

Review

Phosphorous Nanofertilizers for Precise Application in Rice Cultivation as an Adaptation to Climate Change

Raquel Saraiva ^{1,2,*}, Quirina Ferreira ³, Gonçalo C. Rodrigues ^{1,2}  and Margarida Oliveira ^{2,4} ¹ Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal² LEAF—Linking Landscape, Environment, Agriculture and Food Research Center, Associated Laboratory TERRA, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal³ Instituto de Telecomunicações, Avenida Rovisco Pais, 1000-268 Lisboa, Portugal⁴ Escola Superior Agrária, Instituto Politécnico de Santarém, Quinta do Galinheiro, 2001-904 Santarém, Portugal

* Correspondence: raquelcosta@isa.ulisboa.pt

Abstract: Rice is the staple food of more than half of the world's population, which is still growing. The great dependence that agriculture, and rice specially, has on fertilizers alongside extreme events that result from climatic change creates an urge for adaptation. Fertilizers are expensive, finite and a potential environmental problem. Their precise application, by the use of slow-release nanofertilizers, thus avoiding losses and consequently reducing the pressure on water resources, is one step forward in this adaptation. It can reduce costs and protect the environment while ensuring food production. Phosphorous is very important for rice, since it is involved in its flowering and root development, and its low availability to the plants constitutes a serious problem. The delivery of phosphorous through the crop cycle in the form of slow-release phosphorus nanofertilizer (Pnf) instead of the conventional annual bulk application reduces the amount of nutrients applied and increases the absorption by the crop. Combining the fertilizing effect with the use of natural stimulant compounds such as chitosan can protect the crop from diseases and increase its resilience to stress. The use of Pnf reduces the pressure on water resources and avoids imbalances in soil nutrients, thus responding to climatic change challenges and abiotic stresses.

Keywords: crop resilience; food security; *Oriza sativa* L.; slow-release fertilizer; water safety



Citation: Saraiva, R.; Ferreira, Q.; Rodrigues, G.C.; Oliveira, M. Phosphorous Nanofertilizers for Precise Application in Rice Cultivation as an Adaptation to Climate Change. *Climate* **2022**, *10*, 183. <https://doi.org/10.3390/cli10110183>

Academic Editors: Charalampos Skoulikaris and Christina Anagnostopoulou

Received: 14 October 2022

Accepted: 18 November 2022

Published: 20 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Rice is the second most consumed cereal in the world and is a staple food for millions of people. Its consumption is expected to increase and is aligned to global population growth [1]. In contrast to the increase in wheat and maize prices, rice has been subdued, and efforts to curb inflation are notable in averting a worldwide food crisis, but there is no guarantee that this will continue. China, India, Indonesia and Bangladesh produce the largest quantities of rice. The use of fertilizers is essential for plant growth and development in agricultural production [2], and rice is very dependent of it. With rising fertilizer costs and at a time when demand is increasing, there is a potential food availability risk [3].

Phosphorous (P) is an essential macronutrient for plant growth. It is a component of key molecules such as nucleic acids, phospholipids and ATP and, consequently, plants cannot grow without its reliable supply [4]. Furthermore, the availability of P can improve the nitrogen-fixing capacity of plants and support their development throughout the plant's life cycle [5]. However, since P is one of the least available and mobile nutrients in many cropping environments [6], farmers tend to continuously and excessively apply P fertilizers, leading to eutrophication in surface waters and reducing groundwater quality [7].

Eutrophication is one of the greatest threats to freshwater resources. This drives an increase in algal biomass, has implications for greenhouse gas sources [8,9] and promotes the presence of cyanobacterial toxins [10]. Regarding environmental management, it is

compelling to understand how climatic factors interact with nutrients influencing water quality [11]. According to Shuvo et al. [12], climatic variables act synergistically with other factors on water quality degradation. Nutrient management is key to ensuring water quality, especially in the context of climate change [13].

The “farm to fork strategy” [14] intends to reduce at least 20% of fertilizer use by 2030 and to cut nutrient losses in half while ensuring the food supply for the increasing world population. The achievement of these goals will require multiple strategies. Precision agriculture aims to aid in this goal. It allows the optimization of crop yields while minimizing the use of chemical fertilizers, pesticides and herbicides by monitoring environmental variables and supporting more sustainable decision-making. For this, new technologies have been developed aiming to increase crop productivity and reduce the resource costs and environmental impacts related to agricultural production. These technologies can measure crop requirements, allowing a reduction in inputs (e.g., fertilizer). By increasing crop growth and production even under abiotic stress, nanofertilizers can help the availability of food as required [15–17] without the use of more land. This maintains the ratio of farming land and stops the increasing pressure on ecosystems. Slow-release phosphorous nanofertilizers can be tailored to release the nutrient according to the plant’s requirement, thus improving uptake efficiency, targeting the most successful delivery of P and increasing production (Figure 1). This is very important since temperature alterations affect not just seasonality but also soil pH and consequently P availability forms.

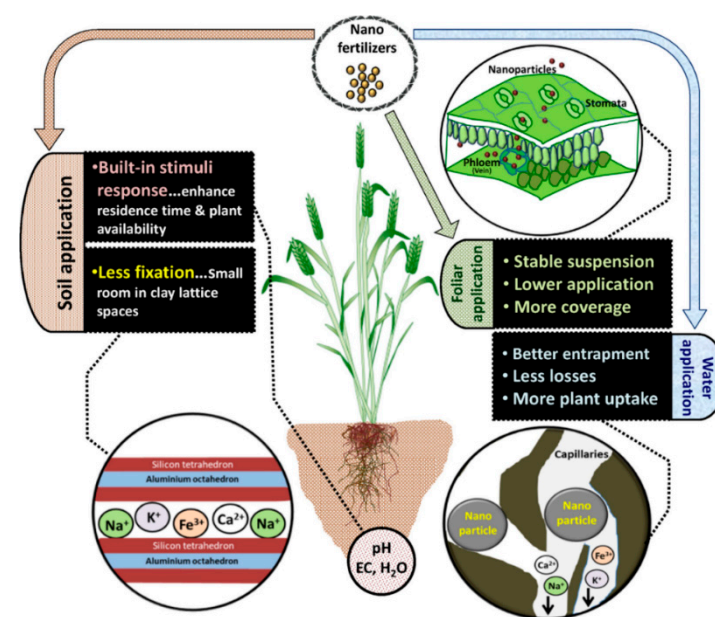


Figure 1. Potential benefits of nanofertilizers under different modes of application for crop production. In [18] under Creative Commons Attribution License (CC BY).

Cutting-edge strategies are crucial, as the costs of inputs are expected to increase drastically due to limited reserves [19], hence the importance of adopting alternative approaches that minimize agricultural costs while maximizing crop sustainability.

Nanofertilizer research appeared in 2011 and has gain relevance in the last years. Pnf research has been focused on soil quality improvement, its effect on soil microorganisms and, more recently, its effect on plant nutrition under abiotic stress.

The data for this review were obtained by research papers in the Web of Science, Science Direct, MDPI and Springer databases as well as the publications of governmental and relevant international institutions. The aim of this paper was to serve as a reference for understanding the benefits of phosphorous nanofertilizers in improving farming and environmental sustainability while promoting food security under climate change.

2. Environmental Impact of Phosphorus Use

Phosphorus is the eleventh most abundant element in the Earth's crust and is present in the biosphere, hydrosphere and geosphere, although, minerals containing it in a concentrated form occur only in very few areas of the Earth [20], mainly located in China, the United States and Morocco, leaving the world very dependent on geopolitics to assure food security. In addition, market demands pose as problem too since phosphorus demand around the world is increasing and the prices are spiking [21].

