Italian Journal of Agronomy 2021; volume 16:1794

Smart fertilizers: What should we mean and where should we go?

Giorgia Raimondi, Carmelo Maucieri, Arianna Toffanin, Giancarlo Renella, Maurizio Borin

Department of Agronomy, Food, Natural Resources, Animals and Environment (DAFNAE), University of Padua, Agripolis Campus, Legnaro (PD), Italy

Highlights

- *A smart fertilizer allows to control the rate, timing and duration of nutrients release.*
- *Nanofertilizers are powder or liquid formulations which involve the synthesis, design and use of materials at the nanoscale level.*
- *Composite fertilizers are formulations containing nutrients mixed or coated with one or more materials that exploit synergy among materials.*
- *Bioformulations are fertilizers containing active or dormant microorganisms capable to trigger physiological growth responses in plants.*
- *Limited information is available for smart fertilizers on herbaceous crops in open field conditions.*

Abstract

The current agricultural system faces several challenges, the most important being the ability to feed the increasing world population and mitigate climate change. In this context, the improvement of fertilizers' agronomic efficiency while reducing their cost and environmental impact is one of the biggest tasks. Available literature shows that many efforts have been made to develop innovative fertilizers defined as 'smart fertilizers', for which, different interpretations and definitions have been used. This paper aims to define, classify, and describe the new frontier of the so-called *smart fertilizers* with a particular focus on field-scale studies on herbaceous species. Most of the analysed papers associate the 'smart' concept to the controlled and/or slow release of nutrients, using both terms as synonymous. Some others broadened the concept, including the controlled release of nutrients to reduce the environmental impact. Based on our critical analysis of the available literature, we conclude that a fertilizer can be considered 'smart' when *applied to the soil, it allows control over the rate, timing, and duration of nutrients release.* Our new definition is: '*Smart fertilizer is any single or composed (sub)nanomaterial, multi-component, and/or bioformulation containing one or more nutrients that, through physical, chemical, and/or biological processes, can adapt the timing of nutrient release to the plant nutrient demand, enhancing the agronomic yields and reducing the environmental impact at sustainable costs when compared to conventional fertilizers*'.

Correspondence: Carmelo Maucieri, Department of Agronomy, Food, Natural Resources, Animals and Environment (DAFNAE), University of Padua, Agripolis Campus, Viale dell'Università 16, Legnaro (PD), Italy.
E-mail: carmelo.maucieri@unipd.it

Key words: Smart fertilizer; nanofertilizers; composite materials; bioformulation; slow-release fertilizers; control release fertilizers; fertilizers bioactivation.

See online Appendix for additional materials.

Received for publication: 23 December 2020.
Revision received: 17 February 2021.
Accepted for publication: 19 February 2021.

Italian Journal of Agronomy 2021; 16:1794
doi:10.4081/ija.2021.1794

Introduction

The current agricultural system is facing several challenges, the most important being: i) feeding the increasing world population (Godfray *et al*., 2010); and ii) mitigate climate change (Metz *et al*., 2007). Current population is 7.8 billion, and in the next 30 years increase will be 2.2 billion based on prediction of 10 billion in 2050 to feed in the framework of soil degradation (Gomiero, 2016) and food-energy-environment trilemma of land use (Tilman *et al*., 2009). Therefore, food production is unlikely to be increased using new land nor increasing nutrients input since plants have a critical uptake limit (Lemaire and Ciampitti, 2020).

Nevertheless, agriculture is a non-point source of pollution for surface and groundwater in the watershed and contributes to greenhouse gas (GHG) emissions, especially N_2O. This gas represents 60% of the total human-made N_2O emissions (Reay *et al*., 2012), and a considerable share is due to fertilization. Concurrently, projections prospect a shortage of nutrients availability that could harm food security (Cordell and White, 2014). This is mainly the case of phosphorous (P), even if the reasons are primarily economic and political than physical (Pahl-Wostl, 2009).

In this scenario, agriculture is required to increase yield per unit and optimize resources (Premanandh, 2011). Fertilization has a basic role in crop production and notably affects its environmental impact, particularly soil nitrogen (N) dynamics. Urea is the most common source of N; however, it has a major limitation: it easily overcomes transformation processes that harm the environment as particulate matter formation (through further reactions of ammonia (NH_3) released into the atmosphere) and contamination of groundwater (through NO_3 leaching after nitrification) (Erisman and Schaap, 2004). Thompson (2012) reported that N use efficiency (NUE) is among the most critical research issues. Alongside N, the overall crop nutrition should be improved.

In this context, a wide range of new fertilizers is being developed to adjust nutrients release to plant requirements and increase nutrients efficiency. This review includes field-scale studies on herbaceous species of new types of fertilizers and aims to define, classify, and describe the new frontier of the generally called *smart fertilizers*.

Materials and methods

Review procedure

Several authors associated the 'smart fertilizers' definition to the broad concept of innovative products improving nutrient management and nutrient use efficiency in the agro-ecosystem. Consequently, the rationale to develop the current review is based on two questions: i) What should we mean by 'smart fertilizer'? ii) What is the current direction of the research, and what it should be (*i.e.*, where should we go)?

The Scopus database was used to investigate the scientific literature through a series of searches refined by journal and source type, year, language, subject area, and specific keywords. Peer-reviewed studies were considered based on a three-step procedure: i) identification; ii) screening system; and iii) inclusion of only those publications relevant for the purpose of the present paper. The three phases are here described.

Identification

Scopus database was chosen due to the high number of scientific journals indexed, keywords searching, citation analysis, and its accessibility and popularity in systematic reviews. A *first identification* was performed using the expression 'smart fertilizers' with the search string TITLE-ABS-KEY ('smart fertilizer*') on 19 September 2020. This search retrieved 20 papers (Figure 1A), of which 13 related to agriculture. The analysis of these 13 articles demonstrates that the 'smart fertilizer' expression, even though it is not widespread in the scientific community, has been attributed to different categories of fertilizers (*e.g.*, nanofertilizer, composite material, bioformulation) and their operational mechanisms (slow/control release, bioactivation, carrier/delivery system). Afterward, a *second identification* was performed, and the name of different types of fertilizers and the names of different operational mechanisms were used to run a second search in Scopus (Figure 1B). The choice of each category's specific names was based on the keywords suggested by Scopus tool 'Refine results' and supported by a previous classification of the types and operational mechanisms of Calabi-Floody *et al.* (2018). Specifically, the second research in Scopus was carried out using the following strings on 20 September 2020: i) TITLE-ABS-KEY ('fertilizer* 'AND

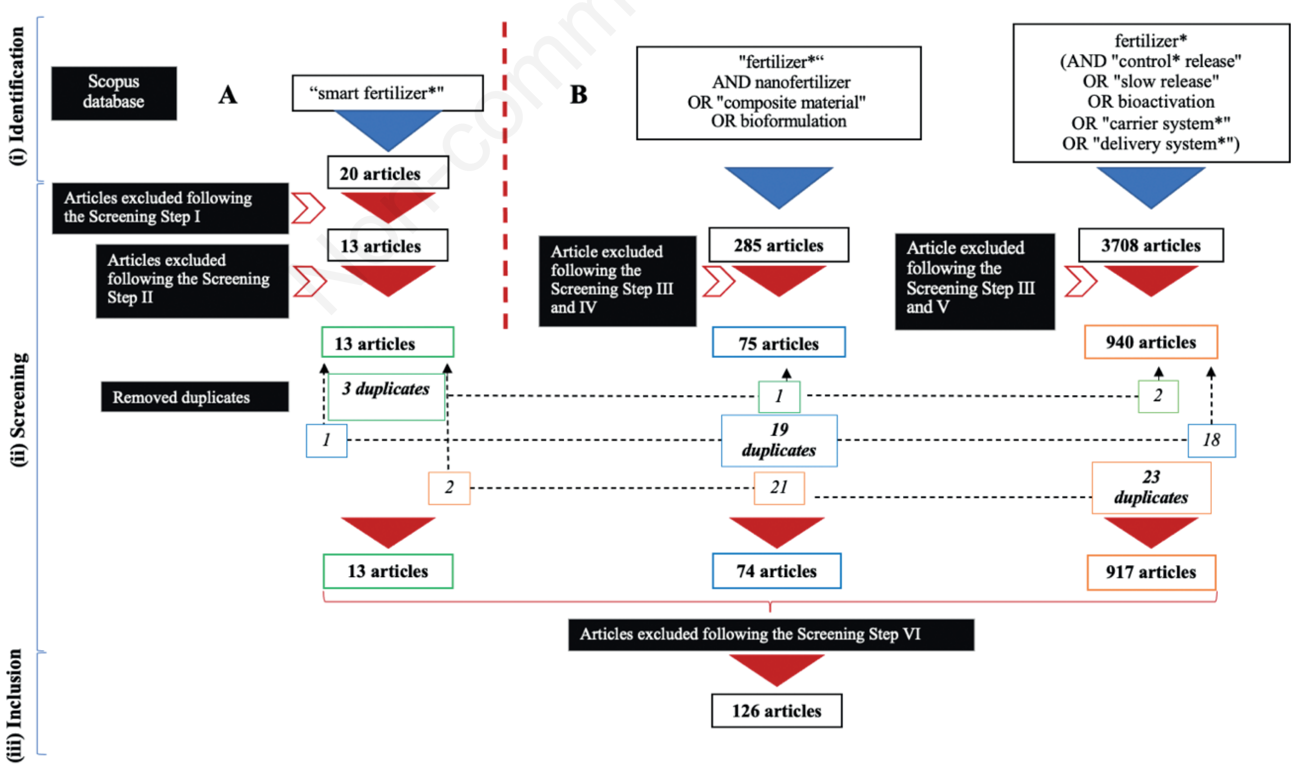

Figure 1. Research scheme. First identification (A); second identification (B).

nanofertilizer OR 'composite material' OR bioformulation), 285 results; ii) TITLE-ABS-KEY ('fertilizer*' AND 'control* release' OR 'slow release' OR bioactivation OR 'carrier system*' OR 'delivery system*'), 3708 results.

