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Review

Nanofertilizer Use for Adaptation and Mitigation of the Agriculture/Climate Change Dichotomy Effects

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Abstract: Agriculture is considered a significant climate change (CC) driver due to greenhouse gas (GHG) emissions and the loss of fertilizers that contribute to water eutrophication. On the other hand, climate change effects are already impacting agriculture, endangering food security. This paper explores the dichotomies of the effects of agriculture on CC as well as of CC on agriculture, focusing on the contribution that nanofertilizers can bring to this complex system in both directions. The strategies to reduce CC while adapting and mitigating its effects must be a global effort. It is not possible to focus only on the reduction in GHG emissions to stop the effects that are already being felt worldwide. Nanofertilizers, especially slow- and controlled-release nanofertilizers, can reduce the nutrient input and also boost productivity while mitigating some CC effects, such as soil nutrient imbalance and agricultural emissions. As so, this review highlights the benefits of nanofertilizers and their role as a part of the strategy to reduce the reach of CC and mitigate its ever-growing effects, and presents some guidelines for the increased use of these materials in order to enhance their efficacy in this strategy.

Keywords: controlled-release nutrients; emission reduction; nanofertilizers; slow-release fertilizer; soil nutrient imbalance

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1. Introduction

Agriculture is essential to feed the world's population, which is projected to reach 9.8 billion by 2050 [1]. It is also essential for the production of many resources that are essential in several economic activities [1]. Agriculture contributes to Climate Change (CC) but is also affected by CC [1]. Consequently, agricultural production has to adapt and evolve in order to maintain the necessary ability to provide food and resources.

Agriculture accounts for 10% of the European Union's (EU) GHGs and 11% of the USA's GHGs [1,2], being responsible for CO_2 and non-CO_2 emissions of methane (CH_4) and nitrous oxide (N_2O) generated by crop, livestock activities, energy, and fertilizer use [3,4]. Combined, N_2O emissions and CH_4 emissions from enteric fermentation account for more than 80% of total agricultural GHG emissions. The slight reduction of 2% registered in the EU's agricultural GHG emissions from 2005 to 2021 is not enough [1]. The United Nations (UN) Sustainable Development Goals (SDG) urges our societies to produce and consume goods in more sustainable ways, while the European Green Deal sets that all sectors shall contribute so that, by 2050, we shall achieve climate neutral economy. In addition, European Climate Law goes further, setting the target of reducing net emissions of GHGs by at least

55% (compared to 1990) by 2030 [5–7]. Therefore, agricultural activities are facing a huge challenge to change the cycle of intensification due to chemical fertilizer use that ultimately increases emissions, contributing to CC. Intensive agriculture and heavy fertilizer use are also related to losses of nutrients to water bodies, causing high concentrations of nutrients and, in the end, eutrophication [1]. Although not directly linked to climate change, this may result in a series of disturbances in the aquatic ecosystem [1]. The effects include shifts in the composition of flora and fauna, which in turn affect habitats and biodiversity, cause the depletion of oxygen in the water, and reduce water quality [1]. Additionally, intensive agriculture can contribute to land degradation, soil salinization, the decline in genetic diversity in crops and livestock, and the use of large amounts of water [8].

On the other hand, by this time, agriculture is already one of the economic sectors with the largest CC effect stress, and the increased demand for food supply adds even more pressure to the production chain [8]. The climate is changing, heating rapidly due to human activities. The Intergovernmental Panel on Climate Change (IPCC) states that the average global temperatures have increased by 1.2 °C since 1880, while all the projections point out that warming beyond 1.5 °C can have irreversible and permanent consequences for humanity. As GHGs contribute more than 2/3 to global warming, CO_2 concentrations are very concerning, and they are at their highest level ever [9–11]. Global warming and CC are increasingly affecting ecosystems around the world, causing natural resource depletion, melting of glaciers, ecosystem changes, increased climate extremes, land degradation, freshwater scarcity, biological invasions, loss of biodiversity, acidification, and subsequently, impacts on human life [10–14]. All of these represent management and policy challenges [15,16].

The susceptibility of a system to be affected and to be unable to cope with CC adverse effects is defined as vulnerability to CC. It is a consequence of a multitude of factors, such as climate exposure, the magnitude of expected CC, ecological sensitivity, and adaptive capacity [15–17]. The world needs to reduce GHG emissions from agriculture and adapt its food-production system to cope with and reduce vulnerability to CC [1]. Strategies for GHG reduction include climate-smart farming methods, run-off reduction, and methods to boost crop resistance, all of which can be achieved by the use of nanofertilizers [18].

Fertilizers are chemical or natural substances that provide nutrients to plants. Nanofertilizers also provide nutrients to plants, but in a much more efficient way. According to Robert Mikkelsen [19], there are three classes of nanofertilizers: nanoscale fertilizers, nanoscale additives, and nanoscale coatings. These classes are characterized as nanomaterials containing nutrients, traditional fertilizers with nanoscale additives, and traditional fertilizers coated or loaded with nanoparticles, respectively. Manjunatha et al. [20] present some potential nanofertilizer designs, such as slow-release, quick-release, specific-release, moisture-release, heat-release, and pH-release nanofertilizers, and the ISO also defines controlled-release fertilizers. In the slow release, the nanocapsule slowly releases nutrients over a long, specified period of time by hydrolysis, biodegradation, limited solubility, and/or other mechanisms, meeting crop requirements and reducing the number of fertilization applications and the amount of fertilizer used, while increasing nutrient use efficiency (NUE) [20–24]. The quick-release nanofertilizers refer to a design where the nanoparticle shell is shattered when it comes in contact with a surface, while in the specific-release design, the shell breaks apart upon contact with a specific chemical or enzyme. In the moisture-release fertilizer, the degradation of the nanoparticle and the nutrient release is due to the presence of water. In the heat-release design, the nanofertilizer is released when the temperature exceeds a set point, and in the pH-release design, the release is dependent on the specified pH conditions. As for the controlled-release nanofertilizer, it is defined as a design in which nutrient release is controlled, releasing nutrients at a known rate and according to the stated time to meet crop requirements [20,24].