Phosphorus is an essential nutrient for sustaining life on Earth, playing a central role in energy transfer within organisms, in the structure of genetic material, in respiration, in photosynthesis and in nitrate reduction [22,23]. Over 99% of natural P is in the form of phosphate, either inorganic or organic. Phosphorus content in natural agroecosystems is generally low, and much of it is not available to plants because it is either absorbed or precipitated [24]. The negative charge of this ion is conducive to binding to any cation, which also restricts the mobility of P in the environment [25]. Phosphorus moves through the soil predominantly by diffusion and is taken up as a dihydrogen phosphate ion or, more slowly, as hydrogen phosphate. In soils with pH lower than 6, the dihydrogen phosphate ion is predominant, while in alkaline soils the hydrogen phosphate ion is the most representative. The latter is not only absorbed more slowly but is also less soluble, making alkaline soils often deficient in P [24].

Moreover, since the diffusion process only occurs in a short distance from the roots, phosphorus is only extracted from a small volume of soil, with only 10–20% of nutrient supplied by fertilizers being taken up by plants in the year of application [24]. In intensive farming systems, the successive annual application of organic or mineral fertilizers leads to the progressive enrichment of soils with this element. Such situations may lead to a lack of crop response to fertilizer application, representing an environmental risk. Consequently, the high concentration of P in the soil and the existence of conditions favorable to leaching and soil erosion lead to the potential contamination of water bodies.

In water bodies, the behavior of P is distinct, with P being more available than in a soil matrix, where sorption is strong and transport to the uptake surfaces is limited by diffusion [25]. Even low concentrations of P are therefore very effective in increasing the biological productivity of aquatic systems, pushing marine and aquatic systems beyond their ecological limits [20,26]. The water system, whether it is lentic or lotic, the water retention time and the mineralization, diffusion and bioabsorption of nutrients are all temperature-dependent variables. Biochemical processes and the chemical profile of water are also directly influenced by temperature. Therefore, a change in water hydrodynamics and/or stratification due to a temperature increase can substantially affect nutrient availability. Lakes with long retention periods may face increasing phosphorus levels [27]. Under borderline conditions, it can speed up the eutrophication of rivers and lakes, with impacts on public health, food security, biodiversity and other ecosystem services. Table 1 summarizes the micro- and macro-effects of traditional phosphorus.

Table 1. Micro- and macro-effects of traditional phosphorus use.

Effect	Impact at Micro Level	Impact at Macro Level
P leaching and soil erosion	Contamination of waterbodies	Endangerment of public health; food security, biodiversity and ecosystems services
Precipitation or adsorption in soil particles	Soil P enrichment but non-available to plants	More resources needed every year

There is increasing evidence that human activities are disrupting the functioning of the Earth's systems to a degree that threatens its resilience. Planetary boundaries delineate a safe operating space for human societies to develop and thrive [28]. Considering the nine planetary boundaries, phosphorus is one of the processes classified with a high risk, even higher than climate change [20]. Crossing these boundaries increases the risk of

generating large-scale abrupt or irreversible environmental changes [29]. According to Asensio et al., [30] climate change will increase phosphorus demand in Mediterranean soils. Seasonal droughts will amplify the imbalance between extractable soil P, C and N due to soil community metabolisms, which will lead to a lower relative P availability for soil organisms and a higher probability of P limitation. In addition, studies conducted by Wang et al. [31] showed that climate warming blocked increases in P fractions within macroaggregates and microaggregates, highlighting the interactions between chemical and biological factors in controlling the distribution of P fractions in soil aggregates.

Conventional assessment methods such as life cycle assessment [32] and consumption-based ecological footprint accounting [33–35] have also been connected to the planetary boundaries framework to provide an assessment on the sustainability of an entity or activity, highlighting potential boundary transgressions.

So, there are strong arguments for an integrated enforcement of “planetary boundaries thinking” at different levels, from nations to basins and regions, where policy decisions might be more influential [36,37]. The global food system cannot remain indifferent to the urgent change in mindset of admitting that agricultural ecosystems are possibly the largest biome on Earth, with a major impact on the planet’s elementary cycles: nitrogen, phosphorus, water and carbon [38]. It is therefore urgent to design and implement more effective and sustainable fertilization systems [20].

3. Nanofertilizers with Phosphorus-Controlled Release of Phosphorus

Most nanofertilizer studies have focused on the use of NPKs and some combination of micronutrients so that nutritional equilibrium is achieved. In these cases, 50% or even 25% dosages are effective when compared to a 100% dosage of conventional fertilizer, mostly because of the controlled or slow-release of the nutrients [39,40]. Nonetheless, Pnf has also been studied for their positive impacts in several crops. Based on their application method, nanofertilizers can be classified into three categories: foliar application, water application and soil application (Figure 1). Regarding plant nutrient requirements, they can also be classified as nanoporous materials, nanoscale additive fertilizers and nanoscale coating fertilizers [41]. The concerns about the fate of nanofertilizers in the ecosystems could be addressed by choosing adequate supports for the nutrients and using green synthesis methods to obtain them [42]. Coated, nutrient-loaded nanomaterials and encapsulated nanomaterials have the advantage of being safer, more stable and able to adapt the release of the fertilizer according to crop requirements better than non-coated nanomaterials [41,43].

Adhikari et al. [44] tested nano-rock phosphate (RP) for field application in maize, and the results showed that the crop utilization of P from nano-RP was similar to the results of superphosphate (SSP), and it was a cheaper P source than SSP. More recently, research efforts have begun to explore nanoformulations of hydroxyapatite (nHAP; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) as a carrier for other nutrients and as a P fertilizer, in addition to its soil bioremediation properties [16]. The application of Pnf in controlled amounts can also increase the biological functions of crops, including the continued and improved uptake of P and other nutrients as the plants grow [16,45]. While it has been pointed out that only 5% to 30% of traditionally applied P is in fact usable by plants [46], the use of slow-release Pnf in several crops emphasizes the suitability of these materials as an effective and precise Pnf. In Priyam et al. [16], slow-release Pnf increased P levels in tomato crops, which led to enhanced germination and growth without any stress caused due to its application in a variety of soils. In addition, Pnf was found to promote a greater physiological efficiency of the shoots and roots for P, stimulating photosynthetic activity and increasing the instant water use efficiency in rice plants while reducing up to 50% of the dosage of P applied [47]. The results obtained by P release over time substantiated the higher nutrient efficiency of the Pnf over traditional fertilizers, which confers several benefits to crops. Similarly, nHAP enhanced growth by around 5% and dry yield by 30% in comparison to traditional P fertilizer in cluster beans [48]. In soybean, the improvement was around 33% in terms of growth rate and 20% in terms of seed yield in comparison to traditional P fertilizer [49].

Pnf has shown to be more effective than control in terms of lettuce growth, which also presented a tendency towards a higher P concentration, although with no significance [50]. In rice, urea-nHAP was used as controlled-release formulation, improving seedling growth and fresh and dry weight when compared to a control [51]. Pnf incorporated in zeolite showed a higher accumulation of P (two times) and K in water spinach plants, in addition to revealing positive effects in the soil after its application, with a better pH, moisture, cation exchange capacity and available P than conventional fertilizer [52].

Phosphorus nanofertilizer can also be effective in soil reclamation processes as showed by Yasmeeen et al. [53], which reported that rock phosphate Pnf promoted plant growth and yield in degraded soil, it being effective especially when encapsulated in a chitosan shell. In their study, the authors used top-soil from degraded agricultural land that had already undertaken 10 years of reconstruction and restoration to perform a pot experiment to evaluate the agronomic potential of rock phosphate Pnf, both encapsulated with chitosan (ERPnf) and non-encapsulated (RPnf). P nutrition and P use efficiency (PUE) under RPnf exhibited minimal but positive effects on maize growth when compared to the control treatment, but ERPnf was the more suitable Pnf due to its higher slow-release capacity, increasing not only P nutrition and PUE but also achieving a higher plant growth and grain yield compared to all treatments. Compared to the control, the authors found that both of the Pnfs used in this study (RPnf and ERPnf) significantly enhanced the abundance of phosphate-solubilizing bacteria, increased biomass and grain yield and considerably enhanced grain P accumulation. In addition, both modalities presented positive effects in the soil rhizosphere and P biological pools, higher root carboxylate secretions and decreased the rhizosphere pH, which could be due to their higher specific area and the crystalline structure of Pnf. The presence of greater P-solubilizing bacteria under the RPnf and ERPnf treatments when compared to the control implies a greater rhizosphere area and a greater P mobilization and solubilization, leading to optimized conditions for plant growth and an enhanced cropping potential in degraded agricultural lands. Thus, chitosan, as an encapsulation polymer, can function as an absorbent for water, promoting microbial activity and emphasizing chitosan's position as an eco-friendly, efficient control-release material for nanofertilizer development [53].