Screening

As reported in Table 1, six screening criteria were adopted to narrow down results to only articles relevant to this review. The objective was to select articles concerning fertilizers included in the categories above only when compared to conventional fertilizers and tested on herbaceous species in field experiments.

Different screening steps were applied for the identification process. The first identification process aimed to perform a broad-spectrum search to read up on the state-of-the-art of the smart fertilization concept. For this reason, no filters were applied and all the results were sorted through, except for those articles off-topic. Starting from the 20 articles, 7 un-related papers were discarded, and the 13 remaining were included for subsequent analyses. The second identification was performed to investigate more specifically on different types and operational mechanisms of non-conventional fertilizers. Different filters were applied to narrow down the results at this stage, and starting from 285 and 3708 articles, only 74 and 917 (duplicates excluded) remained for the fertilizer's types and operational mechanisms categories, respectively. The last screening step was applied to all the articles selected up to that point, and it was used to select only those research studies with field trials of herbaceous species (VI step) of non-conventional fertilizers. 126 articles were finally retained.

Inclusion

The final 126 articles selected through the screening phase were those critically analysed in this review. All these articles reported field experiments conducted on herbaceous crops to test the efficacy of new types of fertilizer compared with conventional fertilizers. Despite many articles dealt with the topic of new fertilizers technologies, few studies presented tests conducted in real farming conditions. However, field experiences are crucial to determine the real effect of fertilization management and, therefore, the efficacy of a new fertilizer type. Field trials, indeed, while retaining some characteristics of the lab trials (such as the control groups and the experimental methods), take into consideration the environmental variability of the actual farming conditions and make the experiment more representative (Henke, 2000).

Furthermore, the experimental unit size was also included among the selection criteria, as it was considered as an important indicator that reflects the level of spatial variability due to a larger occupied area (Hoefler *et al*., 2020). For this reason, only 126 articles were considered, excluding those using lysimeters and those that did not specify the size of the experimental plot. This review aimed to revise only fertilization technologies whose efficacy was effectively tested in real agro-ecosystems and considered the relationship with all the other agro-environmental variables.

Table 1. Screening steps and criteria for each identification stage.

Steps	Screening criteria
(A) First identification	
I	- *Source type*: Journal, Book, Conference proceeding - *Document type*: Articles, Conference paper, Book Chapter - *Language*: English - *Subject area*: Agriculture and Biological sciences; Environmental science, Chemistry, Materials science, Chemical Engineering
II	*Exact words* in the Title, Abstract, Keywords: - Smart fertilizer/s
(B) Second identification	
III	- *Source type*: Journal - *Document* type: Articles - *Language*: English - *Subject area*: Agriculture and Biological sciences; Environmental science
IV	*Exact words* in the Title, Abstract, Keywords: - Fertilizer/s - Nanofertilizer/s - Nanoparticle/s - Nanomaterial/s - Composite material/s - Bioformulation
V	*Exact words* in the Title, Abstract, Keywords: - Fertilizer/s - Control release fertilizer/s - Slow release fertilizer/s - Bioactivation - Carrier system
Common to first and second identifications	
VI	*Field trials* - Included only articles with field trials *Herbaceous species* - Included only articles testing herbaceous species

Smart fertilizers classification

The analysis of the 13 articles found using the keyword 'smart fertilizer' revealed different interpretations and definitions of the 'smart fertilizer' concept. The majority of the papers associated the 'smart' concept with the controlled and/or slow release of nutrients. Some papers attributed the adjective 'smart' to fertilizers able to release their nutrients over a longer period compared to the conventional ones (Giroto *et al*., 2015; Bernardo *et al*., 2018); some others broadened the concept pointing out the ability related to the controlled release of nutrients (Pulat and Yoltay, 2016), or reducing the environmental impact (Bi *et al*., 2020). This is the case of Lü *et al.* (2016), which introduced the concept of a 'multifunctional environmental smart fertilizer' able to decrease the environmental pollution, both reducing the fertilizers' loss and retaining a large amount of water after fertilization. The same authors demonstrated that the addition of specific substances (superabsorbent polymers, *e.g*., L-aspartic acid) improved the fertilizer degradability and soil moisture-retention capacity. Souza *et al.* (2017) reported that biodegradable polymers (*e.g*., chitosan-clay hybrid microspheres) could control the release of N without leaving residues. Giroto *et al.* (2018) proposed in their study a partially polymerized urea-formaldehyde granule where the unreacted urea fraction operates as a fast-release nutrient source while the polymerized fraction acts in longer times. This smart fertilizer was used to significantly reduce the N losses and store the excess of this element for future use by plants. Feng *et al.* (2015) gave another interpretation of 'smart fertilization' as a controlled release mechanism. In their study, the structure and the morphology of the fertilizer were modified using polymer brushes to adapt the nutrient release according to different environmental conditions (mostly soil pH and temperature). Some papers associated the expression 'smart fertilizer' to specific products exploiting nanotechnologies (Calabi-Floody *et al*., 2018; Taimooz *et al*., 2018; Jahangirian *et al*., 2020). Another category of fertilizers using the 'smart' adjective is biofertilizers. Calabi-Floody *et al.* (2019) reported these fertilizers' ability to control the release of the nutrients by integrating microorganisms in the composition of the fertilizer. Mijwel and Jassim (2018) reported the ability of bioactive 'smart' fertilizers to enhance chlorophyll content in potato leaves.

Browsing through the 13 articles found in the first identification process, a first classification of the main categories interpreted as 'smart fertilizer' can be attempted, dividing the fertilizers according to different operational mechanisms and composition. In addition, Calabi-Floody *et al.* (2018), resuming all the new fertilization technologies for food security and environmental health, described some 'smart fertilizers' as composite materials and classified others according to their carrier or delivery system. Based on the above-reported information, a first classification of the smart fertilizers was proposed (Table 2).

Types of new fertilizers

As aforementioned, types of smart fertilizers can be classified as: i) nanofertilizers; ii) composite materials; and iii) bioformulations. In this section, we define each category and assess its impacts. Furthermore, the 126 articles (selected as described in paragraph 2.1.3) are classified and used to critically analyse the available data of open field studies conducted on herbaceous crops within each category: 9 tested nanofertilizers, 113 used composite materials, and 4 included bioformulations. For each category, the main nutrients supplied through innovative fertilizers are shown in Figure 2.

Nanofertilizers

Description

Nanofertilizers are powder or liquid formulations that involve the synthesis, design, and use of materials at the nanoscale level. Although nanoscale particles range from 1 to 100 nm, nanoclay and micronutrient nanoparticles (up to 200 nm and 500 nm, respectively) have been tested (Sarkar *et al*., 2014; Wang *et al*., 2012). They can be produced through physical (top-down approach), chemical (bottom-up approach), or biological (green synthesis) methods (Dimkpa and Bindraban, 2017). Most nanofertilizers are synthesized by a bottom-up approach, which begins at the atomic or molecular scale to build up nanoparticles by chemical reactions, requiring sophisticated instruments (Zulfiqar *et al*., 2019; Pohshna *et al*., 2020). The top-down approach is an alternative method for large-scale and low-cost production (Pohshna *et al*., 2020), based on reducing the bulk materials size to the nanoscale. This approach's limitations are the low control of the size of nanoparticles and the greater quantity of impurities compared to other methods (Zulfiqar *et al*., 2019). The biological method, also known as 'green synthesis', can produce nanofer-

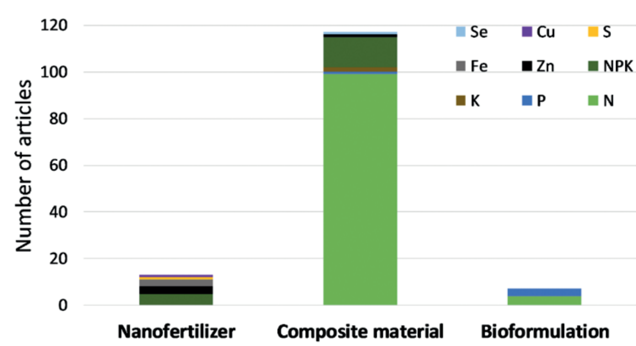

Figure 2. Nutrients composition of fertilization types reported in the selected 126 studies conducted in open field conditions on herbaceous crops (Some articles studied more than one element).

