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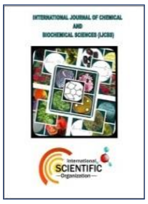

Current trends in the use of Controlled-Release Fertilizers for sustainable agriculture

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Abstract

Fertilizers are fundamental for crop yield, soil productivity, and nutrient supply. However, the overuse of traditional fertilizers can result in consequences such as contamination, decreased soil fertility, and health toxicity. The exponential growth in demand for sustainable crop production has necessitated the development of advanced techniques for fertilizer production. The use of controlled-release fertilizers (CRFs) not only mitigates nutrient loss, but also facilitates the implementation of a well-suited nutrient-release strategy to optimize plant growth. Nevertheless, utilization of CRFs entails significant costs and predominantly relies on petroleum-based synthetic polymers for its coating. Fossil fuel-derived materials, sourced from non-renewable resources and often containing toxic chemicals, can lead to energy and environmental conflicts, such as non-biodegradable soil wastage and fossil fuel exhaustion. To overcome these challenges, it is crucial to come up with biodegradable, cost-effective, and eco-friendly encasing materials. This pursuit has prompted the exploration of nanotechnology. Consequently, the application of nanotechnology plays a crucial role in increasing the efficacy of CRFs. Future CRF technology advancements should enhance nutrient release efficiency, explore low-cost biodegradable materials, improve grower communication, and develop environmentally friendly coating materials for sustainable agriculture practices. This review aims to address the recent advancements in controlled-release fertilizers, focusing on their impact on crop growth, development, yield and global market.

Keywords: Controlled-release fertilizers, CRFs, Nano-fertilizer, Nano-technology, Sustainable agriculture

Full length review article

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1. Introduction

Agriculture has been a significant recipient of technological advancements and research discoveries throughout human history. The integration of technological advancements in the agricultural sector underscores the importance of crop production as a primary source to satisfy the nutritional needs of the burgeoning human populace [1]. Conventional agricultural practices effectively sustain a global population of approximately 6 billion individuals. According to estimates, the human populace will grow by 9.8 billion by 2050. This projection implies that a substantial increase of approximately 70% in food production will be required compared to the levels observed in 2005 [2].

Fertilizers are crucial in improving soil fertility, providing additional nutrients for plant growth, and meeting the escalating food demand [3]. However, overfertilization reduces fertilizer consumption efficiency, worsening environmental issues. Moreover, global warming, urbanization, and the unequal distribution of Earth's resources have caused significant problems for the agriculture business worldwide [4-5]. In developing nations, there are notable economic inefficiencies caused by leaching problems (40-70%) [6]. To effectively handle this mounting issue, it is crucial to introduce an enhanced version of fertilizers that efficiently transport nutrients to targeted plants in a controlled manner, reducing nutrient loss and enhancing crop yield [7]. Controlled-release fertilizers (CRFs) have been developed as a viable solution to address this issue. CRFs are a significant research area for agricultural applications. They reduce labor and fertilizer costs, helping to address resource shortages and rural labor force losses [8-11]. As illustrated in Figure 1, CRFs have received a tremendous deal of attention over the last two decades.

Nanotechnology is believed to significantly improve sustainable agriculture by synthesizing controlled fertilizers. Plants require 16 essential nutrients, of which 13 are obtained from the soil. The continuous application of controlled-released nano-fertilizers to the soil improves nutrient transport to specific plants, leading to accelerated growth, earlier germination, and enhanced nutrient absorption [12]. This comprehensive analysis delves into the ultimate destiny of conventional fertilizers, the classification and mechanism underlying controlled-release fertilizers, and the various factors that influence their performance. Furthermore, it propels the discourse forward by illuminating the utilization of nanotechnology and global market analysis. The consequential effects and advantageous attributes of controlled-release fertilizers are thoroughly investigated, offering invaluable perspectives for individuals with a vested interest in the pivotal role of these fertilizers in fostering agricultural sustainability.

2. Fate and Consequences of Conventional Fertilizers

Fertilizers have been used since agriculture's inception to supplement soil with essential nutrients [13]. They enhance the soil's nutrient composition and integrity by providing deficient nutrients [14]. Fertilizers are synthetic or natural inorganic or organic substances that are applied to agricultural fields to supply essential nutrients for plant development [15]. Table 1 gives an overview of primary nutrients. Farmers have relied on organic fertilizers like manure, compost, legumes, and crop residues for effective agriculture development, since old days. However, these organic fertilizers were slow to reach crops due to decomposition. Synthetic fertilizers overcame this limitation. Conventional fertilizers are more targeted in their application, with known nutrient composition and readily released at the time of application [13]. Figure 2 shows a simple classification of traditional fertilizers. Figure 3 illustrates critical nutrients necessary for plant development, along with indications of nutrient deficiency symptoms.

2.1. *Organic Fertilizers*

Organic fertilizers, which encompass naturally occurring organic materials, are derived from three primary sources. The initial source is of an animal origin. The second source refers to the use of cover crops derived from plants, which enhance soil quality by acting as green manure [16]. The third component, known as the mineral source, comprises naturally extracted powdered limestone, mined rock phosphate, and sodium nitrate [16-17]. These provide essential nutrients for plants through biological processes while also exhibiting the ability to mitigate pest populations [14]. Organic soil components benefit from progressive deterioration. However, soil moisture and temperature affect decomposition, releasing nutrients even when the plant doesn't need them. Moreover, these are low in nutrients and scarce, making it difficult to use them alone to meet crop nutrient needs. This shows that nutrient immobilization before mineralization may cause an early nutrient shortage in crops. Small-scale farmers may struggle to get the massive resources needed [14].

2.1.1. Biofertilizers

Biofertilizers, often known as microbial fertilizers, contain living microorganisms that can colonize plant rhizospheres or tissues. Microorganisms help plants flourish by increasing nutrient availability. These eco-friendly fertilizers can benefit plants if they are applied to plant surfaces, seeds, or soil [18]. Every analytical technique has pros and cons that must be considered based on the inoculant, crop type, environmental conditions, and farmer skills [19]. Several strains, deemed beneficial in scientific studies, are absent from the commercial market [20]. The observed outcome may potentially be attributed to a faulty formulation [21]. Biofertilizer commercialization is also influenced by upstream variables, including the selection of strains, carriers, and marketing considerations [22].

2.2. *Inorganic Fertilizer*

The synthesis of inorganic fertilizer, also known as chemical fertilizer, involves intricate chemical processes. This meticulously crafted product is composed of one or more vital nutrient, specifically designed to improve the crop growth and development [18]. In contrast to the controlled-release capabilities of organic fertilizers, they offer immediate plant nutrients. They exhibit enhanced efficiency, cost-effectiveness, and scalability, rendering them highly compatible with agricultural operations [23].

2.2.1. Nitrogen Fertilizer

Nitrogen is abundant in the atmosphere and essential for all life [13]. Plants need nitrogen (N) to successfully complete their cycles. Insufficient or excessive nitrogen might hinder plant growth [24-25]. The atmosphere's elemental dinitrogen (N_2) gas is 78% nitrogen. Plants cannot absorb or use it since it is inert. Most fertilizers contain nitrogen due to soil nitrogen deficiency [13]. Urea, a nitrogen fertilizer, is a cost-effective and user-friendly choice owing to its notable solubility, limited thermal stability, and relatively low molecular weight. However, it is worth noting that nitrogen fertilizer exhibits a significant potential for losses due to its high solubility characteristics. Unfortunately, volatilization, runoff, and leaching can transmit it to air and aquatic habitats. The ease of dissolution and water runoff of conventional urea fertilizer pose challenges in its fixation by soil particles, leading to a low utilization rate in developing regions [26]. The loss of nitrogen in its different forms has a significant impact on the atmosphere and hydrosphere, which in turn has implications for human and animal health [25].

2.2.2. Phosphorus Fertilizer

Phosphorus fertilizer can affect soil acidity by releasing or acquiring H+ ions, depending on soil pH. Single superphosphate, monoammonium phosphate, and triple superphosphate are typical soil phosphorus fertilizers. However, these fertilizers can lower the pH of alkaline soils with a pH > 7.2, but not acidic soils. Diammonium phosphate can increase the alkalinity of acidic soils, although it does not have any impact on soils with a pH level exceeding 7.2 [13]. The average plant uses 20% of traditional fertilizer's phosphorus. Volatilization and nutrient leaching can slow phosphorus consumption, causing water eutrophication and harmful emissions. Moreover, microorganisms and nutrient hydrolysis might produce pollution and health problems [27]. As phosphorus is rare and valuable, it is imperative to identify and implement efficient strategies for phosphorus generation and utilization [28].