For this review, the data were primarily obtained by research papers in the Web of Science, Science Direct, MDPI, Frontiers, and Springer databases, complemented by governmental and relevant international institutions' publications; this review highlights the benefits of nanofertilizers, their role as a part of the strategy to reduce the reach of CC and mitigate its ever-growing effects, and presents some guidelines for the increased use of these materials, in order to enhance their efficacy in this strategy.

2. Agriculture as a Driver of Climate Change

Agriculture is a significant contributor to anthropogenic global warming and CC, caused by multiple climate pollutants, mainly CO_2, CH_4, and N_2O [1,25,26]. These GHGs are released by farming activities but also by storing, processing, and other related activities in the food chain [1]. It is important to observe that there are significant differences between CO_2, N_2O, and CH_4, since the first is a stock pollutant, and the last two are mainly flow pollutants with less persistence in the atmosphere [26,27].

While the main focus is predominantly on the direct agricultural emissions that are dominated by CH_4 and N_2O [26], it is also important to look at indirect emissions. Indirect agricultural emissions and environment pollution arise from farm machinery, fertilizer production and utilization, use of pesticides, and deficient irrigation strategies, contributing to the total estimated GHGs [28]. Current agricultural practices are focused primarily on boosting yield and, consequently, use large amounts of fossil energy to produce mechanical energy, fertilizers, and other chemicals [29]. The soil surface is a part of the climate system, and it is involved in the carbon (C), nitrogen (N), and phosphorus (P) cycles [30]. Therefore, the total global GHG emissions from agriculture, including farming (10–12%), land use (6–17%), agri-related chemical production and distribution (4%), and farm operations, including irrigation (0.2–1.8%), is quite high (20.2–34.8%) [28,31].

2.1. Nitrous Oxide (N_2O) Emissions

Although its contribution to GHG emission is smaller than other gases, N_2O has 273 times the global warming potential of CO_2 and 109 years of atmospheric lifetime [32]. It was estimated that agriculture accounts for 27% of global N_2O emissions, and this will increase by 35–60%, accounting for 16% of total non-CO_2 emissions by 2030, even though this may be underestimated [29,33–36].

Numerous complex and interacting factors influence N_2O emissions in crop systems [35,37]. The most important to be mentioned are fertilizers, mostly N fertilizers [38,39]. The increase in N_2O emissions from agricultural soils is due to increased N content from fertilizers and the growth rate of its use to meet growing agricultural demand, combined with the consequent growth rate of crop residues [35,40]. The excess of fertilizer use contributes to the buildup of inorganic nitrogen in soils, which results in greater leaching and denitrification when inefficient N utilization, over-doses, or non-synchronized mineral fertilization occurs [41]. The available N is not completely taken up by the plants and is subject to microbial turnover processes that produce nitrous oxide. Inorganic fertilizer has a greater contribution than ammonia-based N sources, such as urea, when applied in unfavorable conditions such as wet, cold, and water-logged soils [28,37]. The excess N is responsible for imbalances in the N cycle, leading to associated increases in environmental risks, including intensification of emissions, soil acidification, biodiversity losses, and risks to human health [41].

Moreover, environmental and management factors such as climate, soil characteristics, the cultivation system, tillage, crop rotation, and operation timing are determinants of soil N_2O production [42–50]. The use of tillage contributes to organic matter breakdown and accelerates the release of N_2O [28]. Other indirect sources of N are volatilization and atmospheric deposition of ammonia and nitrogen oxides from fertilizer and manure application onto agricultural land, coupled with the result of surface run-off and leaching (Figure 1) [35,51].

As a staple food for millions of people around the world, rice cultivation is a special case of attention. Water-logging and soil texture must be considered, since they are key factors conducive to N_2O emission. In water-logging conditions, Panchasara et al. [28] found that the peak N_2O emissions occurred when soil pore space was 70% filled.

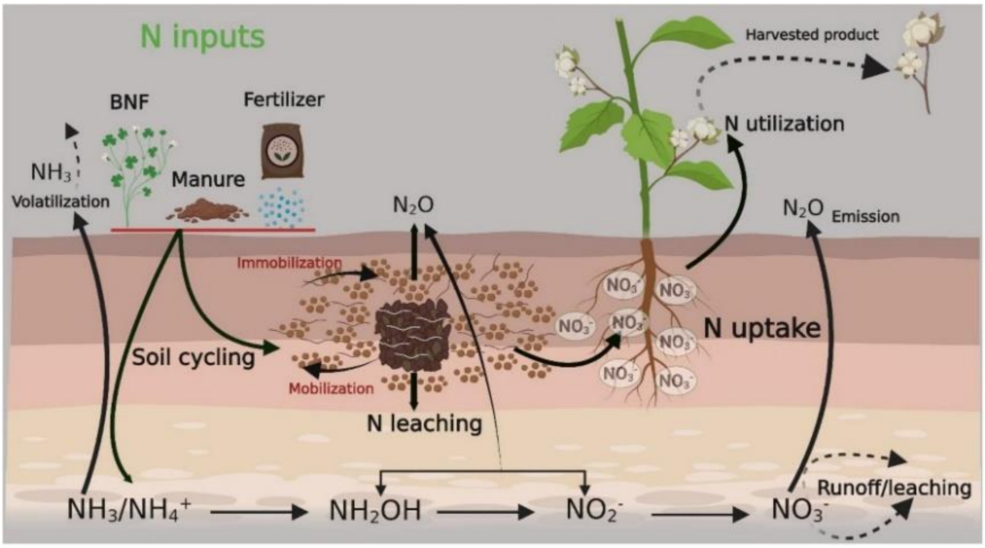

Figure 1. Nitrogen cycle, in [51], under Creative Commons Attribution License (CC BY).