Table 2. First classification of smart fertilizers. Each type of smart fertilizer can have one or more operational mechanisms and it can be made of single or multiple nutrients.

Number of nutrients	Smart fertilizers Types	Operational mechanisms
Single nutrient	Nanofertilizers	Controlled release
Multiple nutrient	Composite materials	Bioactivation
	Bioformulation	

tilizers from various sources such as plants, fungi, bacteria, algae, and yeasts (Prasad *et al*., 2016) with greater control of the toxicity and lower waste production (León-Silva *et al*., 2018). However, in the future, the use of nanofertilizers on a large scale will require a synthesis approach capable of producing vast amounts of them with controlled physicochemical properties at low cost (Raliya *et al*., 2017). The chemical production method is the one that better reflects these characteristics (Zulfiqar *et al*., 2019). Nanoscale nutrients give more advantages compared to conventional fertilizers. They have a high surface-to-volume ratio that enables higher bioavailability resulting in a faster plant nutrient uptake, and a higher nutrient use efficiency (Liu and Lal, 2015; Chhipa, 2017; Kalia *et al*., 2019). Besides the particle size, the performance of nanofertilizers depends on their chemical structure, surface coating, rate, and doses of application (Kah, 2018; Al-Antary *et al*., 2020). Nanotechnologies, manipulating matter at the nanoscale, can exploit these materials' physical, chemical and biological properties that differ from individual atoms, molecules, and bulk matter. Indeed nanomaterials, thanks to their size, can improve the nutrient release dynamics and enhance the plant uptake efficiency (DeRosa *et al*., 2010), leading to: i) increase yield for many crops (Liu and Lal, 2015; Dewdar *et al*., 2018; Abdelsalam *et al*., 2019; Kandil *et al*., 2020); ii) reduction of nutrients losses to the environment (Bley *et al*., 2017); iii) improvement of products nutritional quality and shelf-life (Kalia *et al*., 2019).

As summarized by Mastronardi *et al.* (2015), nanofertilizers can be classified into three main categories:

- *nanoscale fertilizers* - fertilizers that are reduced in size using physical, chemical, or biochemical methods. This category includes particles prepared from urea, ammonium salts, peat, and other traditional fertilizers, and it is usually stated that one of the advantages compared to the conventional fertilizers is the better nutrient efficacy with a lower amount required (Kah, 2018);
- *nanoscale additives* - added to bulk products as supplement materials for secondary reasons. Indeed, they also have a higher water retention capacity compared to conventional fertilizers (Zhang *et al*., 2006; Scott and Chen, 2013) and include nanoscale additives to provide plant pest resistance or antimicrobial properties (Xie *et al*., 2012);
- *nanoscale coating or host materials* - nano-coating materials (zeolites, other clays, and thin polymer) usually used to control the release of the nutrients input or as supportive filling agents to form nanocomposite structures, improving the thermal stability and mechanical properties of bulk material. The common clays used to prepare composite fertilizers are: zeolite, hectorite, laponite, montmorillonite, sapiolite, rectorite, vermiculite, kaolinite, saponite, chlorine, and vermiculate (Nisar *et al*., 2017). Clays are usually modified as pillared layered clays, organoclays, nanocomposites, acid and salt-induced, and thermally and mechanically induced modified clays to adapt their charge and surface properties for specific purposes (Nisar *et al*., 2017). Nutrients are encapsulated by nanoscale films or held into nanopores or spaces within a host material. One of the advantages of this fertilizer type is the strong adsorption of the mineral nutrient within the clays, which can attenuate losses through leaching and allow the slow release of the fertilizer. Zeolites alone or with nanoparticles have been loaded with plant nutrients and found to increase fertilizer use efficiency (Guo *et al*., 2011; Vempati *et al*., 2011).

Impacts assessment

Although these nanofertilizers have demonstrated many advantages in terms of crop nutrition, some studies have been conducted about the side effects and disadvantages related to their application in agriculture. It has been found that the use of some nanoparticles can have negative effects on seed germination, roots elongation, crop growth, translocation, and accumulation of nutrients in plant tissues as well as water transport and transpiration (Mastronardi *et al*., 2015). Some studies were also conducted on the ecotoxicology of nanofertilizers and nanomaterials towards soil microorganisms, demonstrating these fertilizers' ability to impact the microbial communities (Nogueira *et al*., 2012). All these studies demonstrated that the agro-environmental conditions, the specific crop on which the nanofertilizers were tested, and the application doses are crucial in determining their benefits and possible adverse effects. An example is a study conducted by Lin and Xing (2007), where five nanofertilizers tested on six different crops resulted in opposite effects among crops. Nanofertilizers could negatively impact human health due to their size that, as reviewed by Kalia *et al.* (2019) and Surendhiran *et al.* (2020), enables them to enter the human body through inhalation (Geiser *et al*., 2017), ingestion through contaminated drinking water and agricultural produce that have accumulated nanomaterials or dermal absorption (Crosera *et al*., 2009) causing toxicity (Bahadar *et al*., 2016; Dankers *et al*., 2018).

Nanofertilizers in open field experiments

Most nanofertilizers have been produced in research and development divisions, but then almost only tested in laboratories, greenhouses, or small field plots as a pilot (Dimkpa and Bindraban, 2017; Marchiol, 2019). Indeed, only 9 papers among the 126 considered in this review presented field trials with nanofertilizers (Table 3),

Table 3. Studies with nanofertilizers tested in open field conditions.

Category*	Crop	Element delivered	Studied effect	Reference
I	*Ocimum basilicum* L.	Zn	Yield	El-Kereti *et al.*, 2013
I	*Allium cepa* L.	Zn, Cu, Fe	Crop growth and effect on the pathogenic fungus *Pythium aphanidermatum*	Taimooz, 2018
I	*Solanum tuberosum* L.	NPK	Water and nutrient use efficiency	Al-Uthery and Al-Shami, 2019
I	*Vicia faba* L.	Zn, S	Fruit set, number of pods, pod length, and pod weight	Al-Antary *et al.*, 2020
I	*Beta vulgaris* L.	NPK	Yield and quality	Kandil *et al.*, 2020
I	*Solanum tuberosum* L.	NPK	Temporal impact on soil health	Abd El-Azeim *et al.*, 2020
I III	*Lallemantia iberica* (M.B.) Fischer & Meyer	NPK Fe	Yield components and antioxidant traits	Mohammad Ghasemi *et al.*, 2020
III	*Glycine max* (L.) Merr.	Fe	Yield and Fe content in edible parts of soybean	Knijnenburg *et al.*, 2018
III	*Carthamus tinctorius* L.	NPK	Physiological traits	Taghizadeh *et al.*, 2019

*Three categories proposed by Mastronardi *et al.* (2015).

more than 50% of which are related to micronutrients, and showed different results: positive effects were observed on onion (Taimooz, 2018), basil (El-Kereti *et al*., 2013), and broad bean (Al-Antary *et al*., 2020) whereas no effects were found on soybean (Knijnenburg *et al*., 2018). The NPK nanofertilizers have been studied by Kandil *et al.* (2020) and Mohammad Ghasemi *et al.* (2020), who proposed combining this fertilizer with fulvic acid and Fe-chelated nanofertilizers, respectively. The former significantly increased sugar beet shoot, root, and sugar yield, the latter significantly increased Dragon's head seeds production and their oil and total phenols content during winter cultivation. Foliar application of NPK nanofertilizers on safflower has been tested by Taghizadeh *et al.* (2019), reporting, under full irrigation, a significant increase of plant height (+3.7%) and seeds oil content (+11.6%) compared to conventional fertilizer (76.6 cm and 25.3%, respectively). Two open field studies have also been carried out with NPK nanofertilizers application on potato. Al-Uthery and Al-Shami (2019) focused their attention on water and nutrient use efficiency. The authors, applying an NPK nanofertilizer compared to an NPK conventional one, obtained an increase in water, N, phosphorus (P), and potassium (K) use efficiency of 24%, 86%, 178%, and 120%, respectively. The tubers yield per kg of fertilizer was eight times higher with NPK nanofertilizer (250.8 kg) than conventional NPK (27.8 kg). Instead, Abd El-Azeim *et al.* (2020) focused on soil chemical and biological characteristics. They concluded that to improve soil properties and maintain soil health, it is preferable to integrate organic compost with NPK nanofertilizers at a lower dose than conventional doses.

Composite materials

Description

The expression 'composite fertilizer' in this review refers to all the fertilizers structured with multiple materials containing one or more nutrients formulated to exploit synergy among materials (Guimarães *et al*., 2018) and address enhanced plants' nutrition. Composite structures can produce nanofertilizers and bioformulations, but this category contains only innovative fertilizers that are not included in the previous groups.