A new Pnf, which is in development by the authors, uses slow-release technology to ensure the precise and efficient application of P along the rice cycle and is expected to have a biostimulant effect by the use of chitosan [54,55]. This Pnf combines poly-beta-amino-esters (PBAE), graphene oxide (GO), chitosan, poly lactic-co-glycolic acid (PLGA) and P in the forms of active and barrier layers to control the slow-release of P during the first stages of rice production. PBAE was chosen for its tuneable charge density and possibilities for different kinetic profiles, due to it having great potential as delivery vector. Graphene oxide is used in several areas, acting as a barrier agent in slow-release compounds, and some studies have pointed out that it can have an anti-microbial activity effect [56]. The use of GO should be carried out carefully since the information regarding the phytotoxicity of graphene compounds in agriculture is not consensual in the literature. It is suggested, however, that it may have a negative influence on crop germination in quantities greater than $100 \text{ mg}\cdot\text{L}^{-1}$ [57–60]. Frequently used for the encapsulation of substances such as growth regulators and fertilizers, PLGA is a biodegradable copolymer with slow-release and adjustable properties [61]. As for chitosan, it is a polysaccharide, and it is biocompatible and biodegradable with a bio-stimulant effect on the immune systems of crops, promoting antifungal and antiviral properties, bionematicides and the strengthening of catalytic enzymes [62–66]. It has been used as a carrier for other agricultural compounds due to its properties and several studies have reported increased water retention and removal of heavy metals in soil with its use as well as a positive effect in algal contamination control, improving water quality [67,68].

To ensure the safety of GO use, Saraiva et al. [69] conducted a preliminary study where the interaction of GO concentrations ($0.25 \text{ mg}\cdot\text{mL}^{-1}$ and $0.5 \text{ mg}\cdot\text{mL}^{-1}$) with phytotoxicity in *Lepidium sativum* L. was assessed. The results showed that 100% of the seeds germinated

in both GO concentrations, and the seeds exposed to the lower concentration presented the same root length as the control. However, the $0.5 \text{ mg}\cdot\text{mL}^{-1}$ GO promoted a decrease of around 20% in terms of root length. Despite some reduction in root length, the fact that 100% of the seeds germinated in GO concentrations well above those found in the literature (which were expressed in the order of $\mu\text{g}\cdot\text{mL}^{-1}$) is an indication that GO can be safely used in crops [70].

Other studies are being conducted in the field of nanobiofertilizers, which refer to biofertilizers (microorganisms) combined with a nanofertilizer and also to microorganisms encapsulated in nanomaterials, although some microorganisms are not nano sized [71]. Phosphate biofertilizers include phosphorous-solubilizing biofertilizers and phosphorus-mobilizing biofertilizers [72], and although no studies have addressed phosphorous biofertilizers yet, they can pose as an option for development.

4. Benefits of Nanofertilizers for Agroecosystems

The use of nanofertilizers is effective and efficient in crop nutrition and brings several environmental benefits, especially under climatic change and abiotic stress conditions (Figure 2).

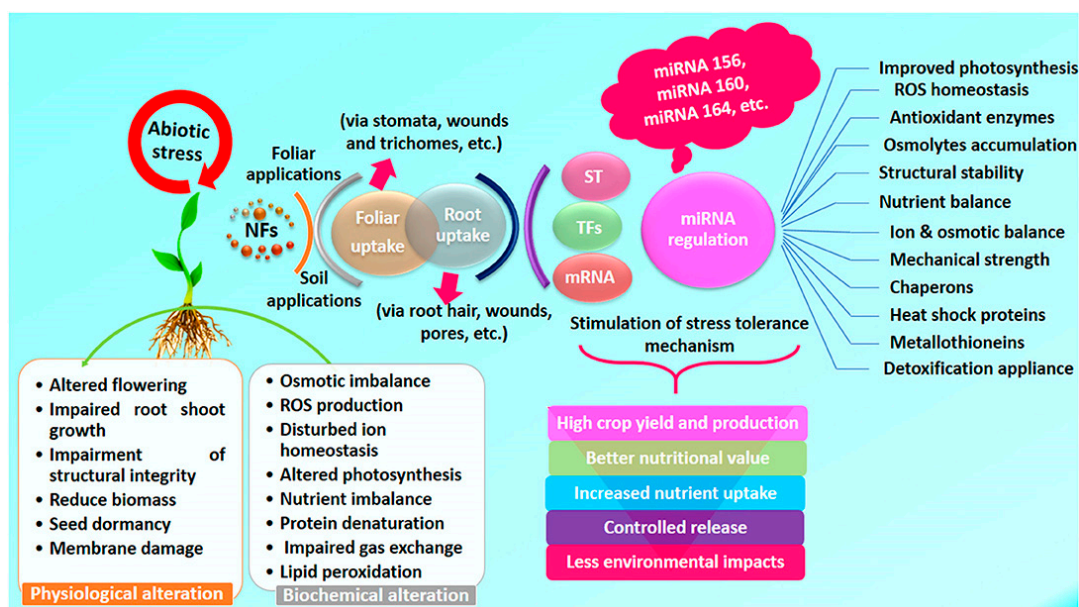


Figure 2. Nanofertilizer benefits in the face of abiotic stress. In [73] under Creative Commons Attribution License (CC BY).

As demonstrated by Yasmeen et al. [53], nano-rock phosphate fertilizer, in particular encapsulated,, improved soil parameters and promote plant growth, aiding the restoration of degraded and abandoned croplands. However, other studies have pursued the understanding of the benefits of nanofertilizer use in presence of ecosystems under abiotic stress. In 2019, Zulfiqar et al. [74] gathered the recent works published about the response effects of nanofertilizers in different crops in the face of different abiotic stresses. Salinity is the most studied abiotic stress and represents a global concern. The review presents the overall positive effects of the pre-sowing application of multi-walled carbon nanotubes, nano SiO_2 , nano silicon and nano urea HAP in cabbage, pumpkin, hollyhock, almond and tomato. The applications resulted in enhanced seed germination, length, diameter, number of secondary roots/plants, plant growth, height, water uptake, net assimilation of CO_2 , total soluble sugars and membrane stability. The application of these compounds also increased the photosynthetic parameters, improved antioxidant enzyme activity and up-regulated the expression profile of salt-stress genes, while reduced the marker for oxidative stress, decreased H_2O_2 , chlorophyll degradation and oxidative damage.. The results for

the application of nano chitosan-PVA and Cu, nano Si and nano Ca in post-transplanting were also positive for tomato and chili pepper, with the plants presenting improved stem diameters, number of flowers, enhanced plant growth, fresh weight, photosynthetic rate, chlorophyll concentration and leaf water content while promoting gene expression and enzyme activity and significantly regulating plant salinity stress. The foliar application of nano Si in peregrine in order to assess the response to salinity stress conducted by Ashour and Mahmoud [75] also revealed enhanced chemical and vegetative parameters (26% higher plant weight, 31% more branches per plant, 19% more leaves and 9% more leaf area in a 4000 ppm salt concentration conditions) while the accumulated content of Na, Cl, total phenolic and flavonoid content was decreased in the peregrina leaves. As P has a positive effect in various crops facing salinity stress, including rice, the use of P nanofertilizers is expected to pose as a suitable adaptation to climatic-change-driven salinity increases.