2.2.3. Potassium Fertilizer

Potassium (K) is an essential macronutrient that exerts a pivotal role in plant development and growth, thereby assuming a critical function in contemporary agricultural methodologies [29]. In terrestrial deposits, sylvite and carnallite are abundant evaporative minerals that provide potassium. Figure 4 shows the four forms in which soil acquires potassium (K) [18]. Potassium fertilizers are soluble in water and adsorb onto soil particles via cation exchange [30]. Most soil matrices may hold potassium ions, making soluble potassium salts easier to incorporate. This fortress prevents potassium fertilizer from leaching, reducing the soil's potassium retention loss [13]. Insufficient potassium in the soil can have several effects, and it is common in many parts of the world, affecting sustainable agriculture practices [31].

2.2.4. Compound Fertilizer

Compound fertilizers are meticulously formulated fertilizers that encompass a harmonious combination of primary nutrients diligently encapsulated within every granule. The constituents should exhibit homogeneity in their mixture, adhering to the desired nutrient grade and ratio, thereby guaranteeing a uniform and efficacious application [32]. In agriculture, compound fertilizers—including secondary and micronutrient elements—are unique. They disperse a predetermined mixture of compounded nutrients within discrete granules, unlike homogeneous fertilizer blending. This eliminates nutrient source segregation during transit or application. Compound fertilizers help distribute important micronutrients evenly across the root zone, in addition to their main purpose [18]. The challenges that necessitate attention pertain to the efficacy of compound fertilizer formulations and their associated costs. The primary constituents of fertilizers, specifically urea, ammonium phosphate, ammonia (NH_3), potassium (K) and sulfur (S) salts, are employed by the manufacturers in the production of compound fertilizers [18].

2.2.5. Micronutrient Fertilizer

Micronutrients, also known as essential nutrients, are required in smaller dosages to fulfill the ongoing nutritional requirements. Plants require micronutrients, which are present in lower quantities than macronutrients. However, the insufficiency of these micronutrients compromises the plant's ability to withstand unfavorable conditions, ultimately leading to diminished agricultural output and compromised product quality. Micronutrients, also known as trace elements, play a pivotal role in maintaining plant homeostasis and serve as indispensable coenzymes in catalytic reactions, thereby facilitating a myriad of biochemical and cellular processes [18-33].

2.3. Limitations of Conventional Fertilizers

The utilization efficiency of chemical fertilizers in direct plant administration has been observed to be relatively low, with only approximately 30-35% of the nutrients being absorbed [34-37]. Urea, a preeminent nitrogen-based fertilizer, has been documented to exhibit nitrogen use efficiency (NUE) levels of merely 50%. Approximately 2-20% of the nitrogen content undergoes volatilization, while 15-25% engages in reactions with soil organic compounds. Additionally, a further 2 to 10% is susceptible to leaching, thereby giving rise to significant apprehensions [35]. Figure 5 illustrates soil conventional fertilizer loss. (A) Run-off, nitrate leaching, ammonia volatilization, and nitrous oxide emissions waste too much nitrogen fertilizer. (B) An excessive amount of phosphorus (P) fertilizer can be lost through processes such as run-off and leaching. It can be immobilized organically, adsorbed inorganically, or precipitated mineral.

The optimization of fertilizer application is imperative to mitigate losses and enhance nutrient utilization. These concerns encompass soil, freshwater, and ocean contamination, alongside a reduction in agricultural ecosystem diversity [38-39]. The primary objective of fertilizer enhancement should revolve around the regulation of fertilizer loss, optimization of nutrient retention, enhancement of efficiency, and mitigation of pollution ramifications [18].

3. Controlled Release Fertilizer – A Novel Approach

The utilization of advanced fertilizers has been recognized as an effective approach to enhance the efficiency of fertilizers and mitigate their negative environmental consequences [18]. The efficacy of providing nutrients and enhanced nutrient utilization efficiency in reducing environmental pollution is contingent upon two key factors: ensuring that nutrient delivery matches the requirements of plants and balancing the availability of nutrients [40]. Controlled-release fertilizers (CRFs) are water-soluble nutrients enclosed within a coating that controls the gradual release of nutrients into the soil [41]. These are granules that are able to intercalate within carrier molecules. This intercalation process enhances the effectiveness of nitrogen release to crops while simultaneously decreasing environmental, ecological, and health risks [42]. These are designed to have a nutrient core that is enclosed by either inorganic or organic materials [43].

Controlled-release fertilizers release nutrients longer than quick-release fertilizers. These release nutrients at varying rates depending on the plant metabolic needs. The CEN Task Force, responsible for European standardization, has provided guidelines for CRF criteria. These rules require slower nutrient release than ordinary fertilizers. The nutrients should not be released more than 15% in 24 hours or 75% in 28 days. Additionally, 75% of nutrients must be released within the prescribed time. Additionally, 75% of nutrients must be released within the prescribed time [44].

3.1. Classification of Controlled Release Fertilizer

A comprehensive categorization has been formulated by integrating the findings of various studies, as illustrated in Figure 6 [27]. In a comprehensive manner, CRFs have been classified into three primary categories.

Inorganic low solubility compounds: There are two types of inorganic low solubility compounds: partially acidulated phosphate rock (PAPR) and metal ammonium phosphates [27]. A group of compounds sharing the formula $MeNH_4PO_4.H_2O$ is commonly used as a fertilizer with a low solubility. "Me" refers to divalent cations like Mg, Zn and Fe. Partially acidulated rock phosphate is commonly used as a controlled-release phosphate fertilizer, particularly in light-textured acidic soils. When the soil has high phosphate fixation, the nutrients quickly convert into a less soluble form right after they are applied.

Organic compounds: They can be classified into two groups: natural organic compounds (e.g., sewage sludge and animal manure) and synthetically produced organic, low-solubility compounds. The compounds can be classified into two categories: biologically decomposing compounds (e.g., urea formaldehyde) and chemically decomposing compounds (e.g., isobutyledene diurea or urea acetaldehyde/cyclo diurea) [27-40]. Factors that influence nitrogen release include granular material size, soil moisture levels, microbial activity, and temperature [40].

Water-soluble fertilizers: These use physical barriers to regulate the release of nutrients. They come in various forms, such as cores or granules, with a special coating to control their dissolution and release. Controlled release matrices, which can be hydrophobic or gel-forming polymers, are less common than coated CRFs. A hydrogel possesses a hydrophilic nature, which hinders the dissolution of fertilizer dispersed within the hydrogel material due to its exceptional water retention capabilities (swelling). There are various types of coated fertilizers available. Coated fertilizers can be organic or inorganic, with some coated with thermoplastics or resins, while others are coated with sulfur or mineral-based materials. The amount of nitrogen released from sulfur-coated urea is influenced by the coating quality. There are three types of sulfur-coated urea granules: damaged, sealed with wax, and perfectly thick. A damaged coating on sulfur-coated urea releases urea upon water contact [27-40].

3.2. General Mechanism of Controlled Release

The liberation of essential nutrients from controlled-release fertilizers (CRF) typically occurs through a triphasic process comprising the following distinct stages: an initial lag period, a sustained release phase, and a subsequent decay period [45]. In the initial phase of the lag period, the interaction between water and fertilizer granules occurs, leading to water infiltration into the outer layer of the granules. Consequently, a portion of the fertilizer undergoes dissolution. The vapor pressure gradient is the main factor that facilitates the process, as it controls the release of nutrients during this phase. The lag phase is achieved by reaching a balance between the aqueous medium and the liberated nutrients, or alternatively, by filling of void spaces within the interval with water [11].

During the subsequent phase of constant release, the penetration of water into the granular matrix commences, leading to the establishment of an equilibrium state between the aqueous medium and the solute present in the fertilizer. The integrity and performance of CRFs coatings are inherently susceptible to the influence of the surrounding environment, thereby rendering them vulnerable to potential degradation and the formation of fissures. Polymeric coatings exhibit remarkable resistance to crack formation, primarily due to their ability to impede water ingress via the minuscule pores present within the coating structure. The nutrient release pattern exhibits notable susceptibility to various environmental factors, including soil moisture, temperature, salinity, soil pH, and microbial activity [46].

In the case that the pressure surpasses a predetermined threshold, it leads to the rupture of the coating material and the subsequent instantaneous release of the fertilizer content [41]. During the decay phase, the process of fertilizer diffusion occurs, wherein the internal core undergoes continuous dissolution, facilitated by the influx of water into the granule. The mechanism is visually depicted in Figure 7 [11]. The observed phenomenon can be characterized by a sigmoidal (S-shaped) release profile, as visually depicted in Figure 8 [11]. The observed phenomenon suggests that the process of release exhibits complexity and non-linearity. The attainment of a sigmoidal release profile is the primary objective pursued by researchers in the realm of formulation development. This desired outcome is characterized by a controlled release pattern that aligns harmoniously with the specific nutrient demands of plants.

3.3. Factors Affecting Nutrient Release

Nutrient liberation from controlled-release fertilizers (CRFs) can be influenced by various chemical, physical, and biological parameters, including temperature, biological activity, soil moisture, pH, and soil composition. The inherent factors that influence the liberation of nutrients from CRFs encompass nutrient composition, coating thickness, granule diameter and shape [11-47-48].