The composite fertilizers are usually made up of organic and inorganic coatings materials (coated granules), hydrophobic matrix material, hydrophilic hydrogel, or inorganic compounds with low solubility (Chen *et al*., 2018; Treinyte *et al*., 2018; Zhou *et al*., 2018; Ramli, 2019; Han *et al*., 2020). According to their physical properties (Jarosiewicz and Tomaszewska, 2003), different materials can determine different nutrients release patterns, either if they are used as a coating or if they are mixed within the fertilizer granule. In any case, all the materials added to the fertilizers are aimed to enhance plants nutrition through one or more of the following processes:

- *Physical control release: decrease the degradation potential of fertilizers in the rhizosphere:* i) reduce the solubility of fertilizers in water; ii) increase mechanical strength; iii) increase abrasion resistance; iv) improve water holding capacity.
- *Biochemical control release: delay nutrients availability exploiting chemical and biological processes in the rhizosphere:* i) utilization of chemical or biological sensors inside fertilizer granules; ii) utilization of materials able to change their properties in response to major environmental factors such as temperature and pH soil value.

Physical control release: coating materials

Among the composite fertilizers, the coated ones are the most diffused for agricultural use. The coating consists of a physical barrier used to control the nutrient release from the fertilizer and can be made of polymeric substances such as thermoplastics and resins (da Cruz *et al*., 2017; Gil-Ortiz *et al*., 2020a, 2020b) or inorganic mineral compounds including sulphur (S) and other nutrients (Wang *et al*., 2017; Guimarães *et al*., 2018; Rajan *et al*., 2021). Among these materials, polymers (thermoplastic, resin), and sulphur are the most commonly used.

Polymers

Polymers can hold together both macro and micronutrients, preventing them from rapid degradation in the rhizosphere environment (Beig *et al*., 2020). The dominant release mechanism depends on the polymer coating's physical properties and the internal solutes, and their interactions with environmental conditions (Adams *et al*., 2013). Polymer-coated fertilizers release nutrients by diffusion. As Irfan *et al.* (2018) described, the release process includes the permeation of water through the coating, the condensation of water molecules on the surface of the nutrient core, the development of osmotic pressure, the dissolution of nutrients, the swelling of the granule. If the membrane resists the internal pressure, the fertilizer is released by diffusion driven by a concentration gradient across the coating, by mass flow driven by a pressure gradient, or by a combination of the two factors (Shaviv, 2000). If the osmotic pressure exceeds the coating membrane's resistance, the release may be massive and called the 'failure mechanism' or 'catastrophic release' (Irfan *et al*., 2018). Therefore, the hydrophobic/hydrophilic coating has a substantial influence on the release rate, with a lower quantity released when the amount of water that diffuses through the coating into the fertilizer core is smaller (Jarosiewicz and Tomaszewska, 2003; Shen *et al*., 2019). In addition, this type of release inversely depends on the product of granule radius, coating thickness (Master *et al*., 2003), and coating elasticity (Shaviv, 2000).

Common polymeric materials used as coating materials in agriculture are polyolefines, polyurethane, polyacrylic, polyacrylamide, polysulfonate, polyvinyl chloride, polystyrene, polylactide, polyacetate, and polydopamine (Timilsena *et al*., 2015). Besides these, many types of biodegradable polymers have been tested (Donida *et al*., 2002; Majeed *et al*., 2015; Senna and Botaro, 2017; Mesias *et al*., 2019; Ibrahim *et al*., 2020), they are usually categorized as degradable synthetic polymers with a small permeability coefficient (biopols, polylactic acids, and polycaprolactone), and modified polysaccharides with a higher permeability coefficient (alginates, starches, agar) (Devassine *et al*., 2002). Zhang *et al.* (2016) reported developing a polymer-coated N fertilizer using biobased polyurethane derived from liquefied locust sawdust as carrier material and found that this fertilizer was more efficient than urea at supplying N to maize. Xie *et al.* (2011) used the straw as skeletal material in copolymerization with other monomers to form superabsorbent N and boron fertilizers. These materials are impressive due to their biodegradability and lower accumulation in the environment than the petroleum-based polymers; however, they show lower efficacy due to their hydrophilic properties and weak coating barrier. These observations suggest that more research is necessary to produce efficient coating materials without adverse environmental impact. Usually, a single coating material is used, but regardless of their origin and biodegradability, more polymers can be combined for the formulation of multilayers granules of fertilizers (Tao *et al*., 2011).

Sulphur

The first studies on S materials date back to 1968 (Rindt *et al*., 1968). These materials have been used for coating because of their ability to reduce the fertilizer granules' solubility and slow the discharge of nutrients. It has been tested in open field crops and turfgrass (Hummel and Waddington, 1984). However, its efficiency as a coating material has been discussed along with its environmental impact. The S coated fertilizers (SCFs) are largely urea-based (Bryant *et al*., 2012; Yang *et al*., 2015; Shan *et al*., 2015a, 2015b). Their release mechanisms are based on the coating layers' breakdown by the hydrostatic pressure, which allows the convective solute encapsulated inside to be released. Indeed, the failure mechanism (above explained) is typical of fragile, nonelastic coatings, such as S (Shaviv, 2000) or other inorganic coatings (Fu *et al*., 2018). S is a difficult material to be processed and it is likely to crack during the manufacturing process. It has been demonstrated to be more sensitive to light, temperature, and mechanical force degradation than polymers (Trenkel, 1997). The coating layer may not be uniform, thin, and discontinuous (Naz and Sulaiman, 2016), leading to an unwanted fast release of nutrients (Lu *et al*., 2012). Despite this inconsistent releasing pattern, S has been widely used (Pollock, 1988; Carreres *et al*., 2003; Zhao *et al*., 2013; Liu *et al*., 2020), and in some cases, it has been combined with various sealants (wax, paraffinic oils, polyethylene) (Shan *et al.,* 2015a, 2015b).

Although S coated fertilizers have been successfully used in different experiments to enhance vegetable and crop nutrition, their effectiveness has often been lower than other slow-release fertilizers (SRFs). It has been demonstrated that S coated urea (SCU) could significantly reduce NH_3 volatilization losses from different crop fields (Rao *et al*., 1987; Knight *et al*., 2007) when compared to conventional urea, but its efficiency was lower compared to polymer-coated urea or urea coated with inhibitors.

Biochemical control release: inhibitors

Nitrification or urease inhibitors can be added to the N-based fertilizer either as coating materials or homogenized in the fertilizer granules and act through chemical effects on soil microbial activity. The two types of formulation can affect the agronomic performances of the fertilizer. When used as a coating, the inhibitors are quickly released in the soil, exerting the main inhibiting effect just after fertilizer distribution. Instead, when inhibitors are homogenized within the granules, they are slowly released along with the nutrients, and in this latter case, N release is slower and more regular overtime.

The main purpose of using inhibitors is to improve N use efficiency of the fertilizer by reducing N losses to the environment. Prevention of ammonium oxidation is the target of the nitrification inhibitors, whereas ammonium release is the target effect of urease inhibitors; therefore, these inhibitor-enriched fertilizers act at two different stages of the N cycle.

Urease inhibitors

The use of urease inhibitors is one of the strategies adopted to improve urea performance in agriculture and mitigate urea-driven pollutants' emission (Kiss *et al*., 2002; Modolo *et al*., 2015; Li *et al*., 2017; Mira *et al*., 2017). Urea hydrolysis is a fast process in the soil that involves proton consumption and thus increases soil pH in the surrounding of fertilizer granules, also conditioning the NH_3/NH_4^+ equilibrium towards the formation of NH_3 (Cantarella *et al*., 2018). The urease is a multi-subunit nickel-dependent metalloenzyme that catalyses urea hydrolysis to two molecules of NH_3 and one molecule of CO_2 (Callahan *et al*., 2005; Real-Guerra *et al*., 2013). As a key enzyme for the global N cycle, urease is widespread in nature, being found in Archaea, bacteria, yeasts, fungi, algae, animals, and plants (Follmer, 2008). A variety of substances have been reported to act as urease inhibitors, and several of them are urea analogues that compete with the natural substrate for the urease active site. The urease inhibitors are a wide variety of inorganic and organic compounds, including metalloids, metals and non-metal ions (*e.g*., F^-, Hg^{2+}, Cd^{2+}, Ag^+), plant crude extracts, or natural organic molecules (Modolo *et al*., 2018). The urease activity can increase the potential NH_3 volatilization (Bock *et al*., 1988; Cameron *et al*., 2013), contributing to the global N gasses emission from agricultural soils (Bouwman *et al*., 2002). Besides the environmental issue, NH_3 volatilization is an economic loss because less N remains available for plants, leading to a reduction in yields. The control of urease activity in the soil may be a technique to increase the plant-available N content (Rawluk *et al*., 2001), because plants can take up urea molecules (Mérigout *et al*., 2008) and synthesize urease for intracellular N mineralization and organization into amino acids, and generally outcompete microorganisms in the uptake of urea from the soil urea stable pool (Harder Nielsen *et al*., 1998). Urea with urease inhibitors can be used as side-dress fertilization to decrease urea-derived NH_3 formation on the soil surface and foster urea movement to deeper soil layer through water infiltration. Silva *et al.* (2017), in a meta-analysis about the use of N-(n-butyl) thiophosphoric triamide (NBPT) as urease inhibitor, showed a significant reduction in NH_3 losses compared to the pure urea across all soil pH values, soil texture classes, SOC contents, N rates, and NBPT concentrations. Furthermore, the authors revealed a potential increase in yield of major crops around 5.3% by NBPT use, but they also indicated limited beneficial effects of NBPT on yields in coarse-textured soils and NBPT rates >1060 mg kg^{-1}. Therefore, the effectiveness of such inhibitors may vary according to the soil type.