As there is no technology for N_2O removal from the atmosphere, it is important to avoid N_2O emissions, which can be achieved by proper fertilizer management [29]. Improving fertilizer formulation, release, and placement can reduce N_2O emissions by delaying nutrient delivery to the roots and increasing plant uptake and use efficiency [29]. EPA [35] points out that a 20% reduction in fertilizer use could potentially achieve 46% of emission mitigation in croplands, and, combined with no-tillage cultivation practices, it could represent 80% of global emission reduction potential [35].

2.2. Carbon Dioxide (CO_2) Emissions

It is not simple to quantify CO_2 emissions from food systems, due to the complex processes involved and the difficulty in applying sectoral boundaries [26]. However, it is admitted that a small portion of agricultural CO_2 emissions occurs directly from agricultural production, resulting from urea application and liming. A larger portion is the result of indirect energy-use from agricultural operations, such as the use of fossil fuel by machinery, CO_2 emissions from land-use change and from input utilization (e.g., fertilizers), production, and transportation [26,52,53].

A huge amount of fossil fuel energy is used to produce fertilizers, with concomitant large CO_2 emissions [54]. Phosphorus is an essential nutrient for crops and livestock production, and the majority of P fertilizers are derived from mined rock phosphate (80%), which requires large quantities of resources and energy [55–57]. According to the Institute for Industrial Productivity [58], ammonia (NH_3) manufacturing, in 2011, contributed 1–2% of worldwide CO_2 emissions. Carbon dioxide is the most important GHG, having multiple years of atmospheric lifetime [32]. Besides fossil fuel energy, obtaining hydrogen from hydrocarbons to produce ammonia is an important source of CO_2 and CH_4 emissions [54]. As N fertilizer is the most used worldwide, and all synthetic N fertilizers are derived from ammonia, this comes with a cost [54].

Ocean acidification is another negative and very concerning consequence of the increase in CO_2 release, since about one-quarter of the total CO_2 emitted is dissolved in the oceans, where it forms carbonic acid and decreases surface water pH [59]. These modifications impact the capability of shell formation and the survival capacity of many marine species at a global scale, since ocean acidification occurs all around the globe [59].

On the other hand, soil can act as a carbon sink, and it is estimated that it could sequester between 0.4 and 6.8 Gt CO_2 year^{-1}, values that could be enhanced by the improvement in fertilizer use efficiency and the application of other best management techniques and practices [60].

The route to reducing CO_2 emissions from crop production can be traversed by changing to green energy production, but decreasing fertilizer needs and improving the efficiency of fertilizer use may also have some reduction potential [26].

2.3. Methane (CH_4) Emissions

Methane is a greenhouse gas that has proximally six times the global warming potential of CO_2 and 12 years of atmospheric lifetime [32]. The emissions of CH_4 are due to numerous cropping practices, such as the application of fertilizers, as described before; soil incorporation of crop residues; the quantity of organic material available to decompose; cultivation of high organic content soils; inappropriate irrigation practices; and livestock waste management [28,35,61]. The growing demand for animal and agricultural products induce growing animal and agriculture waste and, consequently, increases the rate of CH_4 emissions [28,40].

The anaerobic decomposition of organic matter in water-logged fields depletes the oxygen present in the soil and water, and produces CH_4 from the decomposition of soil organic matter via methanogenic microorganisms [35]. Due to the great importance that rice cultivation has, this is also a considerable CH_4 source. It is estimated that rice cultivation will account for 4% of total non-CO_2 emissions by 2030. A 30% reduction in the utilization of fertilizers in rice crops could account for a potential reduction of about 12 MT CO_2eq [35]. The improvement in efficiency in agricultural practices and a shift to sustainable consumption patterns can contribute to reducing methane emissions [1].

2.4. Nitrogen and Phosphorus Flows to Terrestrial Biosphere and Water Bodies

Global warming is not the only consequence of agricultural activities. Nutrient pollution results from livestock and crop production, and although P and N are essential to crops, the use of synthetic fertilizers greatly impacts terrestrial and aquatic ecosystems [62,63]. Human activities cause pressure on N and P cycles, causing imbalances and producing more reactive forms of nutrients. Besides run-off from excess fertilization, the increasing amount of N_2O in the atmosphere can suffer re-deposition in the soil, leading to soil acidification and further water contamination [54,64].

Although soils act, to some extent, as P reservoirs for future crops, the excess fertilization could lead to long-term legacy P [63], particularly as it is predicted that global mineral P inputs will increase from 7.5 to 12.5 Tg year^{-1} from 2005 to 2050 values [63,65–67]. The excess of nutrients is, in this case, lost in run-off water or by leaching and percolation to the groundwater by the lack of assimilation capacity of the crops [59,68,69]. According to the FAO [70], 20% of the applied N accumulates in the soil and biomass, and 35% ends up in the ocean. These lost nutrients accumulate over time, contributing to the proliferation of algae and aquatic plants in rivers and lakes. Globally, an area of 240,000 km^2 is affected by oxygen depletion due to fertilizer-induced eutrophication [70]. N and P run-off from farmland and pastures is the leading cause of eutrophication [71] and, ultimately, is leading marine and aquatic systems to cross their ecological limits [59,63,72,73]. Eutrophication is responsible for poor water quality, impacting drinking water quality, increasing the treatment demand, and posing a threat to animal and human health [72–74].

Li et al. [75] conducted an extensive scientific review where it was concluded that eutrophication is responsible for freshwater's increasing CO_2, CH_4, and N_2O emissions. Not only is it estimated that shallow lakes in a eutrophication situation emit nearly 50% more methane when compared to lakes with no eutrophication, but the large amount of N can also lead surface waters to shift from being N_2O sinks to emitters [75].

The implementation of practices optimizes the circular economy and the efficient use of fertilizers, as their appropriate timing, rate of delivery, and placement can boost crop production, reduce losses and environmental impacts, and ensure food security by reducing the dependency on scarce resources [63,76].

An overview of how agriculture impacts climate change is presented in Table 1.

Table 1. Agriculture as a driver to climate change—overview.