3.3.1. Fertilizer Composition and Shape

Fertilizer composition: Nitrogen, phosphorus, and potassium are vital macronutrients in agriculture [49], wherein their availability exerts influence on the release mechanism from fertilizers [50]. Plants conventionally uptake nitrogen in the form of nitrate or ammonium ions [51], thereby leading to a substantial depletion of the supplied fertilizer. Phosphorus, being the second most abundant macronutrient provided to crops, encounters challenges due to leaching in sandy soils and fixation in acidic and highly weathered soils [52]. The acid phosphate sources can be effectively impregnated with MgO, thereby serving as a viable approach to neutralize acidity and enhance the efficiency of phosphorus utilization [52-53]. The intricate release profile of potassium arises from the intricate interplay of physical interactions and chemical bonding between potassium species and other minerals in controlled-release fertilizers. The small dimensions of potassium ions facilitate their facile ingress into the microporous crevices within the carbonaceous composition of the matrix [54].

The liberation of every nutrient is contingent upon its solubility, diffusivity, interactions, temperature, water content, and medium composition. The rate of nitrate release is the most rapid, followed by ammonium and potassium, whereas phosphate exhibits a comparatively slower rate. The investigation conducted by Wilson and Chem revealed that the fractional rate of nitrate release exhibited a superior magnitude when compared to that of potassium and, notably, phosphate [50].

Fertilizer shape: Granular fertilizers play a vital role within the industrial domain, owing to their numerous advantageous attributes. These include enhanced manipulability, diminished expenses associated with transportation and storage, decelerated nutrient discharge, mitigated segregation, and heightened homogeneity of constituents [53-55-56]. The surface properties of granules play a crucial role in modulating the release kinetics of controlled-release fertilizers (CRFs), whereby granules with irregular morphology induce irregularities and flaws in the coating matrix. The granules' particle size distribution is of utmost importance. Rotational cylinders are extensively employed in the fertilizer industry to produce granulates or pellets. The rate of dissolution of the granules is influenced by factors such as granule size, distribution, and porosity. The granulation process parameters encompass the magnitude of powdered raw material delivery, the angular inclination of the coating drum, the rotational velocity, and the duration of material residence [57].

Coating composition: Seasonal crops uptake nutrients in a sigmoidal pattern, so fertilizers should release nutrients accordingly for optimal plant nutrition and reduced losses [51]. Hydrophobic-coated fertilizers control release rates with different temporal patterns. Coating fertilizers with soluble or biodegradable polymers controls nutrient release effectively [58]. This approach yields high nutrient content per total weight, unlike matrix-based fertilizers that require mixing with inert solids [59]. Table 2 provides an overview of various coatings and their characteristic findings [11]. Polymer-coated CRFs are advanced due to their versatility for different harvests, soils, and weather. The degradation kinetics of polymers play a pivotal role in regulating the nutrient release characteristics of controlled-release fertilizers (CRFs). The rate of degradation is influenced by certain factors, such as the structural characteristics encompassing configuration, chemical composition, and ionic groups. Additionally, physiological aspects like molecular weight, processing conditions, and annealing play a role. Furthermore, morphological attributes, including structure, shape, and site of implantation, also contribute to this phenomenon. Physical properties such as the permeability of water and solubility play a crucial role in determining the rate of polymer degradation [35-60].

3.3.2. Soil Parameters

Soil properties strongly affect release rate and profile [50]. Upon soil contact, the degradation of the coating polymer and the subsequent liberation of nutrients from controlled-release fertilizers (CRF) are regulated by a synergistic triad [48]. Soil factors (pH, temperature, moisture, composition) and microbial activity affect nutrient release [61].

pH: The availability of nutrients is intricately influenced by the pH of the soil. The solubility of nutrients depend on the pH of the soil. The soil pH, if excessively high or excessively low, can impede the uptake of nutrients by the root system [11-62-63]. The pH of the release medium exerts a substantial influence on the chemical species' interactions within the granule and the diffusion coefficient of ions [64]. Rashidzadeh and Olad [65], Emami et al. [66], Wen et al. [67], Uzoh et al. [68], and Salimi et al. [69] have observed that within an acidic environment (pH 2–5), a substantial abundance of H+ ions is present. This results in the protonation of the majority of carboxylate anions (COO−), thereby mitigating anion-anion electrostatic repulsion within the network and subsequently reducing the swelling capacity. In an alkaline milieu (>pH 9), the COO− anion experiences shielding due to the presence of Na+ ions in the solution, thereby impeding anion-anion electrostatic repulsion. This phenomenon has been observed in the context of control release fertilizer coatings, as discussed in the review. Within the pH range of 5–9, or under conditions of neutrality, it is anticipated that the swelling capacity would reach its peak due to the conversion of COOH groups into COO− ions. This conversion leads to the maximization of electrostatic repulsion [41].

Temperature: The release duration of CRF is significantly influenced by temperature, making it the foremost critical environmental factor [11]. The observed phenomenon entails a positive correlation between soil temperature and the rate of nutrient release from controlled-release fertilizers (CRF). As the soil temperature rises, there is an accessory increase in the rate of nutrient release, resulting in a reduction in the overall release duration [47]. In the study conducted by Gandeza et al., it was observed that following a 60-day incubation period in water, a polymer-coated fertilizer (PCF) exhibited a gradual release of nitrogen (N) at different temperatures. Specifically, at 10°C, 20°C, and 30°C, the PCF released 20%, 48%, and 80% of the nitrogen content, respectively [47].

The observed nutrient release pattern exhibits two distinct possibilities, namely a linear or sigmoidal trend that depends on alterations in the prevailing temperature conditions. The observed pattern exhibits a sigmoidal shape, commencing with a discernible lag phase, followed by the attainment of a steady release and subsequent decay phase. CRFs, or controlled release formulations, exhibit a linear release profile characterized by the absence of a lag phase. Instead, they initiate with a consistent release phase followed by a subsequent decay phase [70]. The expeditious liberation of nutrients from granular matrices will inevitably exert an influence on the nutrient release rate. The application of fertilizer onto bare soil is subject to the influence of fluctuating surface temperatures, a factor that can potentially diminish the durability of fertilizer products. To optimize the release time and mitigate the potential impacts of temperature, it is imperative to incorporate the fertilizer into the soil matrix [71].

Soil microbial / biological activity: Soil microorganisms and enzymes degrade fertilizer coatings [48]. The protective layer breaking down releases 15-20% of unused plant nutrients from controlled-release fertilizers due to concentration differences. This phenomenon is influenced by biotic and abiotic factors [48]. Versino et al. explained the degradation mechanism of biodegradable polymer coatings. Microbes colonize polymer substrates and release catalysts to aid hydrolysis, producing oligomeric and dimeric compounds. The monomers can degrade aerobically, producing CO_2, water, minerals, and biomass, or anaerobically, forming CO_2, methane, and humic substances, without harmful substances [35]. Soil activity depends on its composition, temperature, moisture, pH level, and various environmental factors [72]. Jia et al. found that non-sterilized soil releases nitrogen faster and degrades polydopamine-coated fertilizer more quickly than sterilized soil under the same environmental conditions [73]. Soil composition affects the release profile of CRFs. Silt, clay, sandy, and loamy are common soil types found in different environments. Silt is nutrient-rich and fertile, while clay is compact and dense.

Sandy soils have less than 18% clay and more than 68% sand in the top 100 cm [50]. Loam is made up of sand, silt, and clay in the proportions of 40% sand, 40% silt, and 20% clay [50]. Loam soils have more nutrients, moisture, and humus, making them better at draining water and air and allowing water and air to enter. Sandy soils have weak structure, low water retention, high permeability, and are easily compacted. Increased moisture and temperature boost microbial activity, leading to communities with improved abilities to access and break down substances [61]. Table 3 gives information on different coatings and the enzymes and bacteria responsible for their degradation [50].

4. Controlled-Release Fertilizer and Nano-Technology

Utilization of CRF entails significant costs and predominantly relies on petroleum-based synthetic polymers for its coating. Fossil fuel-derived materials, sourced from non-renewable resources and often containing toxic chemicals, can lead to environmental and energy conflicts, such as non-biodegradable soil waste and fossil fuel exhaustion. To overcome these challenges, it is important to come up with biodegradable, cost-effective, and eco-friendly encasing materials. This pursuit has prompted the exploration of nanotechnology. Nanotechnology has emerged as a solution through green nanomaterials, nanofertilizers, nanoagrochemicals, nanopesticides, nanoherbicides, nano-biosensors, and nano-based treatment of agricultural waste. They have shown excellent responses to plant growth and productivity. Nanofertilizers, made up of various nanoparticles like metal oxides and carbon [7], offer controlled, slow-release, and specific concentrations of macro and micronutrients to plants, with proper size and surface area [74].