Nitrification inhibitors

The ammonium present in the soil, either released by ammonification or applied as fertilizer, can be oxidized to nitrate by nitrifiers bacteria through the conversion of the NH_4^+ into NO_2^- and then into NO_3^-, which is not retained by the negatively charged soil exchange complex, making it more mobile towards plant roots via mass flow, leachable into the percolating water, or subjected to microbial denitrification. For these reasons, it is often desirable to control and/or reduce the nitrification process to synchronize N fertilizers release with the plant demand increasing fertilizer N use efficiency.

The use of nitrification inhibitors showed positive results in increasing yield and reducing N losses in many crops (Chen *et al*., 2008a). However, it was also demonstrated that their beneficial effect is affected by soil characteristics (*e.g*., soil pH and texture) and other management factors such as irrigation and N fertilizer rate (Abalos *et al*., 2014). The longevity of the inhibitors under soil conditions, as affected by temperature, is crucial for their effectiveness (Menéndez *et al*., 2012; Guardia *et al*., 2018). There is a broad range of nitrification inhibitors of either natural or synthetic origin, among which the most common and studied are 2-chloro-6-(trichloromethyl)-pyridine (nitrapyrin), dicyandiamide (DCD), and 3,4-dimethylpyrazole phosphate (DMPP) (Rodrigues *et al*., 2018). Along with the requested effect, nitrification inhibitors may have undesirable effects on non-target organisms and potential phytotoxicity. In this context, the development of new types of biological nitrification inhibitors is an ongoing research field, especially for the major grain crops (Norton and Ouyang, 2019). The new nitrification inhibitor 2-(3,4-dimethyl-1H-pyrazol-1-yl) succinic acid isomeric mixture (DMPSA) has been evaluated on maize fertilized with Ca-ammonium nitrate by Guardia *et al.*

(2017), and a reduction of N_2O emission of 58% was reported with no effect on crop yield.

Impact assessment

Polymers demonstrated high efficacy as coating, but some of them (especially those petroleum-based) also raise some environmental concerns (Saleh *et al*., 2003) related to their high pollution potential, high risk of accumulation, toxicity, and low degradability (Naz and Sulaiman, 2016). Furthermore, high environmental impact is also related to the fact that manufacturing polymeric materials requires chemicals and organic solvents challenging to recycle (Beig *et al*., 2020). The use of biodegradable polymers was suggested to solve these adverse effects, although synthetic non-degradable materials generally have a slower release rate than biodegradable and cellulose acetate-based ones.

The S coating can be limited by the extensive processes and equipment necessary for the manufacturing process, making it expensive and environmentally unfriendly (Hergert *et al*., 2011). However, S coating can keep the same crop yield while reducing the environmental impact determined by N losses compared to conventional fertilizers (Sanderson and Fillimore, 2012).

Their use showed many benefits for what concerns inhibitors, although little is known about their potential to enter the food chain (Byrne *et al*., 2020), even if this phenomenon has been already observed (Danaher and Jordan, 2013). In a comparative study on the undesirable effects of DMPSA and DMPP, Rodrigues *et al.* (2018) found that when applied at high doses to red clover, DMPP was absorbed, translocated, and preferentially accumulated in the leaves, whereas DMPSA mostly remained at the root level. The authors also reported that both *in planta* toxicity assays and *V. fischeri* bioluminescence inhibition test only showed detrimental effects at very high doses, which are nearly impossible to be found in agricultural conditions. Also, for NBPT urease inhibitor, a plant uptake in maize, pea, and spinach has been observed (Cruchaga *et al*., 2011; Zanin *et al*., 2015), with potential inhibition of leaf and root urease activity (Byrne *et al*., 2020). In this context, the challenge is to find eco-friendly, non-toxic, and low toxicity for plants and chemically stable inhibitors, efficient at low concentrations, compatible with urea fertilizers, and having sustainable costs.

Composite fertilizers in open field experiments

Most of the composite fertilizers have been tested in the laboratory leading to results that apply to specific and regulated soil and water conditions of pH, temperature, and microbial activity. Nonetheless, 113 articles on composite fertilizers tested in open field conditions have been considered in this study (Appendix 1), and they revealed that the majority of the field experiments were conducted using polymer-coated fertilizers (PCFs; 66 articles), 16 articles tested SCFs, and 18 tested fertilizers with nitrification and urease inhibitors. 41 articles, classified as 'others', tested fertilizers with specific formulations other than those just described (Figure 3). Within the latter group, 5 studies tested isobutylidene diurea, 4 studies urea formaldehyde, 2 studies methylene urea. In contrast, the others either did not specify the type of composite materials used, or the specific composite material was tested only in a single study.

Some studies were conducted on more than one crop, either as a species mixture (Bilgili and Açikgöz, 2011; Hric *et al.,* 2016), or as a rotation (Diez *et al*., 2000; Hu *et al*., 2013). The three most studied crops were rice (*Oryza sativa* L.), primarily in China, followed by maize (*Zea mays* L.) and winter wheat (*Triticum aestivum* L.) (Figure 4). These studies also showed that N was by far the most studied nutrient when evaluating the effectiveness of new fertilizers (Figure 5); 10.6% of the articles used NPK fertilizers, and few studies were conducted on other elements depending on the soil limiting nutrients (Li *et al*., 2020).

Considering the main studied effects in the selected papers (Figure 6), crop yield and the quality of the marketable product were the most common parameters used to test the effectiveness of the composite fertilizer on crop yield (83 out of 113 articles), 55.4% of which also studies nutrients uptake. A substantial share of the total number of papers (31%) focused on the effect of new fertilizers on greenhouse gas (GHG) and NH_3 emissions. Less attention was given to the effect on nutrients losses through runoff or leaching, studied by only 9 articles. Some studies are not included because focusing on other effects such as microbial activity (Jiao *et al*., 2005), strictly soil N dynamics (Diez *et al*., 1996; Kabala *et al*., 2017), or root growth (Li *et al*., 2014).

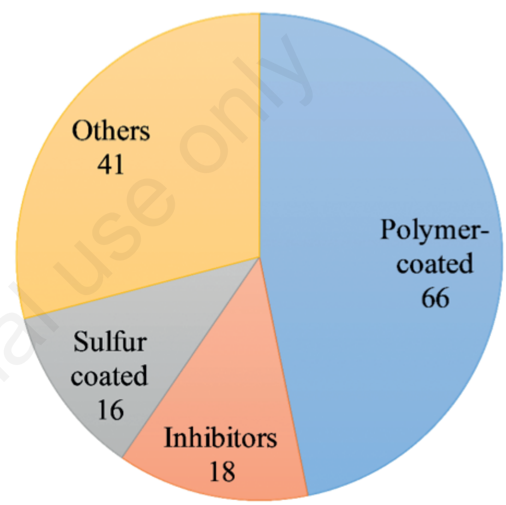

Figure 3. Classification of the articles using composite materials technology according to the type of composite material used (some articles studied more than one material).

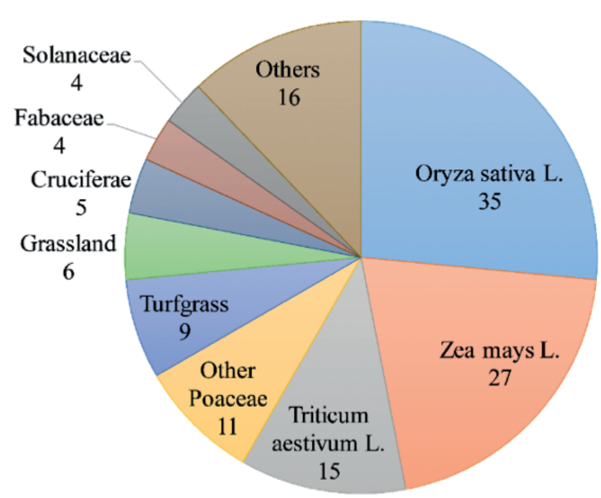

Figure 4. Classification of the articles concerning composite materials technology according to the crop tested (only categories with more than 2 studies were included).

