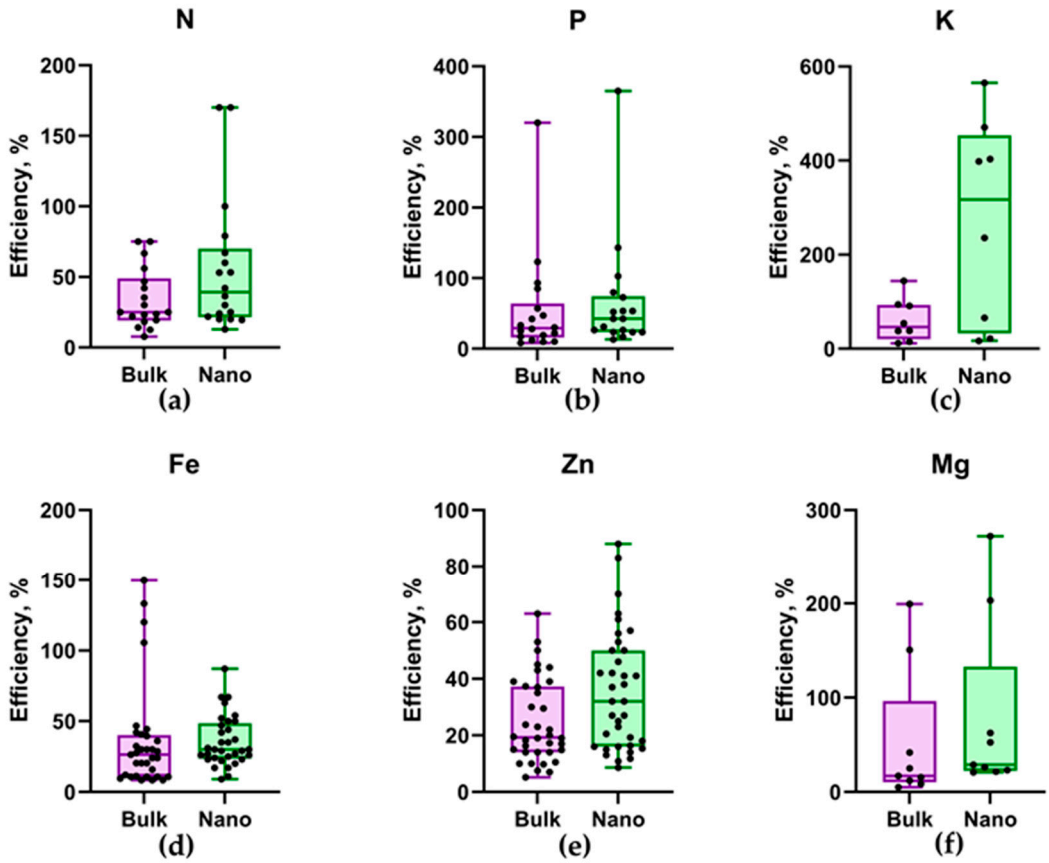


Figure 4. Comparative assessment of the effectiveness of using nanofertilizers containing nitrogen (**a**), phosphorus (**b**), potassium (**c**), iron (**d**), zinc (**e**), and magnesium (**f**) in comparison with their bulk counterparts. Data taken from PubMed database https://pubmed.ncbi.nlm.nih.gov/ from 2012 to 2024. Black dots represent studies that compared the effects of using both nanofertilizers containing a specific element and bulk fertilizers.

From the above graphs, it can be established that the use of nanofertilizers containing phosphorus, iron, and magnesium does not have obvious advantages compared to bulk analogs; however, they are not inferior to them and are able to compete with them in the fertilizer market due to the reduction in the influence on ecosystems with rational application.

The use of nanofertilizers—sources of nitrogen, potassium, and zinc—shows greater efficiency compared to bulk analogs. However, the lack of a sufficient number of studies devoted to testing nanomaterials containing the main macroelements—nitrogen and potassium—delays the release of these nanofertilizers for widespread use. Commercial nanofertilizers containing zinc have already gained popularity in Brazil, India, and the UK [214]. Despite the small amount of research on nanomagnesium, commercial fertilizers based on it are also popular in Latin American countries with high levels of soil degradation.

The investigation of such properties of used nanomaterials as size, shape, and charge is necessary to understand their effect on plants. It is necessary to understand the correlation of these traits with the growth parameters and quality of the resulting crop products. In addition, as studies have shown, selecting different concentrations [27,31,142,149,152–154], modifications [87,149], preparation methods [31], and sizes [29,155], as well as joint use with other nutrition components [84], can influence various parameters of growth and quality of the resulting foods, which, in turn, is important for the production of functional products.

Although macronutrients are very important in plant nutrition, most research on nanomaterials for use as fertilizers focuses on micronutrients. The most promising and important direction from the point of view of environmental safety in the near future may be research into methods for the production and use of nanofertilizers with sources of nitrogen as the main element of nutrition.

Most of the research was carried out in controlled laboratory conditions or in climatic chambers that were only partially close to real field conditions, so extensive field research in this area is necessary to obtain more reliable results. Particular attention in subsequent field experiments should be paid to methods of applying nanofertilizers. Lots of the research on the use of nanofertilizers, especially those containing microelements, was carried out using foliar treatments, which are not always effective in field conditions and are not always applicable due to weather conditions. Therefore, the use of multicomponent nanocomposites with the sustained release of components containing macro- and microelements is considered promising [215]. It is also necessary to develop and adjust strategies for applying nanofertilizers in precision farming systems using unmanned aerial vehicles equipped with hyperspectral cameras that obtain data on the lack of nutrients [8] and the local application of missing elements in order to avoid the excessive application of fertilizers and reduce negative influences on ecosystems.

It is also necessary to take into account the fact that nanoparticles, when they enter plants, move along the food chain to the final consumer: humans. The mechanisms of assimilation and transformation of nanoparticles in plants are not fully understood, so concerns arise about their possible negative cumulative effect on human health. For the widespread introduction of nanofertilizers into agriculture, an integrated approach to the study of their transformations in the "soil-plant-farm animals-human" system is necessary.

4. Conclusions

It can be reasonably concluded that the use of nanofertilizers in agriculture is a promising avenue of research compared to the use of "classical" mineral fertilizers. The principal advantages of nanofertilizers are their more pronounced effect on the growth and yield of agricultural crops and, as a consequence, their high efficiency of use at lower concentrations than that of applied mineral fertilizers. It is important to note that mineral volumetric fertilizers can have adverse environmental effects, including damage to the environment, eutrophication, and the accumulation of excess fertilizers in soil and groundwater. The impact of nanoparticles and nanomaterials is species-specific and contingent upon the application method, size, shape, production method, and concentration of nanoparticles utilized. Despite the considerable number of reports on the high efficiency

of nano-fertilizers, there is a paucity of literature data on the subject. The existing limitations on the introduction of nano-fertilizers in mass production due to the disparate initial parameters of the particles on which research has been conducted (size, synthesis methods, etc.) also present a certain difficulty. Moreover, there is a paucity of comprehensive studies on crops belonging to different botanical families, which would facilitate the development of general principles of the practical application of nanoparticles. It is also notable that there is a paucity of scientific data on the biosafety of nanomaterials used in agriculture. Consequently, it is of the utmost importance to conduct further detailed toxicological studies of nanofertilizers in animals and humans, given the possibility of their ingestion with consumed foodstuffs.

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