Nanofertilizers present novel strategies for implementing smart and sustainable methods in agriculture. However, it is imperative to thoroughly evaluate their potential hazards to plants, soil organisms, and human health prior to their widespread adoption in commercial settings. The potential accumulation of nanomaterials in the environment and subsequent integration into the food chain raises concerns regarding human health risks, as shown in figure 9. Additionally, emerging environmental and health safety concerns may impose limitations on the application of nanotechnology in crop production. The potential consequences of bioaccumulation and nanoparticle exposure on plants in the long term can have significant implications for the food chain [75-76]. Additionally, the utilization of nanofertilizers raises concerns regarding safety, food security, and ethical considerations.

To address these concerns, it is imperative to conduct comprehensive studies that aim to elucidate the effects of nanoparticles on the human body. These studies should also explore the feasibility, risk assessment, hazard identification, and suitability of utilizing smart nanofertilizers. It is imperative to comprehend the phytotoxic consequences of nanoparticles on plants, their interaction with soil, and their potential implications for human health. This knowledge is essential for the practical implementation of nanomaterials in real-world agricultural settings [76]. Some nano-coated or encapsulated based controlled-released fertilizer systems include polymeric nanoparticles, infiltration into porous nanomaterials, intercalation into nanoclays, and hydroxyapatite nanoparticles.

5. Effects of CRFs on Plants and Soil

Soil is crucial for effective agriculture as it provides nutrients for crop growth, water, plant nutrients, and structural support. The interrelationship between soil and plant nutrients is vital. Table 4 presents the application of CRFs to various test crops and the corresponding outcomes [11]. However, fertilizer loss from soil can impact soil fertility [77], leading to lower NUE. Formulating natural fertilizers can enhance soil fertility and support sustainable farming practices [78-83]. CRFs release nutrients [40], matching plant demand and ensuring the longevity of soil fertility. Research shows that CRFs can reduce nitrogen losses by decreasing ammonia volatilization, emissions, and runoff. They maintain balanced soil nutrient concentrations and promote microbial activity for chemical/biological processes. However, CRFs release nutrients through physical processes, reducing soil nutrient loss and increasing nitrogen use efficiency (NUE) through proper plant uptake. Further studies are needed to fully understand their impact on soil [84].

6. Advantages

Utilizing controlled-release fertilizer in the production of bedding plants and other agricultural commodities has numerous benefits. It offers improved mineral nutrition for up to 18 months with a single application. Its consistent nutrient supply reduces leaching and enhances fertilizer use efficiency. In pot experiments, biochar-coated urea increased nutrient use efficiency (NUE) up to 20% [85]. In rice cultivation, controlled-release nitrogen fertilizer (CRNF) improved nutrient use efficiency up to 43.96% [86]. A mixture of polymer-coated urea CRF and urea fertilizer increased NUE up to 26.6% [87]. CRFs play a crucial role in nutrient loading capacity, ensuring optimal nutrient storage and utilization. The polymers employed in CRF walls exhibit valuable characteristics that contribute to efficient nutrient loading.

Crop quality is linked to crop productivity through controlled-release fertilizer (CRF) treatments. Research shows that CRF can enhance crop quality and increase productivity. For example, controlled-release urea fertilizer (CRUF) in a cotton-garlic intercropping system improved yield. Specifically, the yield of lint cotton improved by 17.3% [88]. CRUF also improved yields in rice and oilseed rape, with increases of up to 8.2% and 15.5%, respectively, over a seven-year field study [89]. Overall, CRUF treatments can significantly enhance crop quality and productivity across various crop systems. Fertilizer usage decreases, reducing plant injury risk due to highly soluble salt levels. One application can meet crop seasonal needs, reducing labor and minimizing risks like leaf burning, water contamination, and eutrophication.

7. CRF Market Analysis

Markets and Markets (one of the best consulting firms in America) analysed the future global market trend of controlled release fertilizer from 2023-2028. According to projections, the global market for controlled-release fertilisers is estimated to proliferate at a compound annual growth rate (CAGR) of 5.9%, from USD 2.2 billion by 2023 to USD 2.9 billion by 2028. The market for controlled-release fertilisers has expanded significantly and solidified its position as the industry leader in the world of agriculture [90].

Fortune Business Insights (a global buisness research company) analysed and forecast the controlled-release fertilizer global market for 2019-2026. The market for controlled-release fertilisers was valued at $2.3 billion in 2018 and is estimated to proliferate at a compound annual growth rate(CAGR) of 6.37% to reach $3.86 billion by 2026. In 2019, the North American market had a value of USD 1.09 billion [91].

8. Industry Developments

Pursell Agri-Tech, a U.S.-based company that creates fertilisers to boost agricultural yields, began construction on a cutting-edge production plant near Savannah, Georgia, in May 2021. It will greatly increase the Southeast's and other regions' access to its next-generation coating technology. Controlled-release fertilisers (CRF) for the turf, specialised, agricultural, and ornamental industries will be produced at the factory [91]. The fifth iteration of ICL Group's Osmocote controlled-release fertiliser was released in September 2021. The Israel-based business develops, produces, and sells metals, fertilisers, and other specialty chemical products. Osmocote 5 features an enhanced Optimised Trace Element Availability (OTEA) system that meets the needs of plants throughout the release program, resulting in increased growth, health, and colour. This unique release technology matches nutrients to plants.

Florikan announced a significant increase in staging and short-term storage in September 2021. With these additions, Florikan will be better equipped to meet the increasing demand for its premium ranges of Gal-XeONE^{TM}, YLD^{TM}, and Nutricote® controlled-release fertiliser products [92]. ICL unveiled eqo.x, a ground-breaking, quickly biodegradable release technology intended for open-field agriculture, in September 2022, marking a major breakthrough in controlled-release urea technology. This innovative method, made possible by a specialised coating, allows farmers to maximise crop performance while also reducing environmental impact. It accomplishes these two goals by reducing nutrient loss and increasing nutrient use efficiency (NUE) by an astounding 80%. The release method helps reduce the frequency and volume of nitrogen applications while enabling the possibility of higher or equivalent yields with fewer fertiliser amounts. Moreover, it guarantees a consistent and even release of nutrients, promoting consistency and predictability in the supply of nutrients [90].

In June 2023, Yara Clean Ammonia and *Badische Anilin- und Sodafabrik* (BASF) joined forces to investigate the possibility of constructing a massive low-carbon blue ammonia production plant in the US Gulf Coast region, together with carbon capture technology. With 1.2 to 1.4 million tons of yearly capacity, the factory is expected to meet the growing demand for environmentally friendly ammonia worldwide. This collaboration aims to significantly reduce the carbon footprint of its operations by utilising its prosperous past of collaboration. A necessary component of fertilisers, especially those with controlled release, is ammonia. The clean ammonia produced by Yara, which has a smaller carbon footprint, may improve the controlled-release fertilisers' environmental standing [90].

9. Current Challenges

The following are the current obstacles in CRF research and development and commercial viability:

The release properties of CRFs depend upon various factors, including permeability, microbial decomposition, soil pH, temperature, and moisture content. Every botanical variant possesses distinct nutritional demands, absorption durations, and molecular configurations. The appropriate choice of CRF may be contingent upon these variables. Insufficient rates of release may result in nutrient deficiencies, whereas excessive rates of release may lead to plant toxicity and the forfeiture of advantageous effects [27-93-94]. The production of CRF exhibits a higher cost in comparison to that of conventional fertilizers. The application of sulfur-coated urea consistently results in a reduction of the soil's pH level. The process of acidifying soil leads to the manifestation of nutrient imbalances, specifically causing deficiencies in calcium and magnesium.

Controlled-release fertilizers might exhibit insufficiency as nutrient sources under conditions characterized by soil temperature [40]. Coating with advanced nanomaterials necessitates safer practices, equipment, and handling, and they are expensive. The economic viability of low-cost biodegradable polymer materials should be investigated. Growers struggle to understand the applicability of agrochemical products, leading to a communication gap based on geographical and meteorological factors. CRFs can decrease nitrogen loss in environments with excess water or mismanaged nitrogen, but only if nitrogen application is properly managed, such as method, timing, and rate, to minimize N losses.

CRF coatings, composed of non-biodegradable polymers such as polyurethane and polyethylene, result in the accumulation of microplastics within agricultural soil [95]. This accumulation leads to soil pollution, negatively impacting both soil microbial diversity and plant life [96]. This accumulation leads to soil pollution, negatively impacting both soil microbial diversity and plant life, as shown in figure 10 [96]. Research groups are developing biodegradable coatings and detecting microplastics in agricultural soil.