The responses to Cd stress, Cr stress, drought and both high and low temperature stresses were also studied by several authors. Although the information obtained is specific for crops and specific sites, these studies revealed the important interactions that must be exploited in order to adapt to climatic change effects, and some related directly to rice crops. The abiotic stresses affecting rice include mainly salinity, drought, high and low temperatures, UV radiation and Cd, among others. According to Mahmood-ur-Rahman et al. [76], the way that rice responds to these abiotic stresses is through the activation of signalling pathways, which up- and down-regulate genes to face stress conditions and enable the plant to be more tolerant to challenging growing conditions.

The use of ZnO NPs, Si NPs and magnetite NPs in situations of Cr stress have positive effects in diminishing phytotoxicity in crops, since Prakash et al. [77] demonstrated that the addition of ZnO nanoparticles in a growing medium can reduce the toxicity and improve the growth of rice seedlings in soils contaminated with chromium. The same protection effect and improved seedling growth was observed by Tripathi et al. [78] when nano Si was applied to pea plants, while magnetite successfully reduced the toxicity and accumulation of Cr in wheat [79].

Diminished effects of Cd stress were also found with the addition of several nanoparticles and nanofertilizers in the forms of nano CeO₂, nano TiO₂, nano magnetite, nHAP and nano Si in several crop species including rice [79–82]. In this last study, the authors found that the use of nano Si reduced the Cd content in plants while improved the content of other nutrients such as K, Mg and Fe in grains. In addition, the addition of nano TiO₂ in rice cultures significantly boosted the development of the crops, reduced Cd toxicity and enhanced the photosynthetic efficiency [80]. Nano hydroxyapatite (nHAP) was also found to be effective in the immobilization of Cd in sediments and aqueous mediums. By means of its higher surface area, there was a higher sorption of Cd resulting from surface complexation and the diffusion of the high metal into the structure of nHAP. This reduced its concentration in the water and benefitted subsequent uses, which concurred with water safety and food security [83].

The positive effects of nHAP in crop stress was also observed in cases of Pb contamination, where nHAP was effective in increasing crop growth and biomass in ryegrass due to its effects on soil pH, which was increased by the application of the nanofertilizer and led to a reduction in Pb solubility and mobility in the soil. In sediments and aqueous mediums, nHAP was effective in immobilizing lead, reducing its exchangeable fraction and contributing to restoring polluted agroecosystem environments [83]. While surface complexation and diffusion are the mechanisms responsible for Cd sorption onto nHAP, the dominant mechanisms for Pb sorption are dissolution and precipitation, which is very interesting since both were successfully immobilized but by the means of different mechanisms [83].

Drought is an increasing abiotic stress and is closely related to climatic change, and the use of nanofertilizers and nanoparticles in order to reduce its effects could be very meaningful in the near future. In tomato and sorghum, nano CeO₂ and nano Si were used, respectively, to increase germination with positive results, although Haghghi et al. [84]

suggested its benefits in tomato were concentration-dependent [84,85]. Besides germination, nano CeO₂ increased the photosynthetic efficiency by 38% and grain yield by 31% in sorghum under drought stress, and the 10 ppm treatment induced a reduction in superoxide radicals, H₂O₂ and MDA by over 35% [85].

The use of nanofertilizers can also enhance soil's chemical properties and nutrient status, as seen in Figure 3. Increasing nutrient availability to the plants and reducing plant stress leads to nutrient uptake improvements [86,87], reduces the risk of disease resistance and benefits crop resilience. Soil fertility can also be restored or improved by the application of encapsulated nanoparticles such as nanoclays and zeolites, as nanofertilizers present the capability of combating soil- and groundwater-borne pollutants [88,89].

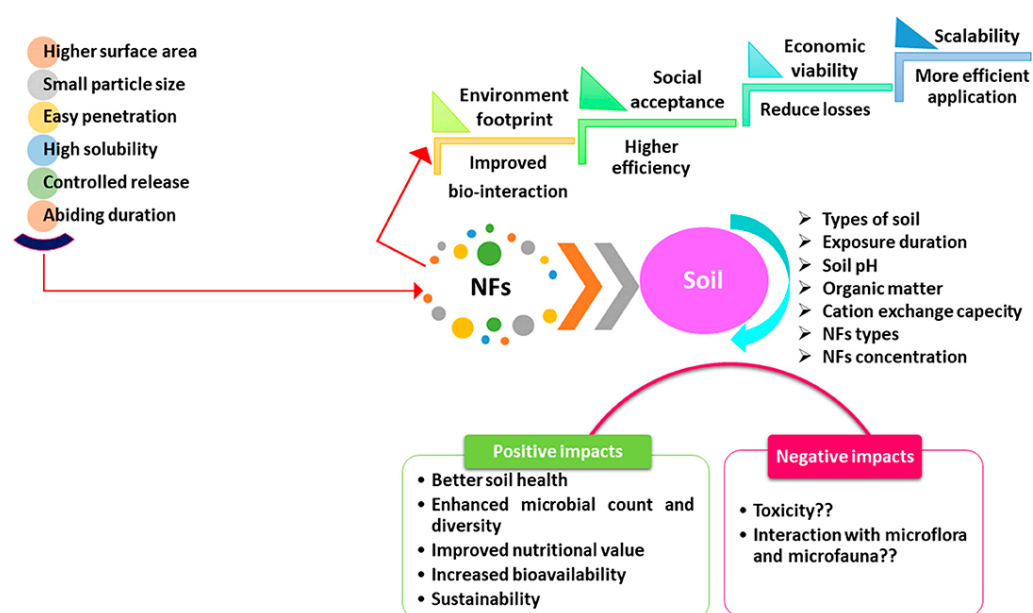


Figure 3. The role of nanofertilizers in soil. In [73] under Creative Commons Attribution License (CC BY).

Green nanoparticles such as agro-nanotechnologies, plant-nanotechnologies or phyto-nanotechnologies can even be a step forward for the sustainability of nanomaterials for agricultural application as they use biologically synthesized nanoparticles [42,90]. Nanofertilizers can increase defence responses and plant growth, as shown in several studies [91], due to the use of materials such as chitosan and their ability slowly release the nutrients, avoiding over dosage and ensuring absorption by the plants. The biodegradability and biocompatibility of chitosan along with its renewable sources (seafood bio-waste) and stimulating effect for plants turns it in an exceptional choice for environmentally friendly nanofertilizers [92]. Several commercially available fertilizers and bio stimulators in the market use chitosan clorhidrate, in which is a clear statement that industry and the public are urging for biodegradable supports for these new materials.

The low nutrient doses applied to crops ensure their non-toxic effects in crops and safety for aquatic biota [93]. The losses of P in agricultural soil involve complicated hydrological and biogeochemical processes and are influenced by climate, soil properties, crop types and other factors such as flooding frequency, which impacts both dissolved and particulate P and is very important in rice paddy fields [94,95], since it has been found that runoff is the major source of P losses [96,97]. The reduction in nutrient size and dosage enabled by nanofertilizers can enhance insoluble nutrient solubility in soil and boost their bioavailability to plants, directly resulting in less input and consequently less resource exploitation, while the slow-release of nutrients reduces or even eliminates nutrient loss and harmful effects on soil [15,42]. Phosphorous use in slow-release nanofertilizers can be delivered in small dosages but at a high efficiency, and it can be tailored to be delivered

at specific times, improving crop tolerance to increasing salinity and opposing the effects of seasonality alterations, ensuring correct fertilization and achieving food security in rice crops.

5. Conclusions

Nanofertilizers offer great promise for sustainable agriculture and for adaptation to climate change challenges such as food security, water and soil safety and environment protection. In addition, this can be achieved, but to do so it is crucial to ensure that the materials and doses being used are safe. It can be achieved by the use of green synthesis, the choice of the right biodegradable compounds and the smart utilization of naturally available compounds such as chitosan that boost plants immunity systems and increases the resilience of crops.