Problem	Cause	Effect	References
N_2O	Agricultural practices: fertilizer use	Increase GHG emission—global warming and imbalances in N cycle	[28,29,32–50]
CO_2	Agricultural practices: fertilizer use; energy required (direct and indirect); land use alterations	Increase GHG emission—global warming	[26,32,52–57,59,60]
CH_4	Agricultural practices: fertilizer use and manure management	Increase GHG emission—global warming and higher O_3 surface concentration	[1,28,32,35,40,61]
Run-off (N; P; others)	Agricultural practices: fertilizer	Eutrophication, reduction in water quality, and imbalance of N and P cycles	[54,59,62–76]

3. Climate Change Effects on Agriculture

To meet the increasing Human need for food, crops require the proper environment to grow. The impacts of CC are already being felt, not only by agriculture, but also by fisheries, aquaculture, and in forest production [1,11]. Furthermore, GHG emissions will have an impact in the years to come, reducing the quality of air, soil, and water, and aggravating climatic effects on yields [11].

In general, the effects of global warming will increase air, soil, and water temperatures. Air temperatures aggravate the melting of glaciers, endanger coastal agricultural land, and could extend growing seasons in several areas, which might require more irrigation, increasing the demand for groundwater and the depletion of water resources [77]. Soil temperature increases organic matter (OM) mineralization, reduces soil capability to capture CO_2 from the atmosphere, lowers the uptake of nutrients by the plants, and reduces microbial activity, water holding capacity, and soil particle size, leading to constraints in cationic exchange capacity while increasing soil evaporation and salinization and/or sodicity, leading to more pressure on water requirements [77]. The increase in air and soil temperatures combined impacts several biologic processes, such as seed germination, plant emergence and growth, root extent, and fruit maturation [78]. Water temperature influences fish stock distributions, and alterations could result in the appearance of invasive species, which endangers habitats and water quality [1,4].

Extreme climatic events, such as droughts and heavy rain, will exacerbate many global warming effects, such as soil erosion, depletion of soil nutrients, increased run-off, lower soil water reserves, and alteration of soil properties such as pH, which is essential for nutrient availability to the plants [77]. Adding to that, the great surface N_2O deposition from the atmosphere will induce acidification, adding up to the nutrient imbalances in the soil [54,64].

Changing temperatures and rainfall patterns are conducive to the expansion of pests and diseases, alter plant biological cycles and pollinator activity, and increase food security risks [79,80].

3.1. Temperature and Rainfall Patterns

Increasing air, soil, and water temperatures impact agriculture and biota. With regard to air temperatures, besides the direct impact on food production, it has a cumulative effect with other derived effects from CC, such as Earth's hydrological cycle [81]. It increases evaporation, causing over-drying effects in some areas, and also results in more storm events in other areas, leading to the disruption of several natural processes that affect plants and animals. In the latter, it could result in higher precipitation and even flood risk [81].

The intensification of glaciers melting due to global warming endangers coastal agriculture, but in high latitudes and in the short term, it could be a drought-resilient source of water [82]. At first, melting glaciers help mitigate water stress downstream, supplying water for agriculture and human consumption, but in the future, this is not a sustainable water source, and ultimately, it will lead to harmful environmental and ecological consequences as the glacier shrinks and the water supply diminishes [82–84]. Glacier melting also contributes to the rising sea level and, being associated with global warming and the increase in sea temperature, results in an increase in salinity from 1 to 33% in coastal agricultural land over the past 25 years [77]. Sea level rise and storms can also cause soil erosion and agricultural area losses, and further intensification of saltwater intrusion [77].

IPCC [11] states, with moderate confidence, that in the last 50 years, Human-induced global warming has been responsible for slowing down the agriculture productivity in the areas located in low and mid-latitudes [11]. Although warmer air temperatures can extend growing seasons in several areas, such as large parts of northern Europe, it can also require more irrigation, increasing the demand for groundwater and further intensifying the stress over water resources [1,77]. Southern Europe is located in an area that will suffer from more frequent extreme heat and water stress in summer months, and is already experiencing severe heat waves. There, higher temperatures and reductions in water availability are already reducing crop productivity. To overcome these, some crops might be cultivated when it is possible later in the autumn or winter [1].

Plants respond to high-temperature stress in various ways, altering physiology, biochemistry, and gene regulation pathways [85]. Usually, heat stress is not an isolated variable, and plants often suffer from drought and/or salt stress at the same time [85,86]. Nonetheless, it has its own effects on plants that depend on species and genotype and has wide variations [85,86]. Furthermore, plants have biological limits related to maximum temperatures that can be tolerated [87]. Higher air temperatures accelerate phenological development and abbreviate each growing stage; while the metabolic activity of plants increases, transpiration rates are intensified, and the yields are reduced [88–90]. Most plants (which include cotton, wheat, rice, barley soybeans, sunflower, potatoes, and vegetables) use a one-step process called C3 pathway to fix C via the Calvin Cycle. In the face of increased temperature, these crops suffer an intensification in photorespiration that leads to a lower net photosynthetic rate [90]. The C4 plants (such as corn, sugar cane, maize, millet, sorghum, pineapple, and flowering plants) have two steps in the process, resulting in higher efficiency. Therefore, for the foreseen higher temperatures, C4 crops present more tolerance than C3 [91]. Some plants (permanent crops) require a specific number of chill hours to break dormancy, and with higher mean average temperatures, these crops could be forced to extend their crop cycles, leading to higher irrigation requirements [90,92].

Pollination is key for crop productivity all around the world, and the effects of warmer temperatures and changing precipitation patterns can induce mismatches between the earlier flowering and harvest dates and the pollinators' hatching time [1,80,93]. These newly imposed conditions are prone to pest and disease proliferation, reducing crop yields even more and contributing to food security risks [1,94].