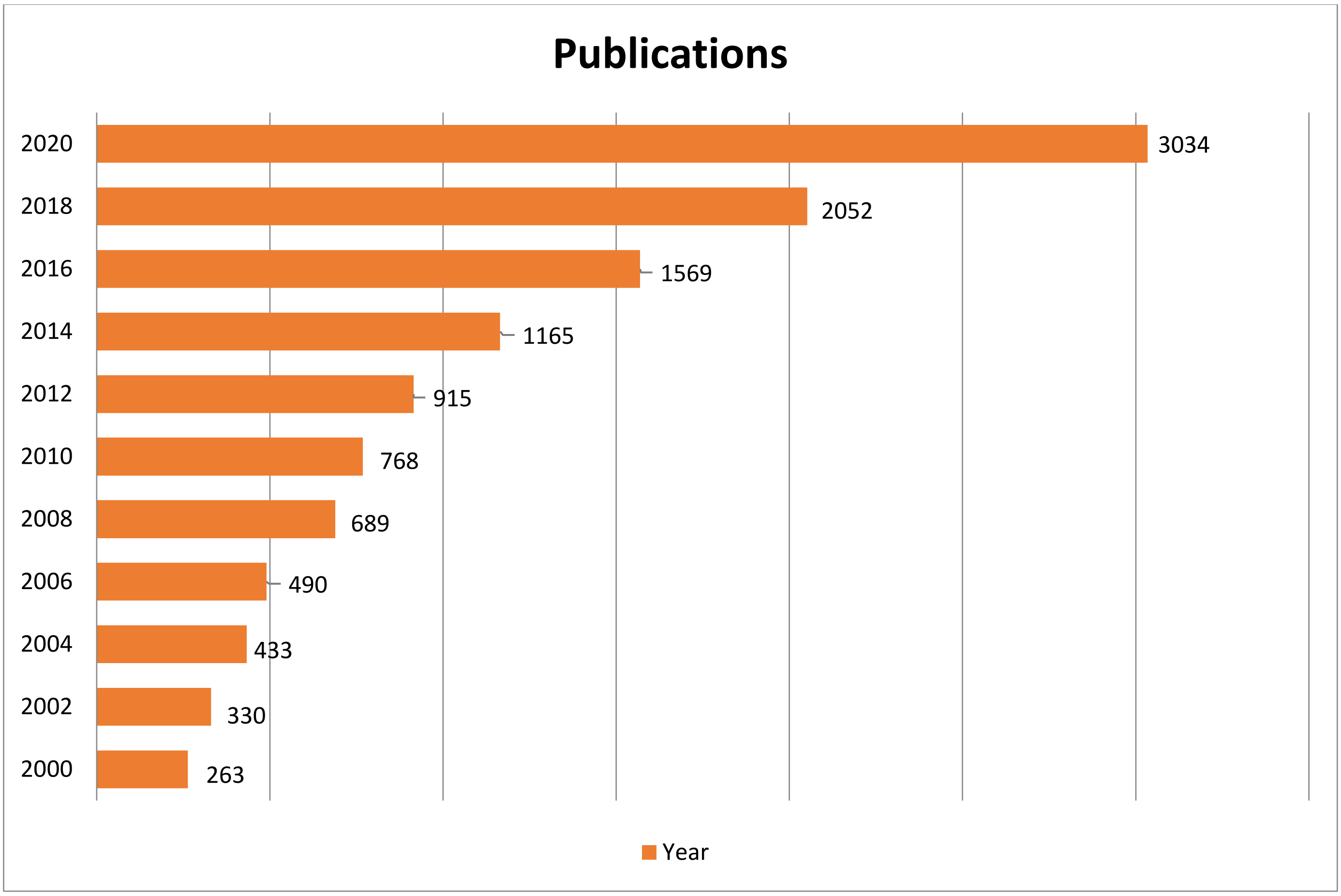

Figure 1. Number of articles published on Science Direct related to controlled release fertilizer during 2000-2020 [84].

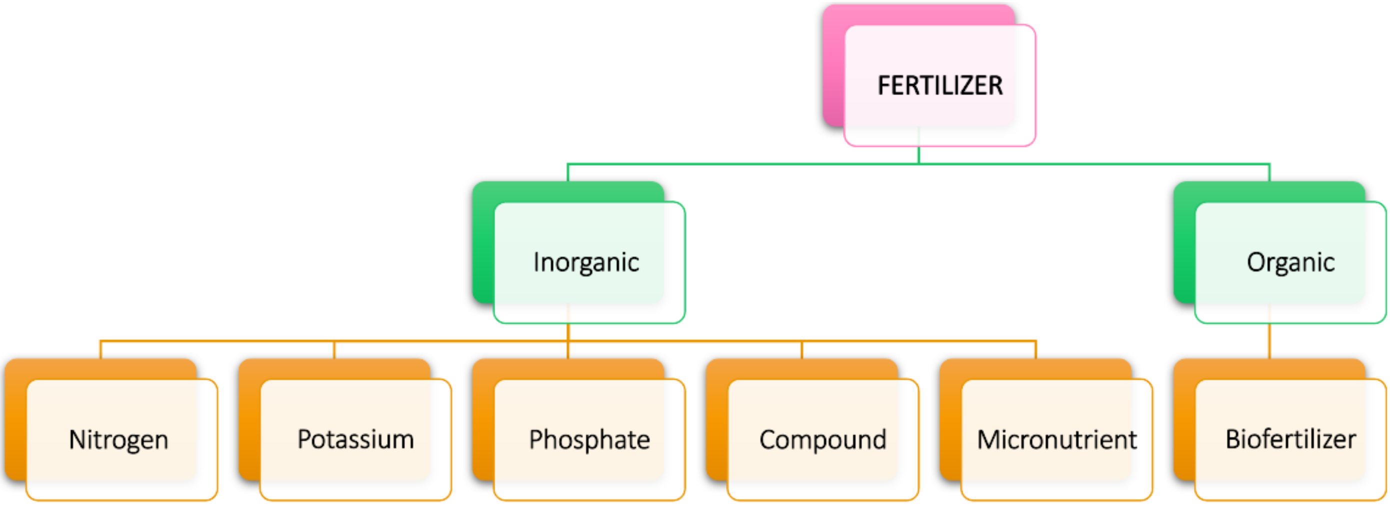

Figure 2. Classification of conventional fertilizers [18].

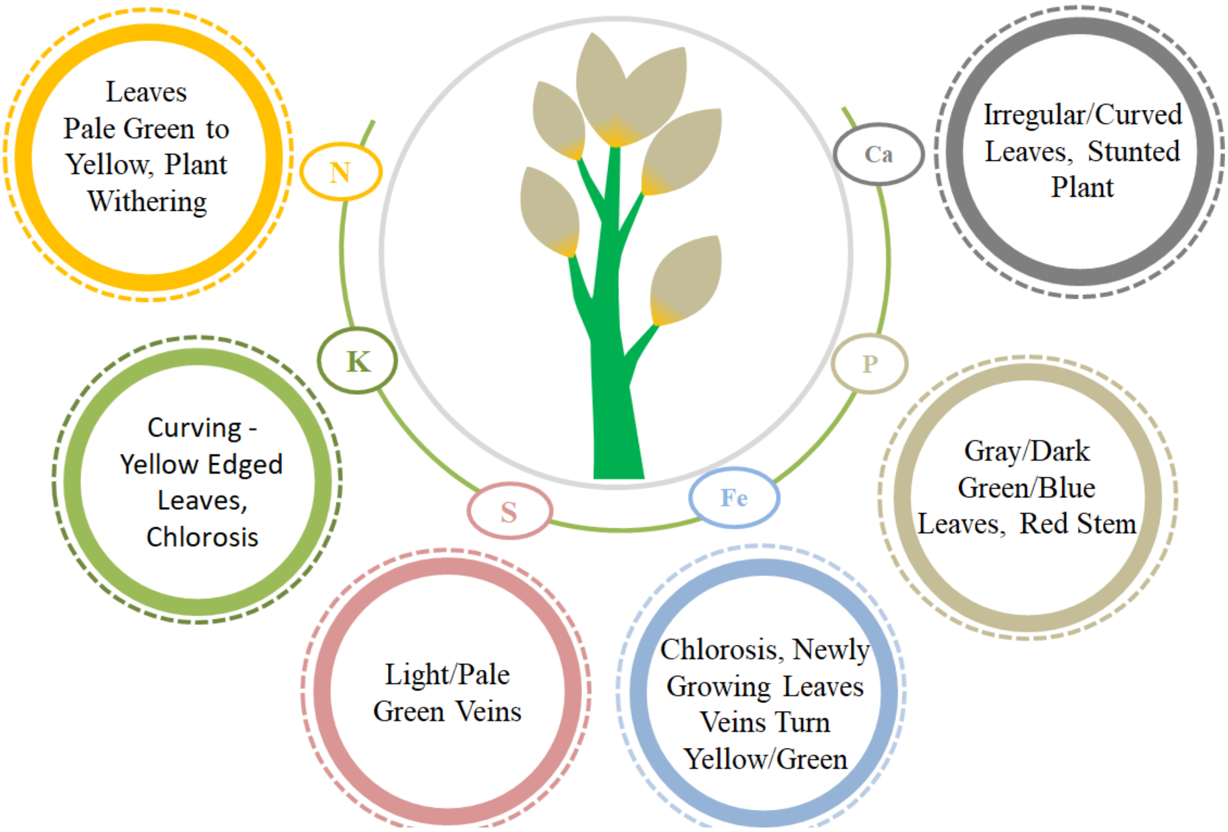

Figure 3. Critical nutrients necessary for plant development, along with the indications of nutrient deficiency symptoms [97].