The main challenge in the application of nanofertilizers is the few commercially available options and public acceptance regarding this technology. This review demonstrated that the precise application of fertilizers, by the use of nanofertilizer forms and slow-release nanofertilizers, allows the use of fewer inputs, avoids losses and reduces pressure on water resources, thus responding to climatic change challenges and abiotic stresses.

6. Future Prospects

Adaptation to climate change involves many actions, and the use of nanofertilizers can be part of the solution, reducing inputs, boosting crop productivity and ensuring water and food safety. Phosphorous nanofertilizers for precise application in rice cultivation as an adaptation to climate change is one step forward, as they can deliver reduced costs and protect the environment while ensuring food production and security. These solutions concur with the UN's Sustainable Development Goals 2, 6, 12 and 13 by the use of slow-release components that improve rice immune systems and thus increase the crop's resilience to climatic change in addition to providing protection against increasing salinity. In addition, the efficient release of nutrients aims to avoid over dosage and losses, protecting aquatic ecosystems and water resources and promoting sustainable agriculture production patterns while ensuring food safety and availability.

Author Contributions: R.S. and Q.F. contributed to the design of the paper. R.S. had the main contribution to the research and manuscript writing. R.S., Q.F., G.C.R. and M.O. contributed to all parts of the article through commenting and as co-authors. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the Fundação para a Ciência e Tecnologia under the scope of Raquel Saraiva's PhD grant 2020.06559.BD, project PTDC/CTM-REF/2679/2020, UIDB/50008/2020 and under the UIDB/04129/2020 project LEAF—Linking Landscape, Environment, Agriculture and Food Research Unit.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. FAO. *World Cereal Production, Utilization, Stocks, and Trade All Likely to Contract in 2022/23*; FAO: Rome, Italy, 2022. Available online: <https://www.fao.org/worldfoodsituation/csdb/en/> (accessed on 3 June 2022).
2. Olad, A.; Zebhi, H.; Salari, D.; Mirmohseni, A.; Tabar, A.R. Slow-release NPK fertilizer encapsulated by carboxymethyl cellulose-based nanocomposite with the function of water retention in soil. *Mater. Sci. Eng. C* **2018**, *90*, 333–340. [[CrossRef](#)] [[PubMed](#)]
3. World Bank. *Commodities Price Data 2022*. World Bank: Washington DC, USA, 2022; Available online: <https://thedocs.worldbank.org/> (accessed on 2 August 2022).
4. Schachtman, D.P.; Reid, R.J.; Ayling, S.M. Phosphorus uptake by plants: From soil to cell. *Plant Physiol.* **1998**, *116*, 447–453. [[CrossRef](#)]
5. Amanullah, A.; Zakirullah, M.; Khalil, S.K. Timing and rate of phosphorus application influence maize phenology, yield and profitability in Northwest Pakistan. *Int. J. Plant Prod.* **2012**, *4*, 281–292.
6. Goldstein, A.H.; Baertlein, D.A.; McDaniel, R.G. Phosphate starvation inducible metabolism in *Lycopersicon esculentum*: I. Excretion of acid phosphatase by tomato plants and suspension-cultured cells. *Plant Physiol.* **1988**, *87*, 711–715. [[CrossRef](#)]

7. Conley, D.J.; Paerl, H.W.; Howarth, R.W.; Boesch, D.F.; Seitzinger, S.P.; Havens, K.E.; Lancelot, C.; Likens, G.E. Ecology—Controlling eutrophication: Nitrogen and phosphorus. *Science* **2009**, *323*, 1014–1015. [CrossRef]
8. Beaulieu, J.J.; DelSontro, T.; Downing, J.A. Eutrophication will increase methane emissions from lakes and impoundments during the 21st century. *Nat. Commun.* **2019**, *10*, 1375. [CrossRef]
9. Webb, J.R.; Leavitt, P.R.; Simpson, G.L.; Baulch, H.M.; Haig, H.A.; Hodder, K.R.; Finlay, K. Regulation of carbon dioxide and methane in small agricultural reservoirs: Optimizing potential for greenhouse gas uptake. *Biogeosciences* **2019**, *16*, 4211–4227. [CrossRef]
10. Hayes, N.M.; Vanni, M.J. Microcystin concentrations can be predicted with phytoplankton biomass and watershed morphology. *Inland Waters* **2018**, *8*, 273–283. [CrossRef]
11. Vaughan, I.P.; Gotelli, N.J. Water quality improvements offset the climatic debt for stream macroinvertebrates over twenty years. *Nat. Commun.* **2019**, *10*, 1956. [CrossRef] [PubMed]
12. Shuvo, A.; O'Reilly, C.M.; Blagrove, K.; Ewins, C.; Filazzola, A.; Gray, D.; Mahdiyan, O.; Moslenko, L.; Quinlan, R.; Sharma, S. Total phosphorus and climate are equally important predictors of water quality in lakes. *Aquat. Sci.* **2021**, *83*, 16. [CrossRef]
13. Quinlan, R.; Filazzola, A.; Mahdiyan, O.; Shuvo, A.; Blagrove, K.; Ewins, C.; Moslenko, L.; Gray, D.K.; O'Reilly, C.M.; Sharma, S. Relationships of total phosphorus and chlorophyll in lakes worldwide. *Limnol. Oceanogr.* **2020**, *66*, 392–404. [CrossRef]
14. EU Commission. *Farm to Fork Strategy*; EU Commission: Brussels, Belgium, 2020. Available online: https://ec.europa.eu/food/farm2fork_en (accessed on 30 November 2020).
15. Ndaba, B.; Roopnarain, A.; Rama, H.; Maaza, M. Biosynthesized metallic nanoparticles as fertilizers: An emerging precision agriculture strategy. *J. Integr. Agric.* **2022**, *21*, 1225–1242. [CrossRef]
16. Priyam, A.; Yadav, N.; Reddy, P.M.; Afonso, L.O.B.; Schultz, A.G.; Singh, P.P. Fertilizing benefits of biogenic phosphorous nanonutrients on *Solanum lycopersicum* in soils with variable pH. *Heliyon* **2022**, *8*, e09144. [CrossRef]
17. Banerjee, S.; Mazumder, S.; Chatterjee, D.; Bose, S.; Majee, S.B. Chapter 7—Nanotechnology for cargo delivery with a special emphasis on pesticide, herbicide, and fertilizer. In *Nano-Enabled Agrochemicals in Agriculture*; Ghorbanpour, M., Shahid, M.A., Eds.; Academic Press: Cambridge, MA, USA, 2022; pp. 105–144. ISBN 9780323910095.
18. Bhardwaj, A.K.; Arya, G.; Kumar, R.; Hamed, L.; Pirasteh-Anosheh, H.; Jasrotia, P.; Kashyap, P.L.; Singh, G.P. Switching to nanonutrients for sustaining agroecosystems and environment: The challenges and benefits in moving up from ionic to particle feeding. *J. Nanobiotechnol.* **2022**, *20*, 19. [CrossRef]
19. Anjum, M.; Pradhan, S.N.; Narayana Pradhan, S. Application of nanotechnology in precision farming: A review. *Int. J. Chem. Stud.* **2018**, *6*, 755–760.
20. Steffen, W.; Richardson, K.; Rockström, J.; Cornell, S.E.; Fetzer, I.; Bennett, E.M.; Biggs, R.; Carpenter, S.R.; de Vries, W.; de Wit, C.A.; et al. Planetary boundaries: Guiding human development on a changing planet. *Science* **2015**, *347*, 1259855. [CrossRef]
21. ESPP. *European Sustainable Phosphorus Platform*; ESPP: Bruxelles, Belgium, 2022. Available online: <https://phosphorusplatform.eu/links-and-resources/p-facts/p-fact-4> (accessed on 4 May 2022).
22. Naher, U.; Othman, R.; Panhwar, Q.; Ismail, M. Biofertilizer for Sustainable Rice Production and Reduction of Environmental Pollution. In *Crop Production and Global Environmental Issues*; Springer: Cham, Switzerland, 2015; pp. 283–291.
23. Amaral, A.; Carvalho, D. Avaliação Do Desenvolvimento da Fava de Indústria (*Vicia faba* L.) na Condições do Vale do Tejo. *Revista da UI_IPSantarém-Unidade de Investigação do Instituto Politécnico de Santarém* **2018**, *6*, 14–25.
24. Varennes, A. *Produtividade dos solos e Ambiente*; Escolar Editora: Lisboa, Portugal, 2003; 490p.
25. Tiessen, H. Phosphorus in the global environment. In *The Ecophysiology of Plant-Phosphorus Interactions*; White, P.J., Hammond, J.P., Eds.; Plant Ecophysiology; Springer: Dordrecht, The Netherlands, 2008; Volume 7.
26. Choudhury, A.; Kennedy, I.R.; Ahmed, M.F.; Kecskés, M.L. Phosphorus Fertilization for Rice and Control of Environmental Pollution Problems. *Pak. J. Biol. Sci.* **2007**, *10*, 2098–2105. [CrossRef] [PubMed]
27. Malmaeus, J.M.; Blenckner, T.; Markensten, H.; Persson, I. Lake phosphorus dynamics and climate warming: A mechanistic model approach. *Ecol. Model.* **2006**, *190*, 1–14. [CrossRef]
28. Rockström, J.; Klum, M. *Big World, Small Planet: Abundance within Planetary Boundaries*; Bokförlaget Max Ström: Stockholm, Sweden, 2015; pp. 1–207.
29. Lychuk, T.E.; Moulin, A.P.; Lemke, R.L.; Izaurralde, R.C.; Johnson, E.N.; Olfert, O.O.; Brandt, S.A. Modelling the effects of climate change, agricultural inputs, cropping diversity, and environment on soil nitrogen and phosphorus: A case study in Saskatchewan, Canada. *Agric. Water Manag.* **2021**, *252*, 106850. [CrossRef]
30. Asensio, D.; Zuccarinia, P.; Ogaya, R.; Marañón-Jiménez, S.; Sardans, J.; Penuelas, J. Simulated climate change and seasonal drought increase carbon and phosphorus demand in Mediterranean forest soil. *Soil Biol. Biochem.* **2021**, *163*. [CrossRef]
31. Wang, W.; Li, Y.; Guan, P.; Chang, L.; Zhu, X.; Zhang, P.; Wua, D. How do climate warming affect soil aggregate stability and aggregate-associated phosphorus storage under natural restoration? *Geoderma* **2022**, *420*, 115891. [CrossRef]
32. Bjørn, A.; Chandrakumar, C.; Boulay, A.M.; Doka, G.; Fang, K.; Gondran, N.; Hauschild, M.; Kerkhof, A.; King, H.; Margni, M.; et al. Review of life-cycle based methods for absolute environmental sustainability assessment and their applications. *Environ. Res. Lett.* **2020**, *15*, 083001. [CrossRef]
33. Fang, K. Assessing the natural capital use of eleven nations: An application of a revised three-dimensional model of ecological footprint. *Acta Ecol. Sin.* **2015**, *35*, 3766–3777.