Physical control release

Polymer-coated fertilizers

Among the 66 articles concerning PCFs, 23 reported results from experimental plots equal to or larger than 20 m^2, and only 6 were conducted for a period longer than two years. The main studied effects were: crop yield, nutrient use efficiency, GHG, and NH_3 emissions. Specifically, studies using resin polymers (10 articles) were tested within the PCFs mainly for their effect on N_2O and CH_4 emissions and NO_3^- leaching, while those using polyolefin polymers (8 articles) were mostly focused on crop nutritional status and nutrients use efficiency.

The PCFs have been demonstrated to have many positive effects compared to conventional fertilizers. Besides their specific formulation, PCFs efficacy is also related to the *placement of application*. In Canada, from 11 field trials over three years, it was observed that the application of the polymer-coated (PC) urea (from 25 to 100 kg ha^{-1}) in the seed raw of spring wheat gave comparable yield to side banded (3 cm beside and 3 cm below sowing raw) conventional urea, while PC urea increased grain N content (+4.2%) across the entire N application range (Haderlein *et al.*, 2001). The lower soil residual N due to higher uptake also reduces the N potential lost due to leaching, runoff, and volatilization (Li *et al.*, 2017). The *timing of fertilization* is also a key factor for both conventional and PCFs. A study conducted on a direct-seeded delayed-flood rice crop demonstrated that a pre-plant application of PC urea jeopardizes its efficacy in rice nutrition, as it released N too rapidly.

In contrast, the application of conventional urea at the five-leaf stage resulted in more adaption (higher rice yield) than a PCF pre-plant application (Golden *et al.*, 2009). Carreres *et al.,* (2003) demonstrated that PC urea produced greater rice yield than conventional urea and SCU, only when applied 15 days before flooding but not two days before flooding. An optimal *irrigation management* is also crucial for PCFs efficacy and ability to reduce nutrient losses. Ye *et al.* (2013) combined alternate wetting and drying irrigation of late-season rice and PC urea fertilization and increased grain yield-reducing water input and enhancing N utilization. Nash *et al.* (2015) reported that both the weather conditions and the drainage system (free *vs* managed) impacted NO_3^- losses in the tile drainage water in corn more than the fertilization regime.

Resin coated fertilizers (RCFs), similarly to all the other PCFs, are generally strongly influenced by the water management as well as by many factors such as the crop species and rotations, land uses, soil types, and farming practices, especially regarding N_2O and CH_4 emissions (Sun *et al*., 2020). Ji *et al.* (2013) reported experiments with a paddy soil managed with alternate flooding and midseason drained periods and showed that RCF inhibited the N_2O emissions in both periods, with higher N_2O emissions reduction (–61%) when the midseason aeration was performed after 30 days of flooding and lower (–21%) when the midseason aeration was performed after 40 days. The authors found lower N_2O emissions (–13%) and grain yield (–5%) with thermoplastic resin-coated urea then urea on the average of the four studied years. Also, the *crop residues management* influence the effect of RCFs as reported by Sun *et al.* (2020) who reported the effects of an RCF incorporated with wheat straw on CH_4 emissions in a wheat-rice rotation. In this experiment, the RCF was used to increase the N use efficiency reducing the soil N substrate for methanogenic bacteria present after plowing wheat straw back into soil (Hou *et al*., 2013), and lower CH_4 emission reduction (1-3%) compared to the use of conventional urea were showed. However, with straw incorporation, the RCF increased the rice grain yield by 10%. Differently, Shi *et al.* (2018) reported that the application of an RCF did not increase yield in a wheat-maize rotation cropping system but reduced the NO_3^- losses compared with conventional urea and duck manure. This experiment using RCF, besides the same yield, showed the same N use efficiency (48%) and residual N than conventional urea. However, its slow-releasing pattern, which depends on the nutrient concentration in the soil outside the RCF granule, prevented a fast accumulation of nutrients in the shallow soil layers and a consequent migration of NO_3^- through the profile.

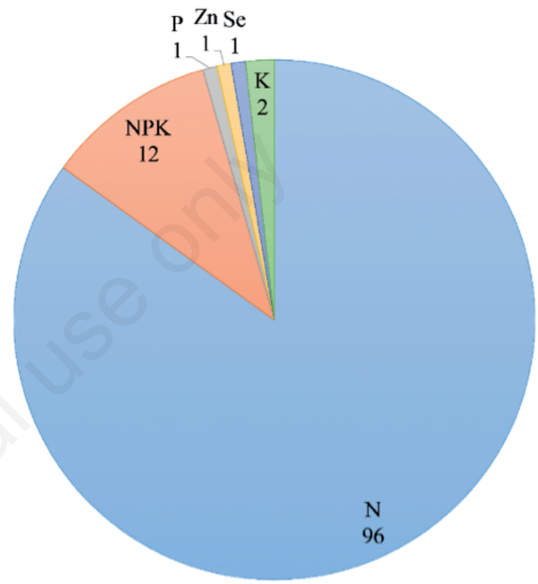

Figure 5. Classification of the articles that used composite materials technology according to the nutrient tested.

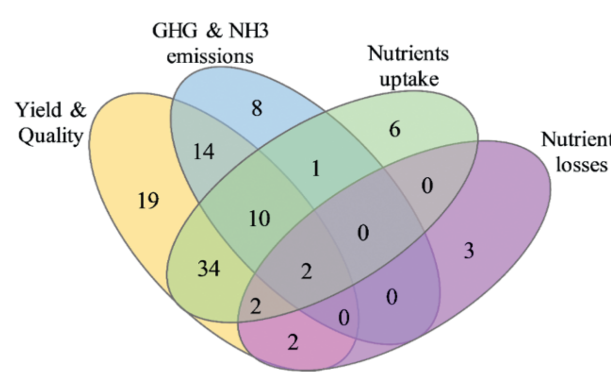

Figure 6. Classification of the articles using composite materials technology according to the main studied effects (nutrients losses refer to runoff and leaching dynamics).

The polyolefine-coated (POC) fertilizers are formulated to increase nutritional efficiency while reducing the application rate, enhancing crop yield, and reducing the environmental impact. Zvomuya and Rosen (2001) applying N as POC fertilizers on potato, obtained an average yield greater than 3.9 Mg ha^{-1} compared to conventional urea. In addition, comparing the POC urea application rates, the authors did not find significant differences in net return, suggesting that the POC urea can be a favourable option. The use of RCF among different crops did not always show an increase in yield; in some cases, these types of fertilizer reduced the environmental impacts of fertilization and decreased crop yield (Ji *et al*., 2013). In a study conducted by Chen *et al.* (2008b), a POC fertilizer did not satisfy cotton N demand because it did not release N fast enough to supply the plant's requirements.

S coated fertilizers

The SCFs were tested in 16 studies conducted in open field conditions, with 50% of them presenting experimental plots equal to or larger than 20 m^2. All experiments were conducted for three or four years, except for 3 articles that reported a length of two years or shorter. The main effect studied in these 16 articles was the ability of SCFs in reducing N losses through runoff, leaching, and volatilization, along with their efficiency in enhancing crop yield. Two studies, conducted in the same experimental site on cabbage crop by Shan *et al.* (2015a, 2015b) on the effects of SCU, significantly reduced NH_3 volatilization and N surface runoff, and found to be less effective compared to other SRFs. Specifically, the SCU reduced NH_3 volatilization on average by 64.8% compared to conventional fertilizers, but other enhanced fertilizers such as biological carbon power urea and the bulk blend controlled-release fertilizer (CRF) resulted in higher reductions (75.4% and 80.4%, respectively). Lower NH_3 volatilization with SCU than conventional has also been observed in rice by Sun *et al.* (2016) (–22.8%) and Liu *et al.* (2020) (–18.4%). Considering the surface N runoff, the SCFs showed a higher reduction (–61.1%) than the biological carbon power urea (–56.1%), even if lower than the bulk-blend CRF (–63.5%). No significant difference between SCU and conventional urea in terms of crop yields was reported by Sanderson and Fillimore (2012) for carrots and by Yang *et al.* (2015) and Yang *et al.* (2020) for rice. A rice yield decreases of approximately 7.5% using SCU was instead observed by Jang *et al.* (2016).

Globally, these studies demonstrated that S coatings could be a reasonable solution to reduce N fertilization's direct environmental impact, but other innovative fertilizers should be considered to maximize crop yield.

Biochemical control release

Several studies have shown that N sources formulated with nitrification inhibitors (NIs) and urease inhibitors (UIs) often reduce soil N_2O, CH_4, CO_2, and NH_3 emissions from the cropping systems (Drury *et al*., 2012; Halvorson and Del Grosso, 2013; Mohanty *et al*., 2017) even though their effectiveness might be affected by the specific formulation. Halvorson *et al.* (2016) conducted a study with a fertilizer containing both urease and nitrification inhibitors that enhanced the N use efficiency by plants while reducing the N_2O emissions compared to conventional urea and solid dairy manure. Besides the fertilizer formulation, the reduction of N_2O emissions by nitrification and urease inhibitors depends on the soil red-ox status and the mechanisms of N_2O formation in soil. Mohanty *et al.* (2017) studied the effects of neem-coated urea (NCU) fertilizer, a natural nitrification inhibitor, in two rice cropping systems and showed that it regulated the formation of NO_3^- and reduced N_2O emissions (–18%) compared to prilled urea in aerobic rice cultivation. The same NCU did not significantly reduce N_2O emission compared to prilled urea in puddled transplanted rice under flooded conditions. In the same study, the NCU increased rice yield by 10.5% compared to prilled urea. In a previous study, Kumar *et al.* (2010) reported that urea coated with a neem-oil thickness of 1000 mg kg^{-1} significantly increased rice yield (+29%) and N uptake (+25%) with respect to uncoated urea.