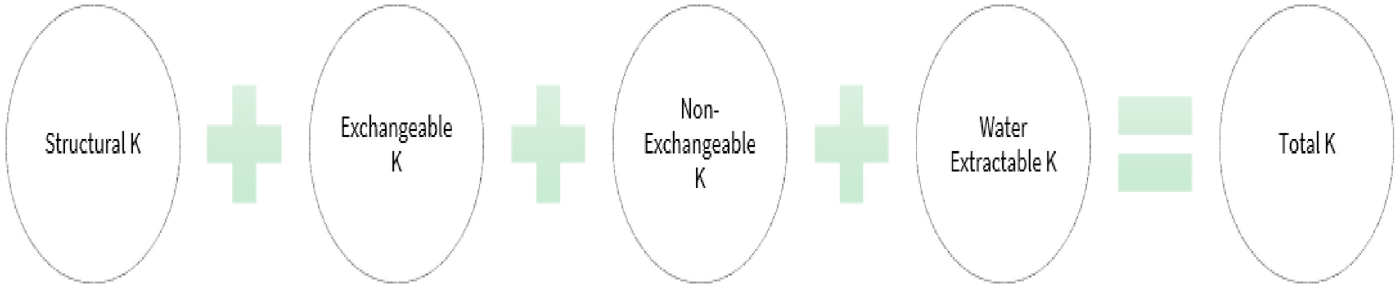

Figure 4. Different forms of soil total K

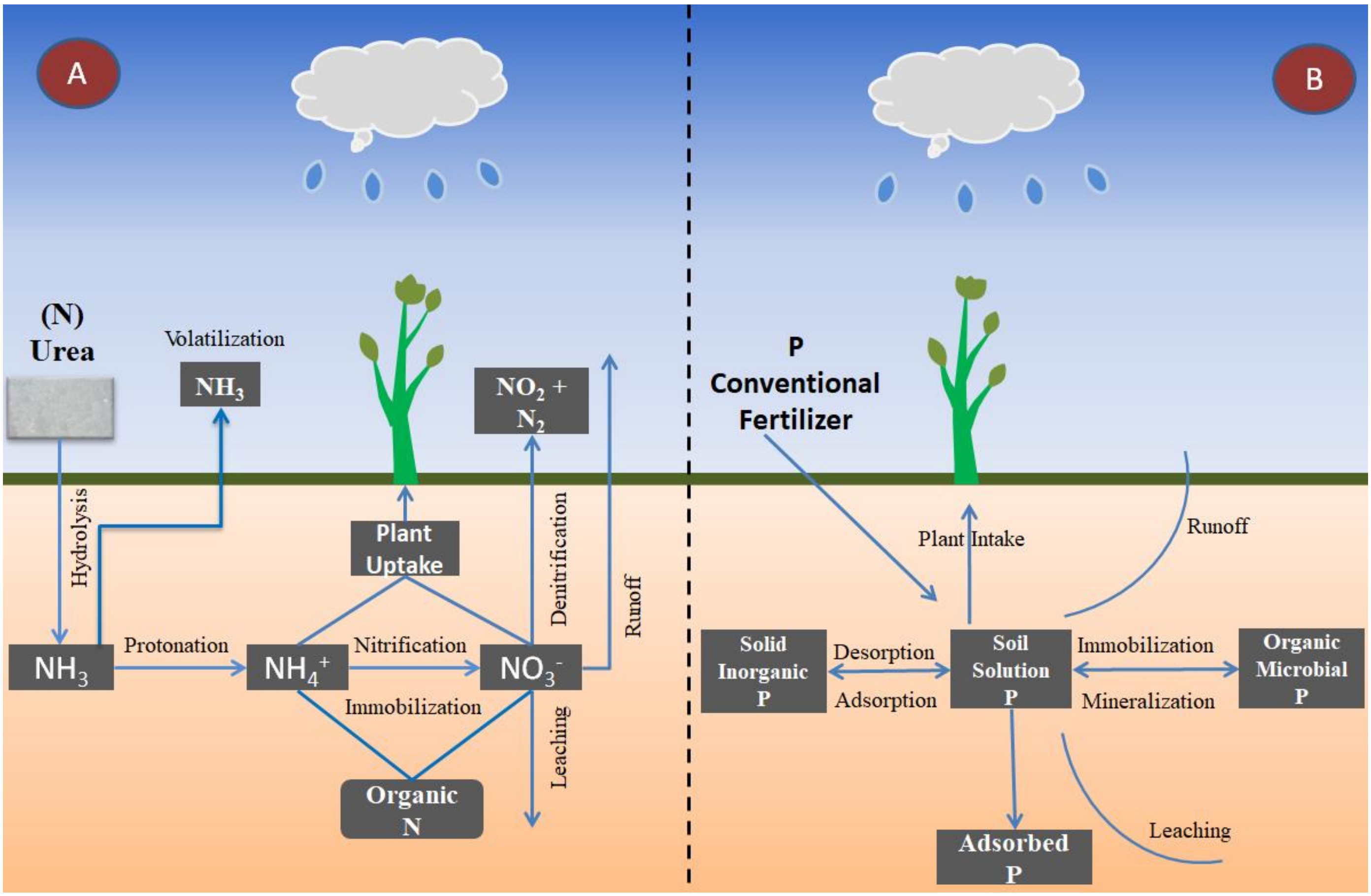

Figure 5. A simplified representation of loss of conventional fertilizers in soil [98].

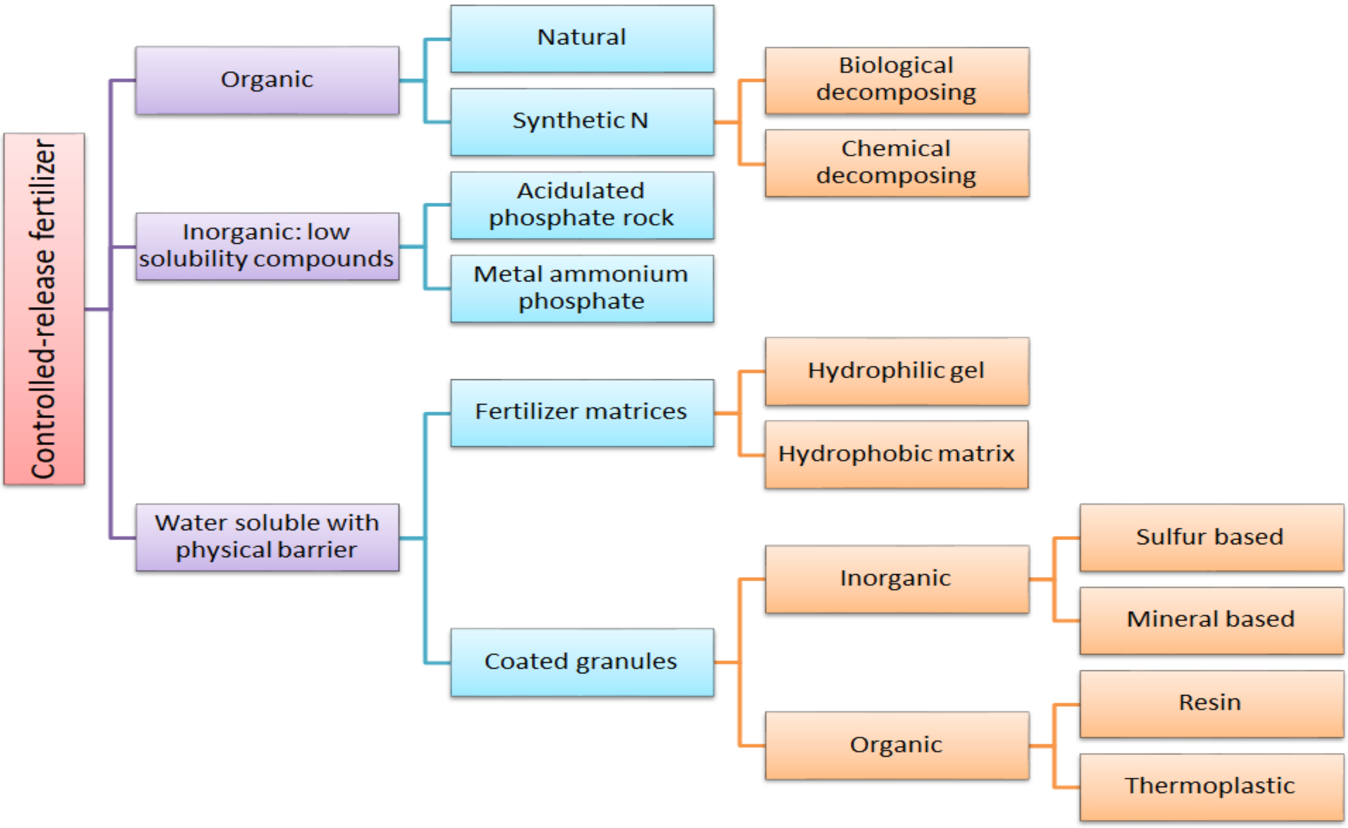

Figure 6. Categorization of controlled release fertilizers [27]