34. Li, M.; Wiedmann, T.; Hadjikakou, M. Towards meaningful consumption-based planetary boundary indicators: The phosphorus exceedance footprint. *Glob. Environ. Chang.* **2019**, *54*, 227–238. [[CrossRef](#)]
35. Li, M.; Wiedmann, T.; Liu, J.; Wang, Y.; Hu, Y.; Zhang, Z.; Hadjikakou, M. Exploring consumption-based planetary boundary indicators: An absolute water footprinting assessment of Chinese provinces and cities. *Water Res.* **2020**, *184*, 116163. [[CrossRef](#)]
36. Li, M.; Wiedmann, T.; Fang, K.; Hadjikakou, M. The role of planetary boundaries in assessing absolute environmental sustainability across scale. *Environ. Int.* **2021**, *152*, 106475. [[CrossRef](#)] [[PubMed](#)]
37. Dearing, J.A.; Wang, R.; Zhang, K.; Dyke, J.G.; Haberl, H.; Hossain, M.S.; Langdon, P.G.; Lenton, T.M.; Raworth, K.; Brown, S.; et al. Safe and just operating spaces for regional social-ecological systems. *Glob. Environ. Chang.* **2014**, *28*, 227–238. [[CrossRef](#)]
38. Rockström, J.; Edenhofer, O.; Gaertner, J.; DeClerck, F. Planet-proofing the global food system. *Nat. Food* **2020**, *1*, 3–5. [[CrossRef](#)]
39. Ramirez-Rodriguez, G.B.; Dal Sasso, G.; Carmona, F.J.; Miguel-Rojas, C.; Perez-de-Luque, A.; Masciocchi, N.; Guagliardi, A.; Delgado-Lopez, J.M. Engineering biomimetic calcium phosphate nanoparticles: A green synthesis of slow-release multinutrient (NPK) nanofertilizers. *ACS Appl. Bio Mater.* **2020**, *3*, 1344–1353. [[CrossRef](#)]
40. El-Azeim, M.M.A.; Sherif, M.A.; Hussien, M.S.; Tantawy, I.A.A.; Bashandy, S.O. Impacts of nano- and non-nanofertilizers on potato quality and productivity. *Acta Ecol. Sin.* **2020**, *40*, 388–397. [[CrossRef](#)]
41. Basavegowda, N.; Baek, K.H. Current and future perspectives on the use of nanofertilizers for sustainable agriculture: The case of phosphorus nanofertilizer. *3 Biotech* **2021**, *11*, 357. [[CrossRef](#)] [[PubMed](#)]
42. Agrawal, S.; Kumar, V.; Kumar, S.; Kumar Shahi, S. Plant development and crop protection using phytonanotechnology: A new window for sustainable agriculture. *Chemosphere* **2022**, *299*, 134465. [[CrossRef](#)]
43. Cheng, Y.; Yin, L.; Lin, S.; Wiesner, M.; Bernhardt, E.; Liu, J. Toxicity reduction of polymer-stabilized silver nanoparticles by sunlight. *J. Phys. Chem. C* **2011**, *115*, 4425–4432. [[CrossRef](#)]
44. Adhikari, T.; Kundu, S.; Meena, V.; Rao, A.S. Utilization of Nano Rock Phosphate by Maize (*Zea mays* L.) Crop in a Vertisol of Central India. *J. Agric. Sci. Technol.* **2014**, *4*, 384–394.
45. Mikhak, A.; Sohrabi, A.; Kassae, M.Z.; Feizian, M. Synthetic nanozeolite/nanohydroxyapatite as a phosphorus fertilizer for German chamomile (*Matricariachamomilla* L.). *Ind. Crops Prod.* **2017**, *95*, 444–452. [[CrossRef](#)]
46. Xiong, L.; Wang, P.; Hunter, M.N.; Kopittke, P.M. Bioavailability and movement of hydroxyapatite nanoparticles (HA-NPs) applied as a phosphorus fertiliser in soils. *Environ. Sci. Nano* **2018**, *5*, 2888–2898. [[CrossRef](#)]
47. Karimi-Maleh, H.; Miranda-Villagómez, E.; Trejo-Téllez, L.L.; Gómez-Merino, F.C.; Sandoval-Villa, M.; Sánchez-García, P.; Aguilar-Méndez, M.A. Nanophosphorus Fertilizer Stimulates Growth and Photosynthetic Activity and Improves P Status in Rice. *J. Nanomater.* **2019**, *2019*, 5368027.
48. Shylaja, S.; Prashanthi, Y.; Rao, T.N. Synthesis and evaluating the effects of nano hydroxyapatite on germination, growth and yield of cluster beans. *Mater. Today Proc.* **2022**, *64*, 917–921. [[CrossRef](#)]
49. Liu, R.; Lal, R. Synthetic apatite nanoparticles as a phosphorus fertilizer for soybean (*Glycine max*). *Sci. Rep.* **2014**, *4*, 5686. [[CrossRef](#)]
50. Taşkın, M.B.; Şahin, O.; Taskin, H.; Atakol, O.; Inal, A.; Gunes, A. Effect of synthetic nano-hydroxyapatite as an alternative phosphorus source on growth and phosphorus nutrition of lettuce (*Lactuca sativa* L.) plant. *J. Plant Nutr.* **2018**, *41*, 1148–1154. [[CrossRef](#)]
51. Pradhan, S.; Durgam, M.; Mailapalli, D.R. Urea loaded hydroxyapatite nanocarrier for efficient delivery of plant nutrients in rice. *Arch. Agron. Soil Sci.* **2021**, *67*, 371–382. [[CrossRef](#)]
52. Rajonee, A.; Zaman, S.; Huq, S. Preparation, Characterization and Evaluation of Efficacy of Phosphorus and Potassium Incorporated Nano Fertilizer. *Adv. Nanopart.* **2017**, *6*, 62–74. [[CrossRef](#)]
53. Yasmeen, T.; Arif, M.S.; Shahzad, S.M.; Riaz, M.; Tufail, M.A.; Mubarik, M.S.; Ahmad, A.; Ali, S.; Albasher, G.; Shakoar, A. Abandoned agriculture soil can be recultivated by promoting biological phosphorus fertility when amended with nano-rock phosphate and suitable bacterial inoculant. *Ecotoxicol. Environ. Saf.* **2022**, *234*, 113385. [[CrossRef](#)]
54. Saraiva, R.; Ferreira, Q.; Rodrigues, G.; Oliveira, M. Nanofertilizantes—A precisão na cultura do arroz. In Proceedings of the Encontro Ciência 2021, Lisboa, Portugal, 28–30 June 2021.
55. Saraiva, R.; Rodrigues, G.; Ferreira, Q.; Oliveira, M. The use of nanofertilizers to increase precision in rice production. In *16th SDEWES2021 Conference: Book Abstracts*; Faculty of Mechanical Engineering and Naval Architecture: Zagreb, Croatia, 2021; p. 545.
56. Chen, J.; Peng, H.; Wang, X.; Shao, F.; Yuan, Z.; Han, H. Graphene oxide exhibits broad-spectrum antimicrobial activity against bacterial phytopathogens and fungal conidia by intertwining and membrane perturbation. *Nanoscale* **2014**, *6*, 1879–1889. [[CrossRef](#)] [[PubMed](#)]
57. Hu, X.; Kang, J.; Lu, K.; Zhou, R.; Mu, L.; Zhou, O. Graphene oxide amplifies the phytotoxicity of arsenic in wheat. *Sci. Rep.* **2014**, *4*, 6122. [[CrossRef](#)] [[PubMed](#)]
58. Liu, S.; Wei, H.; Li, Z.; Li, S.; Yan, H.; He, Y.; Tian, Z. Effects of graphene on germination and seedling morphology in rice. *J. Nanosci. Nanotechnol.* **2015**, *15*, 2695–2701. [[CrossRef](#)]
59. Mukherjee, A.; Majumdar, S.; Servin, A.D.; Pagano, L.; Dhankher, O.P.; White, J.C. Carbon Nanomaterials in Agriculture A Critical Review. *Front. Plant Sci.* **2016**, *7*, 172. [[CrossRef](#)]
60. Chen, J.; Yang, L.; Li, S.; Ding, W. Various Physiological Response to Graphene Oxide and Amine-Functionalized Graphene Oxide in Wheat (*Triticum aestivum*). *Molecules* **2018**, *23*, 1104. [[CrossRef](#)]