Air temperature influences soil temperature, which is crucial for crop production. Therefore, global warming is responsible for soil temperature increase in recent years and can compromise yields around the world [95,96]. The dynamic of air/soil temperature is also relevant as it influences the energy flux from the soil [78]. Despite its importance, studies about soil temperature increase and its effects on soil properties as well as on crops are scarce. Nonetheless, they reveal some important information. In the last 10 years, studies show that soil temperature across the United States (US) suffered an alteration of +0.32 °C, whereas records in China report a 1.9 °C amplification in 50 years (1961 to 2011), and in Germany, reports are for a ≈1.8 °C increase in 67 years (1951 to 2018) [78,97–99]. Soong et al. [100] used a model to simulate and predict the global mean soil temperature increase for the end of the century, and the results show the same rate of warming in the subsurface and at 100 cm depth. Additionally, 2.3 ± 0.7 °C and 4.5 ± 1.1 °C were found for Representative Concentration Pathways (RCPs) 4.5 and 8.5, respectively. The IPCC RCPs describe different 21st century scenarios of GHG and air pollutant emissions and atmospheric concentrations, in addition to land use. RCP4.5 refers to an intermediate scenario, while RCP8.5 refers to a very high GHG emission scenario [95]. Although asymmetric, the results show soil warming worldwide and cause alarm, considering that an increase of 2.3 °C in 100 cm soil depth is critical for ecosystems, numerous soil processes, and crops' growing phases [99]. Among these effects are seed germination, plant growth, root extension and development, and fruit maturation, which are affected by both soil and air temperature as well as by the dynamic between air and soil temperatures [78,98,101].

Change in soil temperature also influences soil moisture content, water-holding capacity, and soil particle size. Increasing the temperature at the soil surface raises the evaporation rate and the mineralization rate of soil organic matter, and impairs the soil's capacity to sequester C [102]. It constrains the movement of water and impairs water holding capacity [102,103]. Increased soil temperature can also reduce clay size and organic matter content, causing lower cation exchange capacity [104,105] while increasing soil salinization, especially in arid and semi-arid climates [103]. Nishar et al. [106] mimic soil warming by studying thermal sites and found that higher soil temperature decreases root biomass and retarded vegetation regeneration. The authors found that higher temperature is correlated with low soil moisture, pH, and an imbalance in soil chemistry. These results were also found by Jiao et al. [107] when studying soil temperature coupled with increase aridity and reduction in precipitation. The authors reported that the soil from more arid and warmer ecosystems presented lower soil organic C and total N and P, provoking imbalances in C/P/N ratios. In these conditions, C/P and N/P ratios decrease while C/N increase, negatively affecting the provision of nutrients to the plants and possibly leading to impaired plant growth and yield production [107].

Water temperature is rising and, coupled with air temperature, is contributing to rising sea levels. A direct consequence is flooding coastal areas with saltwater and gradually contaminating the soil with increased salt content [108]. Additionally, all species have a preferred temperature range to live in and a limit that cannot be crossed under the penalty of annihilating the species from the ecosystem [109]. In lakes and reservoirs, water temperature is also responsible for chemistry alterations, such as the amount of dissolved oxygen, whose reduction depletes water quality and alters natural processes. The higher amount of soluble salts present in the water can directly injure roots, reducing water and nutrient uptake. Poor water quality is responsible for slow plant growth, unaesthetic yields, and in the worst cases, crop death [110]. Evaporation is exacerbated by air and water increase temperatures, making native species more susceptible to competition and disease [109].

3.2. Extreme Climatic Events

Extreme climatic events will exacerbate the effects of global warming and are already affecting global food production. Extreme climatic events cause food insecurity and economic losses as droughts, floods, wildfires, and marine heatwaves impact and impair food availability [11].

Droughts occur in most climatic zones, but some areas are most susceptible to them. For instance, in the Mediterranean area, large increases in temperature, as well as longer drought periods and extreme rainfall events, are already impacting production and are forecasted to worsen in the next decades [11,111]. Longer, dryer, and hotter seasons will require more irrigation in vast areas, and have been found to significantly decline crop productivity [11,112,113].

Global warming has increased aridity, and global drought areas are expanding due to decreased precipitation and an increase in evaporation processes, exacerbating land degradation, desertification, and nutrient imbalances in soil [107]. Nutrients suffer different extents of decoupling, and C, N, and P responses to drought could result in severe C-N-P imbalance and ultimately lead to crop and biodiversity loss [107]. Additionally, Sardans and Peñuelas [114] establish that drought effects can be more important on P uptake than on N uptake, decreasing the adjustment of P uptake efficiency and triggering reductions in plant storage, which can further affect N/P ratios [114,115]. Additionally, heavy precipitation events will contribute even further to soil erosion, increase agricultural run-off, and cause depletion of soil nutrients and alterations to soil properties, leading to a net loss of farmland [77,116]. Mean rainfall reduction causes serious consequences in soil salinity that are spreading, and it is estimated that more than 50% of global farmlands will be salinized by 2050 [117]. Salinization affects the environmental quality, nutrient cycle, and agricultural productivity via osmotic stress and ion toxicity [118]. Osmotic stress is a short-term effect caused by the reduction in osmotic potential between root and soil solution resulting from Na^+ and Cl^- uptake, which reduces water availability [119]. Ion toxicity, however, affects crops when Na^+, Cl^-, or ${SO_2}^{4-}$ are in very elevated concentrations and affect nutrient uptake, reducing crop development and yields [120–123].

Some studies point out that CC, specifically alterations in temperature and rainfall, will influence other soil properties, such as pH, due to increased acidification of soil. This will occur because extreme rainfall events contribute to the leaching of basic cations from the soil exchange complex into surface and groundwater, transferring alkalinity and then leaving acidified soils [124]. As a critical variable, pH affects several conditions in ecosystems, impacting nutrient and toxic elements' bioavailability, root physiology, and rhizosphere microorganisms [107,125].

3.3. GHG

Besides global warming, increasing GHG concentration in the atmosphere can directly affect agriculture [126]. As observed before, in high concentrations, N_2O can suffer volatilization and re-deposition, contributing to soil acidification [54,64]. Increased methane concentration leads to increasing surface ozone (O_3) concentrations which can be absorbed by plants, reducing photosynthesis and growth while increasing their sensitivity to diseases, resulting in compromised crop yields [4,11].