Bioformulations

Description

The bioformulations include all fertilizers containing active or dormant microorganisms (MOs) capable of triggering physiological growth responses in plants, enhancing plants' nutrition and development, or protecting plants from pathogens (Khan *et al*., 2009). In this review, by 'bioformulations', we mean the fertilizers made of specific carrier materials designed to protect or enriched with beneficial plant MOs. These fertilizers overcome the direct inoculation of beneficial MOs into the soil, the plants, or the seeds, that generally do not survive at sufficient density or die due to adverse environmental conditions. The MOs inoculated in the seeds can easily be damaged during storage and sometimes lack good adhesion to seeds (Ma, 2019), and in the soil environment, MOs have only a transient impact on the composition of the community (Qiao *et al.,* 2017), probably due to competition with the native soil microorganisms (Cunliffe and Kertesz, 2006).

There is a wide range of beneficial MOs and carrier materials, which can be selected according to their specific functions. Materials used as MO carriers can be alginate gels, synthetic gels, polyacrylamide, agar and agarose, polyurethane, vermiculite and polysaccharides, peat, perlite, charcoal, lignite, and products based on agro-by-products (Liu *et al*., 2008; Maheshwari *et al.*, 2015; Suresh *et al.*, 2018; Sahai *et al.*, 2019). Saranya *et al.* (2011) reported coconut shell-based biochar as a better alternative to lignite to produce a bio-fertilizer based on *Azospirillum lipoferum* inoculants. Spent mushroom-based substrate showed good shelf life and survival of *Trichoderma viride* and *Rhizobium* (Shitole *et al*., 2014), suggesting that carrier material should be developed considering the specific MO species. Even compounds used to produce composite materials, such as clay or nanoclay, nanocomposite, and biodegradable polymers, can be used as MO carriers, for example, the enzyme–nanoclay complexes proposed by Menezes-Blackburn *et al.* (2014).

Common functions of beneficial MOs reported in the literature are listed as follows: i) increase efficiency and duration of nutrients release time; ii) increase of nutrients availability in the rhizosphere; iii) release and production of phytohormones; iv) production of antibiotics and siderophores; v) N fixation.

Specifically, three major groups of microorganisms are commonly used for bioformulations (Malusá *et al.,* 2012): i) arbuscular mycorrhizal fungi (AMF), ii) plant growth-promoting rhizobacteria (PGPR); and iii) N-fixing rhizobia. Others are the P-solubilizing and mobilizing bacteria, K-solubilizing bacteria, Si and Zn solubilizing bacteria, S-oxidizing microorganisms, and phytate-mineralizing microorganisms.

The AMF are obligate symbiotic microorganisms that need a living host plant to grow and complete their life cycle, found in the roots of about 70%-90% of land plant species (Parniske, 2008; Berruti *et al.,* 2014). They establish a mutualistic symbiosis with the host plant providing water, soil mineral nutrients, mainly P and N (Delavaux *et al.,* 2017), and pathogen protection (Gough *et al.,* 2020) benefiting from organic C from photosynthetic compounds (Bonfante and Genre, 2010). Positive effects of AMF on soil physical characteristics (Yang *et al.,* 2017; Parihar *et al.,* 2020) and plant resistance at abiotic stress (Porcel *et al.,* 2012; Latef *et al.,* 2016) have also been widely reported.

The PGPR were initially intended as rhizospheric bacteria able to promote plant growth (Kloepper and Schroth, 1978), while in the following decades, it has been observed that they were also able to enhance the crop nutrients uptake (Vejan *et al.,* 2016), and suppress crop diseases through multiple mechanism activities (Sivasakthi *et al.,* 2014; Mehmood *et al.,* 2018). Some PGPR bacteria can also excrete physiologically active compounds such as phytohormones (*e.g*., indole acetic acid, gibberellic acid, and cytokinins), and metabolites (*e.g*., siderophores, hydrogen cyanide, and antibiotics) (Babalola, 2010; Bhattacharyya and Jha, 2012) and stimulate plant growth by alleviating abiotic stress effects (Goswami and Suresh, 2020) and increasing resilience to climate change conditions (Nazari and Smith, 2020). According to the PGPR-roots interface, PGPR can be classified as reported by Gray and Smith (2005): i) *endophytic* PGPR, producing nodules or residing inside plant tissues; and ii) *external* PGPR living outside the plant in the phyllosphere and the rhizosphere, enhancing plant growth through the production of signal compounds that directly stimulate plant growth, improve plant disease resistance, or improve mobilization of soil nutrients.

The N-fixing rhizobia bioformulations have been applied to crops for more than a century and represent one of the N deficiency solutions in the agro-ecosystems (Arora *et al.,* 2017). In addition, some N-fixing rhizobacteria are also able to solubilize K from orthoclase, muscovite, feldspar, biotite, mica, and illite (Sattar *et al*., 2019). However, the shelf-life of these bioformulations though improved in recent years by using different carriers, additives, and delivery systems (Kumar, 2014; Brahmaprakash *et al.,* 2020), is still a critical aspect. Besides rhizobial, other MOs used in bioformulations are:

- *P-solubilizing and mobilizing bacteria* (*e.g*., *Pseudomonas*, *Bacillus*, *Aspergillus*, and *Penicillium*) which supply plants with soluble P, facilitate other nutrients, produce phytohormones, and protect plants from biotic and abiotic stresses (Kudoyarova *et al.,* 2017; Nassal *et al.,* 2018; Shrivastava *et al.,* 2018). Phytates represent the most important pool of organic P in soil, but they are poorly available to plants; therefore, phytase/phosphatase enzymes play an important role in increasing P availability (Ramesh *et al.,* 2011). Microorganisms are the main source of phytase activity in rhizosphere and bulk soil (Gaind and Nain, 2015), and several bacterial and fungal species such as *Sporotrichum thermophile*, *Discosia* sp. FIHB 571, *Pseudomonas* sp. and *Bacillus amyloliquefaciens* (see Singh and Satyanarayana, 2012) improve P's plant acquisition from the organic pool. Phytase-based biofertilizers in soil have been tested as P-biofertilizers (Menezes-Blackburn *et al*., 2011, 2014), but the results indicated no significant beneficial effects.

- *solubilizing bacteria* such as *Acidothiobacillus ferrooxidans*, *Paenibacillus* spp., *Bacillus mucilaginosus*, *B. edaphicus*, and *B. Circulans*, solubilize K from insoluble forms (Etesami *et al.,* 2017; Jha, 2017), through acid and polysaccharides secretion and biofilm formation on mineral surfaces (see Sattar *et al.,* 2019). Although these microorganisms are ubiquitous in soil, their activity is influenced by soil properties such as structure, texture, and organic matter content.

- *silicate solubilizing bacteria*. Though Si plays an important role in plant tolerance to biotic and abiotic stress (Mandlik *et al*., 2020) such as infection by fungi, nematodes, viruses, abiotic salinity, heavy metal toxicity, heat and UV-B radiation, Si's mechanisms as plant nutrient are still poorly known. Si can be released from quartz by the silicate solubilizing activity of *Burkholderia cenocepacia* KTG, *Aeromonas punctata* RJM3020, and B. vietnamiensis ZEO3 (Santi and Goenadi, 2017).

Silicate solubilization by *Burkholderia eburnea* CS4-2 has been found by Kang *et al.* (2017), together with the ability to produce indole acetic acid under high pH values conditions. Silicate solubilizing bacteria also increased the plant macronutrient uptake, decreases the translocation of Cd and As in edible plant parts, and contributes to increasing crop yield (Mącik *et al.,* 2020).

- *Zn-solubilizing bacteria*: Zn plays a key role in plant physiology, being present in several enzymes of the fundamental metabolism (Cakmak, 2000). The Zn deficiency in plant is due to low total concentration or low solubility in soil (Bunquin *et al.,* 2017; Suganya *et al.,* 2020), even if added with fertilizers. Various microbial strains capable of improving Zn availability in soil such as *Pseudomonas* sp. and *Rhizobium* sp. strains, *Bacillus aryabhattai*, *Azospirillum* sp., *Bacillus* sp., *Thiobacillus thioxidans, Gluconacetobacter diazotrophicus*, *Burkholderia cenocepacia*, *Serratia liquefaciens,* and *S. marcescens* (Mącik *et al.,* 2020) have been used to prepare bioformulations with potential to alleviate the crop Zn deficiency (Gontia-Mishra *et al.,* 2017).