61. Chen, X.; Tongxin, W. Preparation and characterization of atrazine-loaded biodegradable PLGA nanospheres. *J. Integr. Agric.* **2019**, *18*, 1035–1041. [[CrossRef](#)]
62. Kulikov, S.N.; Chirkov, S.N.; Ilina, A.V.; Lopatin, S.A.; Varlamov, V.P. Effect of the molecular weight of chitosan on its antiviral activity in plants. *Appl. Biochem. Microbiol.* **2006**, *42*, 200–203. [[CrossRef](#)]
63. Sathiyabama, M.G.; Akila, R.; Einstein, C. Chitosan-induced defense responses in tomato plants against early blight disease caused by *Alternariasolani* (Ellis and Martin) Sorauer. *Arch. Phytopathol. Plant Protect.* **2013**, *47*, 1777–1787. [[CrossRef](#)]
64. Silva, M.; Nunes, D.; Cardoso, A.R.; Ferreira, D.; Britol, M.; Pintadol, M.E.; Vasconcelos, M.W. Chitosan as a biocontrol agent against the pinewood nematode (*Bursaphelenchus xylophilus*). *For. Pathol.* **2014**, *44*, 420–423. [[CrossRef](#)]
65. Hossain, M.S.; Iqbal, A. Effect of shrimp chitosan coating on postharvest quality of banana (*Musa sapientum* L.) fruits. *Int. Food Res. J.* **2016**, *23*, 277–283.
66. Pandey, P.; Verma, M.; De, N. Chitosan in agricultural context—A review. *Bull. Environ. Pharmacol. Life Sci.* **2018**, *7*, 87–96.
67. Angelim, A.L.; Costa, S.P.; Farias, B.C.; Aquino, L.F.; Melo, V.M. An innovative bioremediation strategy using a bacterial consortium entrapped in chitosan beads. *J. Environ. Manag.* **2013**, *127*, 10–17. [[CrossRef](#)]
68. Liu, L.; Luo, X.B.; Ding, L.; Luo, S.L. Application of Nanotechnology in the Removal of Heavy Metal from Water. In *Nanomaterials for the Removal of Pollutants and Resource Reutilization Micro and Nano Technologies*; Luo, X., Deng, F., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; pp. 83–147.
69. Saraiva, R.; Ferreira, Q.; Rodrigues, G.; Oliveira, M. A fitotoxicidade de óxido de grafeno como base para nanofertilizantes. In Proceedings of the Encontro Ciência 2022, Lisboa, Portugal, 16–18 May 2022.
70. Chen, J.; Mu, Q.; Tian, X. Phytotoxicity of graphene oxide on rice plants is concentration dependent. *Mater. Express* **2019**, *9*, 635–640. [[CrossRef](#)]
71. Arora, S.; Murmu, G.; Mukherjee, K.; Saha, S.; Maity, D. A comprehensive overview of nanotechnology in sustainable agriculture. *J. Biotechnol.* **2022**, *355*, 21–41. [[CrossRef](#)] [[PubMed](#)]
72. Sharma, S.; Rana, V.S.; Kumari, M.; Mishra, P. Biofertilizers: Boon for fruit production. *J. Pharm. Phytochem.* **2018**, *7*, 3244–3247.
73. Verma, K.K.; Song, X.-P.; Joshi, A.; Rajput, V.D.; Singh, M.; Sharma, A.; Singh, R.K.; Li, D.-M.; Arora, J.; Minkina, T.; et al. Nanofertilizer Possibilities for Healthy Soil, Water, and Food in Future: An Overview. *Front. Plant Sci.* **2022**, *13*, 865048. [[CrossRef](#)]
74. Zulfiqar, F.; Navarro, M.; Ashraf, M.; Akram, N.A.; Munné-Bosch, S. Nanofertilizer use for sustainable agriculture: Advantages and limitations. *Plant Sci.* **2019**, *289*, 110270. [[CrossRef](#)]
75. Ashour, H.A.; Mahmoud, A.W.M. Response of *Jatropha integerrima* plants irrigated with different levels of saline water to nano silicon and gypsum. *J. Agric. Stud.* **2017**, *5*, 136–160.
76. Mahmood-ur-Rahman; Ijaz, M.; Qamar, S.; Bukhari, S.A.; Malik, K. Chapter 27—Abiotic Stress Signaling in Rice Crop. In *Advances in Rice Research for Abiotic Stress Tolerance*; Hasanuzzaman, M., Fujita, M., Nahar, K., Biswas, J.K., Eds.; Woodhead Publishing: Sawston, UK, 2019; pp. 551–569.
77. Prakash, V.; Rai, P.; Sharma, N.C.; Pratap, S.V.; Kumar, T.D.; Sharma, S.; Sahi, S. Application of zinc oxide nanoparticles as fertilizer boosts growth in rice plant and alleviates chromium stress by regulating genes involved in regulating oxidative stress. *Chemosphere* **2022**, *303*, 134554. [[CrossRef](#)] [[PubMed](#)]
78. Tripathi, D.K.; Singh, V.P.; Prasad, S.M.; Chauhan, D.K.; Dubey, N.K. Silicon nanoparticles (SiNp) alleviate chromium (VI) phytotoxicity in *Pisum sativum* (L.) seedlings. *Plant Physiol. Biochem.* **2015**, *96*, 189–198. [[CrossRef](#)]
79. López-Luna, J.; Silva-Silva, M.J.; Martínez-Vargas, S.; Mijangos-Ricardez, O.F.; González-Chávez, M.C.; Solís-Domínguez, F.A.; Cuevas-Díaz, M.C. Magnetite nanoparticle (NP) uptake by wheat plants and its effect on cadmium and chromium toxicological behavior. *Sci. Total Environ.* **2016**, *565*, 941–950. [[CrossRef](#)] [[PubMed](#)]
80. Ji, Y.; Zhou, Y.; Ma, C.X.; Feng, Y.; Hao, Y.; Rui, Y.; Wu, W.; Gui, X.; Le, V.N.; Han, Y.; et al. Jointed toxicity of TiO₂ NPs and Cd to rice seedlings: NPs alleviated Cd toxicity and Cd promoted NPs uptake. *Plant Physiol. Biochem.* **2017**, *110*, 82–93. [[CrossRef](#)]
81. Rossi, L.; Sharifan, H.; Zhang, W.L.; Schwab, A.P.; Ma, X. Mutual effects and in planta accumulation of coexisting cerium oxide nanoparticles and cadmium in hydroponically grown soybean (*Glycine max* L. Merr.). *Environ. Sci.-Nano* **2018**, *5*, 150–157. [[CrossRef](#)]
82. Chen, R.; Zhang, C.B.; Zhao, Y.L.; Huang, Y.C.; Liu, Z.Q. Foliar application with nano-silicon reduced cadmium accumulation in grains by inhibiting cadmium translocation in rice plants. *Environ. Sci. Pollut. Res.* **2018**, *25*, 2361–2368. [[CrossRef](#)]
83. Zhang, Z.; Li, M.; Chen, W.; Zhu, S.; Liu, N.; Zhu, L. Immobilization of lead and cadmium from aqueous solution and contaminated sediment using nano-hydroxyapatite. *Environ. Pollut.* **2010**, *158*, 514–519. [[CrossRef](#)]
84. Haghighi, M.; Da Silva, J.A.T.; Mozafarian, M.; Afifipour, Z. Can Si and nano-Si alleviate the effect of drought stress induced by PEG in seed germination and seedling growth of tomato? *Minerva Biotechnol.* **2013**, *25*, 17–22.
85. Djanaguiraman, M.; Nair, R.; Giraldo, J.P.; Prasad, P.V.V. Cerium oxide nanoparticles decrease drought induced oxidative damage in sorghum leading to higher photosynthesis and grain yield. *ACS Omega* **2018**, *3*, 14406–14416. [[CrossRef](#)]
86. Kaur, H.; Kalia, A.; Singh, S.J.; Singh, D.G.; Kaur, G.; Pathania, S. Interaction of TiO₂ nanoparticles with soil: Effect on microbiological and chemical traits. *Chemosphere* **2022**, *301*, 134629. [[CrossRef](#)] [[PubMed](#)]
87. Babu, S.; Singh, R.; Yadav, D.; Rathore, S.S.; Raj, R.; Avasthe, R.; Yadav, S.K.; Das, A.; Yadav, V.; Yadav, B.; et al. Nanofertilizers for agricultural and environmental sustainability. *Chemosphere* **2022**, *292*, 133451. [[CrossRef](#)] [[PubMed](#)]
88. Sangawe, V.; Inamdar, A.; Adhapure, N. Chapter 18—Rhizospheric health management through nanofertilizers. In *Rhizosphere Engineering*; Dubey, R.C., Kumar, P., Eds.; Academic Press: Cambridge, MA, USA, 2022; pp. 329–353.