Higher surface O_3 concentration leads to stomatal uptake of O_3 into the leaf's interior instead of normal direct plant surface deposition, causing crop damage [127]. Stomatal uptake of O_3 is strongly dependent on stomatal opening and closing and concomitant environmental conditions [128,129]. Thus, the closure of the stomata, caused by several factors, such as CO_2 concentration increase, reduces the uptake of O_3 and its damage [130]. On the other hand, higher CO_2 also enhances photosynthesis, which could impair O_3/CO_2 relationships in crops [131]. Besides the increase in photosynthetic rate and stomatal conductance reduction, CO_2 reduces plant transpiration, improving water and light use efficiency [132]. However, the extent of the improvement effect of CO_2 on crops is also influenced by factors such as water and nutrient availability, diseases, or pest presence [90]. Under higher atmospheric CO_2 levels, C3 plants are more efficient in using ammonium as an N source in comparison to C4 plants [133], having a more relevant increase in productivity due to the fertilizer effect on photosynthesis [91,134,135]. However, under drought conditions, C4 crops may have an improved benefit from CO_2 increase [91]. According to Hinsinger et al. [125], CO_2 concentration buildup can result in a decrease in rhizosphere pH by the formation of carbonic acid in the rhizosphere and may dissociate in neutral to alkaline soils, altering the bioavailability of nutrients.

An overview of how climate change impacts agriculture is presented in Table 2.

Table 2. Climate change effects on agriculture—overview.

Problem	Cause	Effect	References
Temperature and rainfall patterns	GHG—Global warming	Disruption of natural cycles such as crop phenological phases; nutrient imbalances; pests and diseases; and reduction in crop yield and quality	[1,11,77,78,80–110]
Extreme climatic events	GHG—Global warming	Increased water requirements; soil erosion; nutrient imbalances; alteration in soil properties and loss of farmland; and reduction in crop yield and quality	[11,77,107,111–125]
Excess GHG	GHG	Nutrient imbalances; N cycle imbalance; soil acidification; O_3/CO_2 imbalances in plants affecting photosynthesis; and reduction in crop yield	[4,11,54,64,90,91,125–132,134,135]

4. Agriculture Potential for Reduction

According to the FAO [70], the principal measure to mitigate pressure on aquatic ecosystems is to impose a limit on the export of nutrients at the farm level. Agricultural run-off can be diminished in three general ways: source control, process control, and end treatment. In the first case, the aim is to decrease the application of nutrients through the better application of fertilizers, which is allied to conservation tillage and meticulous irrigation practices [136–138]. Controlled-release fertilizers are found to have a great contribution to agricultural run-off control and, coupled with no tillage, can achieve a N and P run-off reduction of more than 60% [139]. Process control uses technologies such as ecological ditches to effectively reduce or eliminate the contaminants in the run-off, using the principle of a surface-flow-constructed wetland [140–142]. Finally, end treatment is the last possibility to reduce the impact of run-off. Drainage systems, buffer bands, and constructed wetlands are common examples of end-treatment technologies [143,144]. The limits to its mitigation could be accomplished by policies and incentives such as taxes and subsidies [70]. Tradeable rights for every kg of nutrient surplus, such as N surplus permits, are more representative of environmental impacts than nutrient inputs as they consider several chemical forms [145,146] and can be more cost-efficient in addressing eutrophication [147]. Other, more traditional regulatory instruments, such as water quality standards, pollution discharge permits, mandatory best practices, and others, are still vital to reducing agricultural pollution [70].

The potential of environmental impact reduction for agricultural emissions involves the decarbonization of energy production, the use of the best available practices, the implementation of precision agriculture practices and climate-smart farming techniques, the improvement of irrigation management practices, better fertilizer usage practices for the improvement in NUE [1,26,28,35,148], as well as the retrieval and reprocessing of resources [63]. All the pointed-out options come with constraints, from technical challenges to economic cost, or from farmer's acceptance to political constraints; nevertheless, to comply with the climate objectives of the Paris Agreement and Green Deal, all sectors must take measures to decrease their emissions and negative impacts [26,149].

Despite the great volume of GHGs that agriculture emits, better integration of innovative techniques into production methods, more efficient application of fertilizers, and better manure management can effectively reduce its weight [26]. Reducing agricultural emissions and nutrient loss from fertilizers could play a significant role in climate change mitigation [26,150]. In Ahmed et al.'s study [151], it is observed that "variable rate fertilization", "controlled-release and stabilized fertilizers", and "improved fertilization timing" represent important technical GHG mitigation potentials of 176 MMT CO_2e, 65 MMT CO_2e, and 40 MMT CO_2e, respectively. Moreover, in the top 15 measures recognized by the global agriculture marginal abatement cost curve, "Reduce nitrogen over application in China and India" could contribute to reductions of 88 Mt CO_2e, and "expand adoption of controlled-release and stabilized fertilizers" could contribute to reductions of 75 Mt CO_2e. Furthermore, rice cultivation is highlighted with "improve fertilization practices" potential to contribute to reductions of 449 Mt CO_2e, and "improve paddy water management" could contribute to reductions of 296 Mt CO_2e. Nonetheless, all this comes with a cost [151].

5. Reducing the Impact of Climate Change on Agriculture

The level of impact that crops are subjected to can be diminished by altering agricultural practices, acknowledging the effects of CC, and adopting climate-smart farming practices and technologies.

The alteration of crop rotation to meet water availability, the adjustment of sowing dates, the protection of pollinators, and the usage of resilient crop varieties, can make a huge difference in mitigating yield loss [1,152]. Other practices that can be widely applied are the systematic use of climate forecasting tools, plant cover crops, improved methane recovery from organic residues, and improved NUE and plat resilience. The use of smart fertilizers, such as slow-release fertilizers, controlled-release fertilizers, and nanofertilizers (including controlled-release nanofertilizers and slow-release nanofertilizers), to deal with nutrient imbalances and losses to the environment is a viable option [153]. Moreover, irrigation practices need to continue to shift to precise application practices based on real-time information and crop vegetative indexes, avoiding over-irrigation and, ultimately, nutrient run-off [4]. However, although these can be effective measures, the IPCC brings to attention the fact that it is not enough and cannot prevent all changes related to CC, and that the reduction in GHG emissions is fundamental [11].