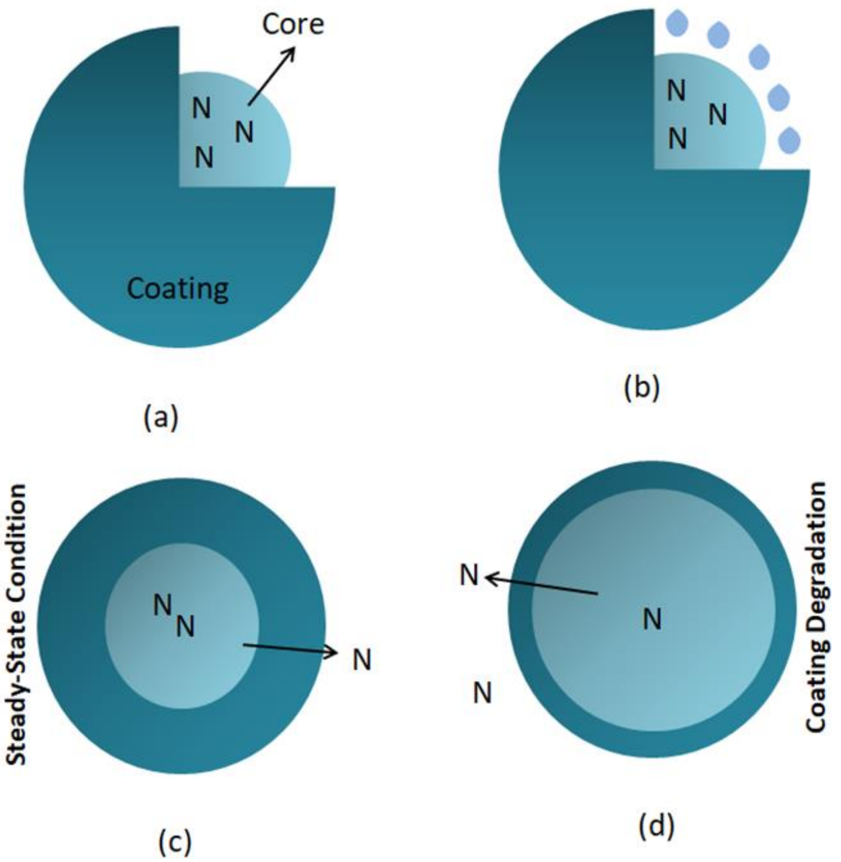

Figure 7. The process of nutrient release (N = Nutrient). (a) Fertilizer granules featuring a protective covering. (b) Infiltration of water during the lag period. (c) A state of equilibrium and maintains a consistent discharge of nutrients by the use of a pressure gradient. (d) Degradation of a coating and its corresponding decay stage [11-27-41].

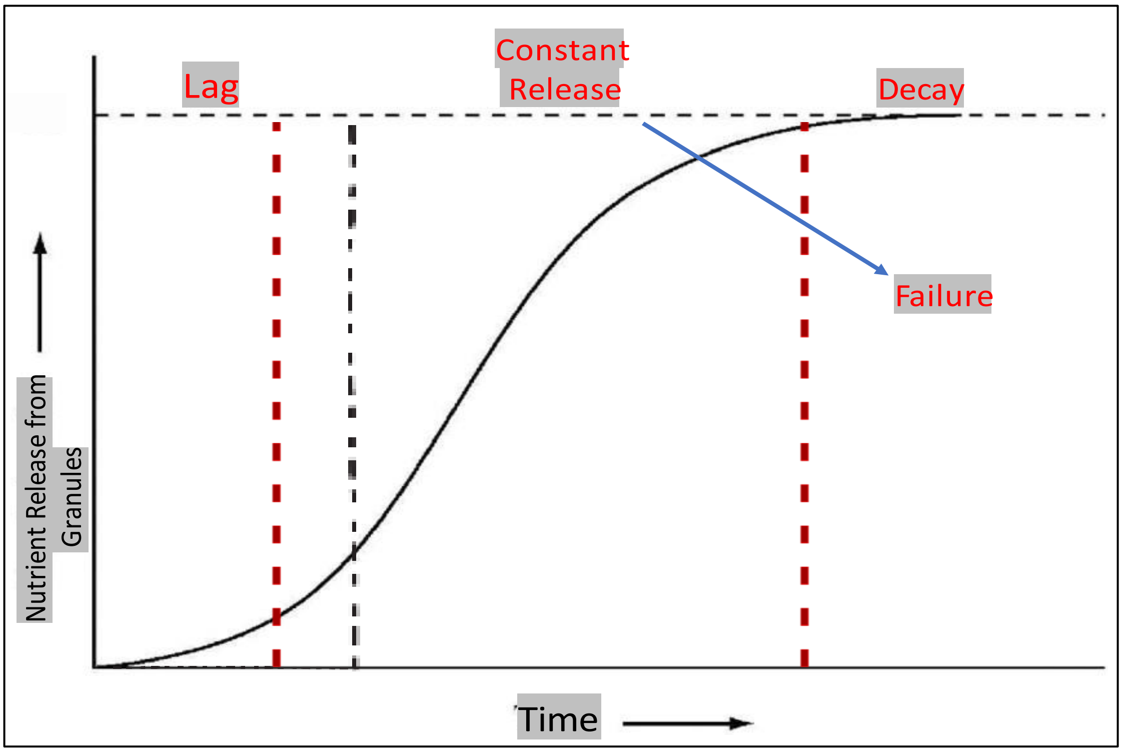

Figure 8. The release of nutrients follows a sigmoidal curve characterized by three distinct stages: the Lag, the Constant release, and the Decay phase.

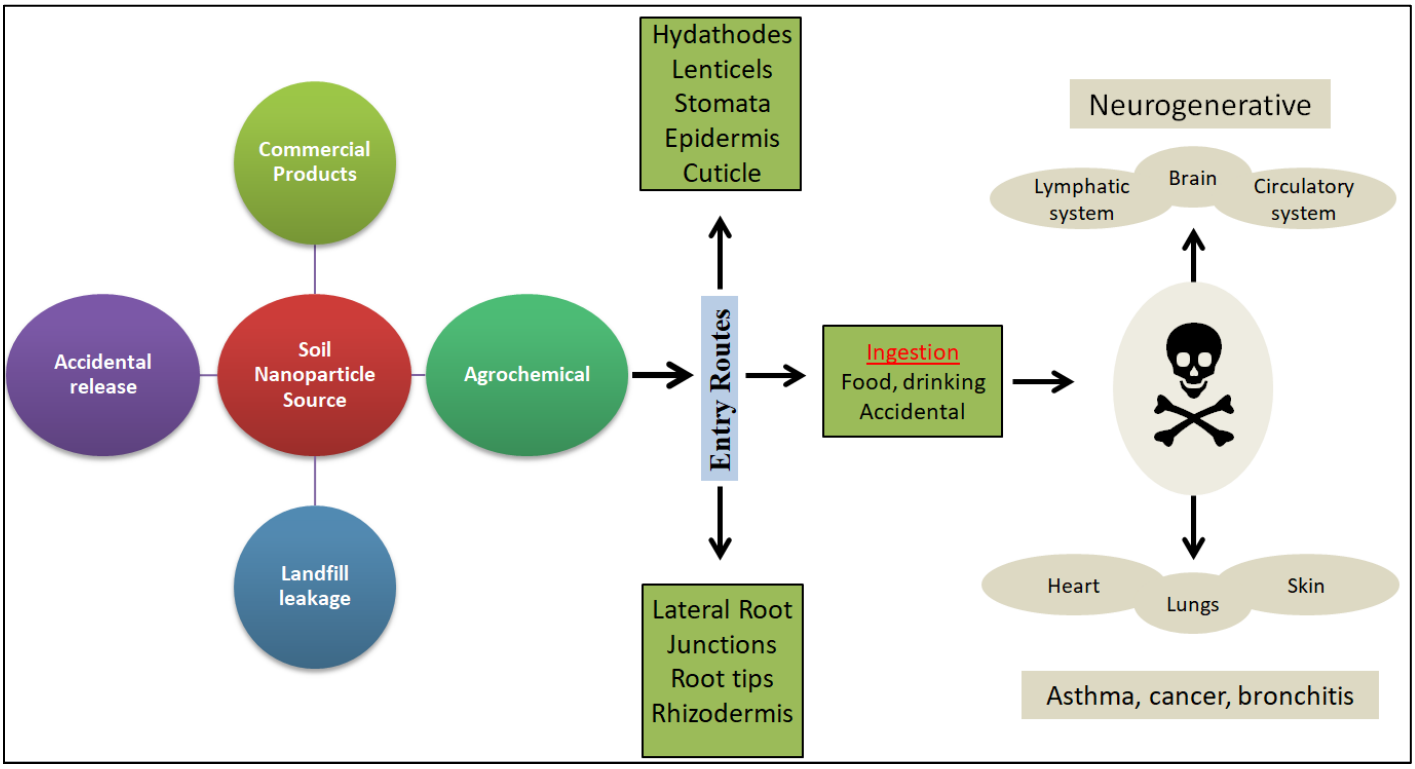

Figure 9: Contamination of soil by NPs and their impacts of human [99].