89. Boregowda, N.; Jogigowda, S.C.; Bhavya, G.; Sunilkumar, C.R.; Geetha, N.; Udikeri, S.S.; Chowdappa, S.; Govarthanan, M.; Jogaiah, S. Recent advances in nanoremediation: Carving sustainable solution to clean-up polluted agriculture soils. *Environ. Pollut.* **2022**, *297*, 118728. [[CrossRef](#)]
90. Mahapatra, D.M.; Satapathy, K.C.; Panda, B. Biofertilizers and nanofertilizers for sustainable agriculture: Phycoprosects and challenges. *Sci. Total Environ.* **2022**, *803*, 149990. [[CrossRef](#)] [[PubMed](#)]
91. Choudhary, R.C.; Kumaraswamy, R.V.; Kumari, S.; Sharma, S.S.; Pal, A.; Raliya, R.; Biswas, P.; Saharan, V. Cu-chitosan nanoparticle boost defense responses and plant growth in maize (*Zea mays* L.). *Sci. Rep.* **2017**, *7*, 9754. [[CrossRef](#)]
92. Prajapati, D.; Pal, A.; Dimkpa, C.; Singh, U.; Devi, K.A.; Choudhary, J.L.; Saharan, V. Chitosan nanomaterials: A prelim of next-generation fertilizers; existing and future prospects. *Carbohydr. Polym.* **2022**, *288*, 119356. [[CrossRef](#)] [[PubMed](#)]
93. Batley, G.E.; Kirby, J.K.; McLaughlin, M.J. The fate and risks of nanomaterials in aquatic and terrestrial environments. *Acc. Chem. Res.* **2013**, *46*, 842–862. [[CrossRef](#)]
94. Hyland, C.; Ketterings, Q.; Geohring, L.; Stockin, K.; Dewing, D.; Czymmek, K.; Albrecht, G. *Agronomy Fact Sheet Series—Fact Sheet 13*; Cornell University Cooperative Extension: Ithaca, NY, USA, 2005.
95. Zhan, X.Y.; Zhang, Q.W.; Zhang, H.; Hussain, H.A.; Shaaban, M.; Yang, Z.L. Pathways of nitrogen loss and optimized nitrogen management for a rice cropping system in arid irrigation region, northwest China. *J. Environ. Manag.* **2020**, *268*, 110702.
96. Liu, J.; Zuo, Q.; Zhai, L.; Luo, C.; Liu, H.; Wang, H.; Liu, S.; Zou, G.; Ren, T. Phosphorus losses via surface runoff in rice-wheat cropping systems as impacted by rainfall regimes and fertilizer applications. *J. Integr. Agric.* **2016**, *15*, 667–677. [[CrossRef](#)]
97. Hua, L.L.; Liu, J.; Zhai, L.M.; Xi, B.; Zhang, F.L.; Wang, H.Y.; Liu, H.; Chen, A.; Fu, B. Risks of phosphorus runoff losses from five Chinese paddy soils under conventional management practices. *Agric. Ecosyst. Environ.* **2017**, *245*, 112–123. [[CrossRef](#)]