6. Nanofertilizers as Mitigation and Adaptation Strategy

Nutrient management is pointed out as one of the effective measures to be taken both to reduce agriculture impact in CC and to mitigate the effects of CC in agriculture. As such, fertilizer production and utilization must be considered carefully. Nanofertilizers, as a new and improved fertilizer option, contribute to the reduction in nutrients needed and to its incremented use efficiency [154]. Several studies point to the effectiveness of nanofertilizers in crop production and account for the improved nutrient management achieved by its use, even in unfavorable conditions, such as in salinity soil [155–159]. Due to nanofertilizers's unique properties, their use is noted as a promising strategy to solve land quality degradation, low crop productivity under abiotic stress, nutrient deficiency in plants, nutrient imbalances in soil, and nutrient leaching losses [160,161]. A greater surface area exhibited by materials at the nanoscale results in a larger reaction surface, aiding the occurrence of metabolic reactions in plants, including higher, slower, and more adequate nutrient uptake, as needed by crops [156,162–167]. Several release mechanisms are possible with the use of these materials, such as target delivery and slow- and controlled-release mechanisms, responding to environmental triggers and biological demands.

Das et al. [154] achieved nutrient savings and crop improvements by pre-treating seeds of beetroot, carrot, fenugreek, and mustard, with nano-iron pyrite (FeS_2). Soaking the seeds for only 12h in an aqueous suspension of nano-iron disulfide/pyrite (FeS_2) resulted in a significant yield increase in all crops under study. At maturity, beetroot presented a 47% yield increase; carrot presented a 19% increase; mustard obtained a 65% increase in the seed yield; and fenugreek crop achieved a significant increase in leaves per plant, leaf area, and average chlorophyll concentration [154]. For tomato, the application of 8 g L^{-1} of silica nanoparticles ($nSiO_2$) significantly enhanced seed germination potential, achieving a seed germination percentage improved by 22%, mean germination time improved by 4%, seedling vigor index improved by 508%, seed germination index improved by 22%, seedling fresh weight improved by 117%, and seedling dry weight improved by 117%, when compared with control [168]. Tarafder et al. [169] used urea-modified hydroxyapatite and incorporated copper (Cu^{2+}), iron (Fe^{2+}), and zinc (Zn^{2+}) nanoparticles to use in a field experiment with lady's fingers (or okra). The dose of nanofertilizer applied was 100 times less than the conventional fertilizer and resulted in a significant increase in Cu^{2+}, Fe^{2+}, and Zn^{2+} nutrient uptake as a consequence of slow release. Enhanced vegetative growth, flower number/plant, photosynthetic pigments, and yield were also found in common bean plants when a combination of zinc oxide (ZnO), Manganese dioxide (MnO_2), and molybdenum trioxide (MoO_3) nanoparticles was supplied to the crop via foliar application [170]. Furthermore, although not linearly correlated to concentration, all the foliar applications of nanofertilizer had a significant induced improvement in nitrogen, copper, manganese, potassium, zinc, and phosphorus uptake [170]. Another interesting discovery resulting from the application of nanofertilizers was made by Abdel-Aziz et al. [155], who, besides obtaining higher yield in wheat using nano-chitosan–NPK, also observed the acceleration of plant growth, resulting in a reduced life cycle (40 fewer days), which can be an advantage concerning irrigation requirements in CC conditions.

As abiotic stresses are a major concern for crop production and are exacerbated by CC, the nanofertilizers' positive results found in salt stress and high-temperature stress conditions are a breakthrough finding. Under salt stress conditions, Wahid et al. [157] found that green synthesized silver (Ag) nanoparticles had a positive effect on wheat survival and development by positively regulating numerous metabolic traits such as seed germination, antioxidant, amino acid, potassium, and nitrogen content [157]. Furthermore, in these conditions, the foliar application of nano-silicon (Si) in peregrine by Ashour and Mahmoud [171] also reflected enhanced plant weight, number of branches, leaves per plant, and higher leaf area. Under high-temperature stress, plants suffer declined pollen germination, seed set, and seed yield percentages [172]. In a study where high temperature (38/28 °C) and optimal temperature conditions (32/22 °C) were compared, selenium (Se) nanoparticle treatment in grain sorghum aided in alleviating the stress effects on the crop. Using 10 mg L^{-1} Se nanofertilizer via foliar application, the authors verified enhancing antioxidant enzyme activity that resulted in a stimulated antioxidant defense system, improved the pollen germination percentage (14%), and thus significantly increased seed yield (26%) under high-temperature stress [172].

As nanofertilizers can provide controlled or slow-release nutrients according to crop demand, they could also contribute to the synchronization of macro and micro nutrients, achieving better balance in soil and synergetic effects for crops [166]. Thus, soil properties and health are also improved as nanofertilizer can release nutrients at a slower rate than conventional fertilizers, opposing nutrient imbalances, contributing to better soil fertility and organic matter content, amending problems in soil structure, and contributing to food quality and safety [161,173–176].

Besides evident crop and soil benefits, the use of nanofertilizers can reduce GHG emissions to the atmosphere, not only by the reduction in input for the same result, but also by reducing soil emissions after nanofertilizer use as demonstrated by Mohanraj et al. [177]. In their study, the authors applied nano-zeolite-based nanofertilizers carrying NO_3^- or NH_4^+ forms of N in rice soils and evaluated N_2O and CH_4 emissions compared to the control. The results showed that, although not having the same effect, both nanofertilizers reduced emissions when compared to control. The lowest N_2O emissions were recorded for nanofertilizer-NH_4^+ (0.88 mg m^{-2} day^{-1}, compared to 1.67 mg m^{-2} day^{-1} of control, which was the highest recorded), and the lowest CH_4 emission was obtained by nanofertilizer-NO_3^- (13.6 mg m^{-2} day^{-1}, compared to 14.5 mg m^{-2} day^{-1} of control and nanofertilizer-NH_4^+), which suggest that the better release of nutrients achieved by the nanofertilizers contributes positively to crop NUE and to the reduction in soil emissions [177].