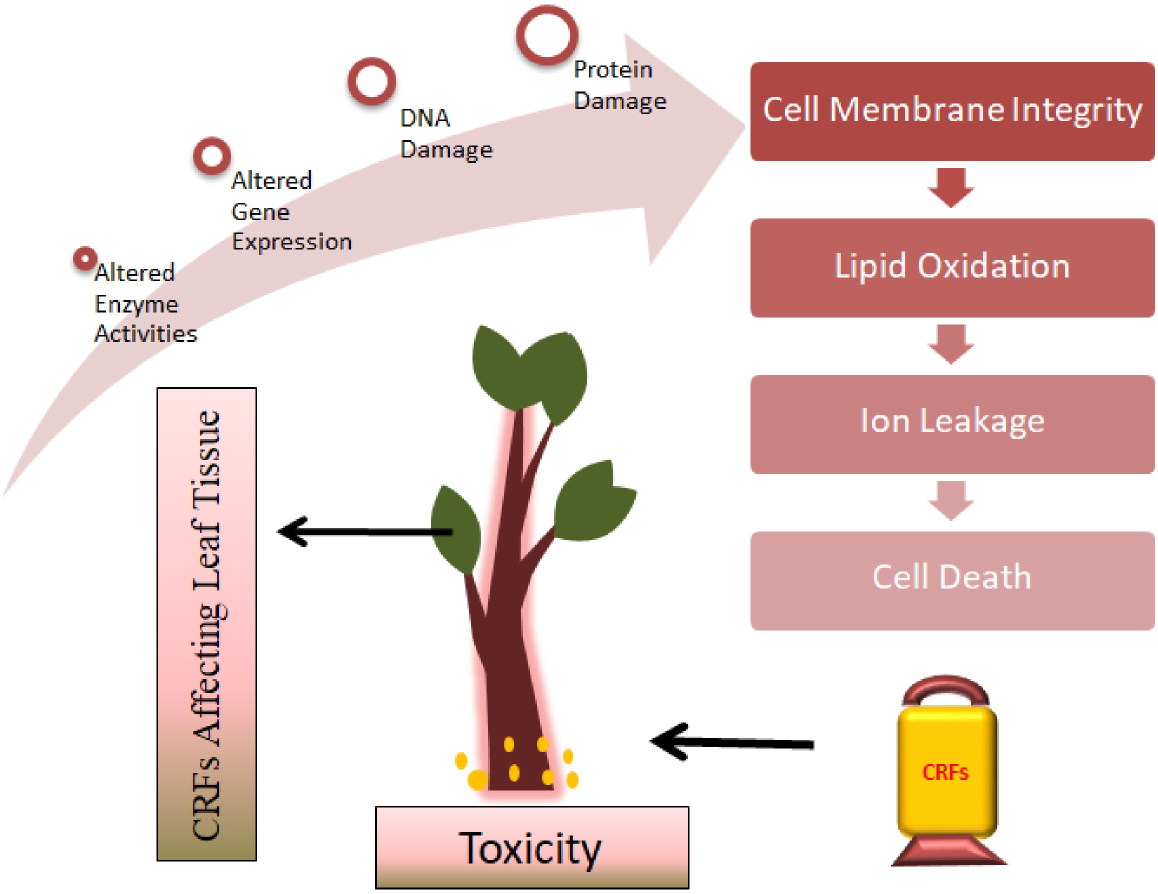

Figure 10. Accumulation of CRFs in plant causing cell toxicity.

Table 1. Plants that need primary nutrient, their deficiency symptoms and effects of excess [100].

Plant Nutrient	Plants most likely to suffer	Deficiency symptoms	Effects of excess
Nitrogen	• Farm crops (except legumes like beans, peas, and clover) • Leafy crops like grass, kale, cereals, and cabbages.	• Stunted Growth • Chlorosis • Reduced Protein Content • Reduced Flowering • Early Maturity	• Delayed Ripening • Lodging in Cereals • Lower Sugar and Starch • Susceptibility to Frost.
Potassium	• Potatoes • Carrots • Barley • Beans • Clovers • Sugar beet .	• Leaf Chlorosis • Scorching • Stunted Growth • Weak Stems • Lodging • Reduced Seed and Fruit Size.	• Delayed Ripening, • Cause magnesium deficiency.
Phosphorous	• Root crops • Lucerne • Clovers • Kale .	• Stunted Growth • Leaf Discoloration • Delayed Maturity • Poor seed and fruit development.	• Early ripening resulting in yield reduction.

Table 2. Different coatings and their characteristic findings.

Materials	Findings	Author
Sulfur	• Enhances nitrogen assimilation. • Enhances yield. • Needs an additional wax or polymer coating to ensure durability.	[101-102]
Minerals	• Enhance the soil's ability to retain water. • Improve soil’s chemical and physical properties. • Reduce fertilizer need. • Process adjustments are required to accommodate changes.	[103-105]
Agriculture residues	• Nourish plants. • Extend the irrigation cycle. • Reduce production expenses.	[106]
Synthetic polymer	• Greater soil durability. • Hydrophobic. • Resistant to water. • Reduced impact on environmental parameters.	[107]
Natural polymer	• Abundant in nature. • Inexpensive. • Biodegradable. • Cannot be utilized directly for coating application.	[108-110]

Table 3. Soil microflora role in degrading different coatings.

Polymer Coating	**Biodegradability**	**Enzyme/Bacteria/Fungi**
Polyurethane	Partially biodegradable	Enzyme: • Polyurethanase Bacteria/Fungi: • *Petalotiopsis micropora* • *Enterobacter agglomerans*
Chitosan	Complete Degradation	Enzyme: • Chitosanases Bacteria/Fungi: • *Kitasatospora* spp • *Mortierella* spp • *Streptomyces* spp
Alginate	Complete Degradation	Enzyme: • Alginate lyase Bacteria/Fungi: • *Agrobacterium tumefaciens*
Starch	Complete Degradation	Enzyme: • Amylases • Transglucosidases • Amyloglucosidases Bacteria/Fungi: • *Bacillus amyloliquefaciens*
Lignin	Complete Degradation	Enzyme: • Laccase Bacteria/Fungi: • Actinomycetes • g-Proteobacteria • a-Proteobacteria

Table 4. Application of CRFs on different test crops and their results.

Type of crop/vegetable/ornamental/ fruits	Results	Author
Rice	In a field test, it was shown that using 20% less nitrogen (N) with CRF led to the same crop output as using conventional fertilizers.	[111]
Cotton	The output of lint cotton went up by 8.1% to 32.1% and by 3.7% to 20.8% in a 2 year polymer coated KCl (CRK) pot experiment.	[112]
Geranium	When CRF was applied to potted geraniums, the amount of flowers, umbels, and plant height were all high.	[113]
Phalaenopsis	Using CRF helped the growth of flowers, leaves, and the number and length of leaves.	[114]
Peach	Field experiments for three consecutive years showed that BCRF (bag-controlled release fertilizer) improved yield by 21.35% when compared to spreading fertilizer.	[115]
Banana	A controlled-release fertilizer at 75% or 50% of the conventional fertilizer dose yielded the same fruit yield. CRF made the soil less acidic and maintained suitable P and K concentrations for banana cultivation, regardless of split applications.	[116]
Apples	When CRF was used on apple trees, plant height, trunk diameter, chlorophyll content, and output all went up by 8.82%.	[117]
Maize	Fertilization enhanced nitrate content in crops, increasing maize grain yield and protein. Combining coating and nitrification inhibitors improved nutrient release for maize growth.	[118]
Orange	When compared to the usual method (fertigation), the CRF treatment caused the fruit girth, yield, and weight to go up by 0.13%, 1.48%, and 0.84%, respectively.	[119]

10. Conclusions:

Crop production depends on the effective use and distribution of nutrients, since overuse of these resources can harm the environment. The use of conventional fertilizers results in nutrient leaching, overfertilization, and financial waste. Thanks to technological improvements, controlled-release fertilizers, or CRFs, have become more and more prevalent in modern agriculture. It is crucial for global CRFs manufacturers and scientists to place a strong emphasis on sustainability and environmental responsibility. This involves meticulously selecting materials that are both efficient and cost-effective while still maintaining the high quality of CRFs production. With the development of nano-enabled controlled-release fertilizers, which increase crop yields and economic value while preserving environmental compatibility, nanotechnology has completely changed the composition of fertilizers. Further research is necessary to fully comprehend the effects of CRFs on crop quality, environmental compatibility, productivity, and non-targeted organisms to gain valuable insights for the future.

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