Despite the uncertainties, good nutrition boosts crop resistance to abiotic stress, but furthermore, the nanofertilizer formulations can include biostimulants that can promote crop health and resilience (Figure 2). Nanofertilizers can also improve the ability of plants to absorb carbon dioxide (CO_2) by increasing photosynthetic efficiency. At the same time, the use of nanofertilizers can contribute to improved yields and reduce emissions from soil, confirming the IPPC [153] statement that nanotechnology is a very promising advance in technology that contributes to plant health and improves crop resilience against several risks, including CC.

As revealed, the utilization of nanofertilizers can have advantages in reducing the effects of the CC/agriculture dichotomy, but to actually achieve some level of relevance, its use must be more effective and widespread. Nonetheless, these materials have some limitations to their use as public acceptance, safety assessment methods, exposure levels, and other possible nano-toxicological effects on the environment and human health that are not yet perceived. To overcome these concerns, a greater investigation into the properties and biological reactivity of nanomaterials must be carried out, and specific regulatory policy must be produced, as well as specific safety testing guidelines [178–180]. To increase the widespread safe application and concomitant efficacy of nanofertilizers in reducing agro-related CC and CC effects in agriculture, some guiding principles should be followed:

- The materials to be used in nanofertilizers must be studied for their safety. A good example is to use the ones that have already been proven to have high biodegradability, high biocompatibility, and decreased cytotoxicity, such as the ones studied for medical devices or resulting from green synthesis;

- Nanofertilizers should be studied and applied to specific crops in order to eliminate the nano-phytotoxicity effect in a fit-to-purpose, precision application;
- When available, commercial nanofertilizer formulations should be chosen over traditional ones, increasing yields, improving soil conditions, and reducing emissions;
- The commercially available nanofertilizer options must be increased to become a viable and consistent alternative for producers;
- The inclusion of biostimulant substances in the formulations should be considered in order to increase crop resistance and resilience.

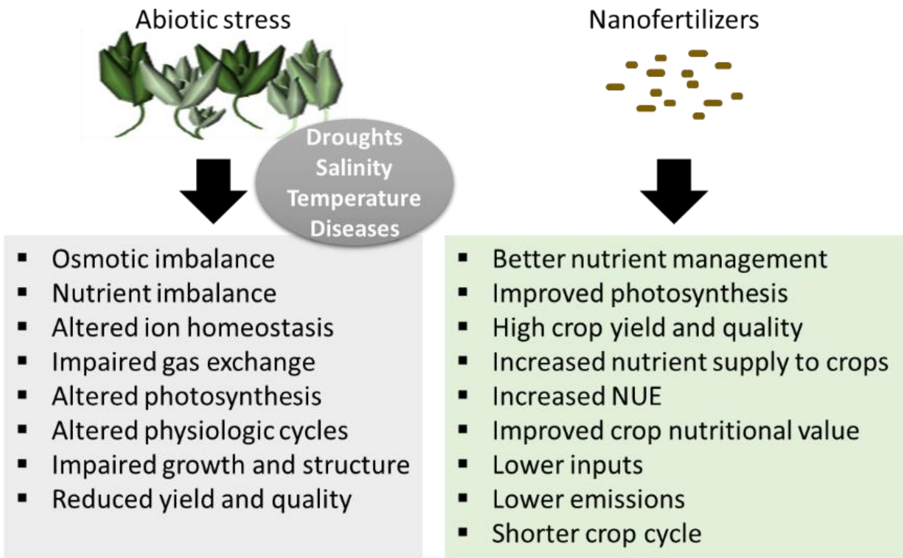

Figure 2. Nanofertilizer benefits to crops under abiotic stress due to CC.

The encouragement to increase nanofertilizer improvement and utilization can arise from policy. Establishing limits for synthetic fertilizer allowed per ha/crop or economic benefits for the utilization of new fertilization forms could be a strategy to create change. Alternatively, the market is already promoting change as the cost of conventional fertilizers increases and the demand for more efficient options rises.

7. Conclusions and Perspectives

This paper addressed the dichotomy between agriculture and climate change, referring to the questions raised by agricultural activities that produce effects on CC and, on the other hand, the effects and consequences that CC has on agricultural activity. Climate change is negatively impacting agriculture, and the need to provide food for the world's growing population results in the pressing need to intensify this activity. Ultimately, this also adds pressure to agricultural systems and thus exacerbates climate change. To mitigate the effects of this dichotomy several actions can be taken, including the decarbonization of energy in all sectors of the economy, the effective reduction in GHG emissions, and the change in cultural practices, including the adoption of climate-smart practices, which comprise a more efficient use of nutrients and the careful and efficient use of water resources through the change in irrigation techniques.

Due to their physicochemical characteristics, nanofertilizers present some potential applications to combat the increase in CC and mitigate the effects that are already in place. The reduction in inputs and nutrient loss is a truthfully appealing fact. Thus, the effect on soil nutrient imbalance and the reduction in soil emissions due to the application of nanofertilizers are compelling arguments for their utilization.

To increase the efficacy of nanofertilizers in the adaptation and mitigation of the agriculture/CC dichotomy effects, some guidelines were formulated from the increased number of research studies for fit-to-purpose nanofertilizers to eliminate nano-toxic concerns for crops and humans, as well as the increment of commercially available nanofertilizers options, to create a viable alternative for producers to use.

In conclusion, the increase in nanofertilizers brings several benefits, and they are viable assets for the adaptation of agriculture to CC effects and to mitigate agriculture contributions to CC.

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