- *S-oxidizing microorganisms*. S deficiency negatively affects crop yield and quality by decreasing protein synthesis (Cazzato *et al.,* 2012). The S phyto-availability in soil depends on its microbial mineralization rate by sulfatase and other enzyme activities (Vidyalakshmi *et al*., 2009). Soil microorganisms that are capable of oxidizing S belong to various bacterial genera (*e.g*., *Xanthobacter*, *Alcaligenes*, *Bacillus*, *Pseudomonas, Thiobacillus*) and species (*e.g*., *Thiobacillus ferrooxidans*, *T. denitrificans*, *T. thiooxidans*, *T. thioparus*), fungi (*e.g*., *Fusarium* sp., *Aspergillus* sp., *Penicillium* sp.), and actinomycetes (*e.g*., *Streptomyces* sp.), but the most active sulfate oxiders are bacteria (Mącik *et al*., 2020).

Bioformulations in open field experiments

Relatively few studies on bioformulation have been carried out in real open field conditions. Among the 126 studies on innovative fertilizers in open field trials, only 4 involved bioformulations (Table 4). Kumar *et al.* (2014, 2015) tested the same bioformulation (*Azotobacter chroococcum* + *Bacillus subtilis*) on wheat and rice, using charcoal as carrier material and applying it alone or entrapped in organic agro-waste materials like cow-dung, neem leaf powder, clay soil, and *Acacia* gum. The authors also tested two application doses on wheat (the recommended dose and a double dose) and two application timings on rice (0 and 30 days after sowing). For both crops, entrapped bioformulations showed better performance than bioformulation alone, especially when applied at a double dose (wheat) and at sowing time (rice). For wheat, twice the recommended dose entrapped in the organic matrix increased the availability of nitrate, nitrite, ammonium, and phosphate in the rhizosphere and the concentration in plant leaves, which are directly correlated to growth and productivity. For rice, a significantly lower grain yield (–18.2%) with entrapped bioformulation than conventional urea (2.2 Mg ha^{-1}) was observed, even though no differences in grain protein (9.4%), starch (64.3%), and wet gluten (23.8%) content was shown.

A bioformulation based on *Azotobacter chroococcum, Azospirillum brasilense,* and *Pseudomnas putida* entrapped in the same organic matrix used by Kumar *et al.* (2014, 2015) was tested by Rai *et al.* (2017) on growth and alkaloid content of reserpine, and in this study the two- and three-fold doses than the recommended one increased the availability of the nutrients in the rhizosphere and improved plant growth. Indeed, 75 days after sowing, the authors noticed significantly higher shoot length (+25.9%), leaves number (+16.4%), and flowers number (+40.9%) using the triple dose of entrapped bioformulation compared to conventional urea (32.5 cm, 29.7 leaves plant^{-1}, and 7.3 flowers plant^{-1}). Instead, different behaviour was observed comparing shoot and root fresh and dry weight. The triple dose of entrapped bioformulation significantly increases fresh root weight (+61.0%), dry weight (+100.3%), and shoot dry weight (+8.2%) compared to conventional urea (9.35, 3.02 and 26.94 g plant^{-1}, respectively), while fresh shoot weight was not different. Based on this, it can be hypothesized that the bioformulation stimulated the plant photosynthesis also influencing the water use efficiency (WUE). This hypothesis is supported by the results of Akhtar *et al.* (2020), where the effects of *Bacillus licheniformis* were evaluated on maize growth and physiology under well-watered and drought stress conditions, showing an increase of 15% for root and shoot dry weight and a WUE up to 46% at the two different irrigation levels.

Field trial results on the effects of rhizobia and/or exopolysaccharides (EPS) bioformulations on pigeon pea crop showed that EPS and rhizobia significantly enhanced seed germination, pod number, seed yield, and protein content by 1.14, 1.38, 1.31, and 1.37-fold, respectively, compared to untreated control (Tewari and Sharma, 2020). In addition, this blended formulation increased the nodule number per plant, which is generally reduced by mineral fertilizers (Hu *et al.,* 2017; Pampana *et al.,* 2018).

As reported above, few studies have been carried out in open field conditions and none in large plots and for a long period. For this reason, general indications for bioformulation use on a large scale are not conclusive. Several studies compared conventional fertilization with bioformulation without considering nutrient mass balance that could represent a limiting factor in the long term. Indeed, MOs entrapped in an organic matrix and supplied at higher doses than recommended increase crop yield compared to MOs supplied alone. Given this, we think that bioformulations can be considered eco-friendly methods integrated into crop fertilization management according to specific agro-ecosystem characteristics and not as a substitute for fertilization. Among the unclear points to be elucidated, future research for the preparation of 'smart bioformulation' fertilizers needs to identify the microbiome associated with the specific plant varieties and cultivars, and the delivery technology (*e.g.*, seed coating, microbial inoculation) to achieve a mechanistic understanding of the bioformulation functioning in the rhizosphere.

Operational mechanisms

All the innovative fertilizers described so far can exploit one or more operational mechanisms. However, most of the papers report new types of fertilizers formulated for nutrients' slow or controlled release in the soil.

Slow and/or controlled release fertilizers

The terms *SRF* and *CRF* are generally considered analogous, and a clear distinction between these two operational mechanisms has not been specified in many papers even though their introduction by the fertilizers industries dates back to 1960 (Shoji, 2005). Indeed, some studies referred to them as synonymous (Azeem *et al*., 2014). A first differentiation was proposed by Trenkel (1997), based the distinction on the formulation and its impact on soil microbiome. They claimed that only microbially degradable fertilizer (*e.g*., urea-formaldehyde) could be referred to as 'SRFs', whereas all the coated or encapsulated products should be considered 'CRFs'.

The SRFs and the CRFs are designed to modulate the timing of nutrients release and overcome the continuous nutrient release of conventional fertilizers (CFs), responsible for the low nutrient utilization efficiency by crops and high leaching, runoff, or gaseous emissions in the atmosphere. The current paradigm is that CF cannot be available at 100% due to environmental losses, with a different effect on crops depending on species and local pedo-climatic conditions (Beig *et al*., 2020). It is estimated that 20% to 70% of the conventional urea applied in open field conditions escapes to the environment through nitrification leaching and volatilization (Naz and Sulaiman, 2016). Farmers manage these major limitations with timely side dressing or multiple fertilizer applications, but such practices are generally not efficient for crop nutrition (dotted line in Figure 7). To deal with these challenges, the global fertilizer industry has developed new forms of fertilizers able to provide crop nutrition with slow or controlled release mechanisms (Robbins, 2005) that aim to slow down nutrients release (SRFs) and to match nutrients demand (CRFs). Crop nutrient demand is dynamic along the plant's growth cycle: it is low in the early growth stages, increases sharply in the middle stage, and decreases in the late stage, as shown by the solid curve in Figure 7. Generally, CFs rapidly release nutrients immediately and linearly after application, not synchronized with crops requirements. With a single application, an ideal fertilizer should be able to match the crop's nutrient requirements throughout the whole growing cycle (dot-dashed curve in Figure 7), thus preventing nutrients losses.

Table 4. Studies with bioformulations tested in open field conditions.

Beneficial microorganisms	Carrier materials	Crop	Effect on yield	Reference
Azotobacter Chroococcum (N fixing bacteria) and *Bacillus subtilis* (phosphate solubilizing bacteria)	Charcoal	*Triticum aestivum* L.	Bioformulation alone +70% and bioformulation with carrier +112% than unfertilized control (1.1 Mg ha^{-1})	Kumar *et al*., 2014
Azotobacter Chroococcum (N fixing bacteria) and *Bacillus subtilis* (phosphate solubilizing bacteria)	Charcoal	*Oryza sativa* L.	Bioformulation alone –55% and bioformulation with carrier –18% than conventional urea control (2.2 Mg ha^{-1}).	Kumar *et al*., 2015
Azotobacter chroococcum, *Azospirillum brasilense* and Pseudomnas putida	Charcoal	*Rauwolfia serpentina* L.	+8% in yield of bioformulation (maximum tested dose) compared to urea application	Rai *et al*., 2017
Rhizobia		*Cajanus cajan* L.	No significant difference between bioformulation and unfertilized control	Tewari and Sharma, 2020

A CRF, be either organic or inorganic, should control the rate, pattern, and duration of nutrients release in response to plant needs, not only delay the nutrient release, which is the typical mechanism of SRFs. Based on their different operational mechanisms, SRFs and CRFs can be distinguished as different enhanced fertilizers. The SRFs effectiveness is highly dependent on soil microbial activity, soil moisture, and temperature (Steiner *et al.*, 2009). Liu *et al.* (2014) included in this category also organic fertilizers such as plant manures, green manure, and cover crops, all animal manures and compost, due to their slowly release of nutrients affected by the local climatic conditions. However, we argue that these organic matrices' nutrient release is hardly predictable nor controlled by standard agronomical practice.

According to Shaviv and Mikkelsen (1993), the CRFs, differently from the SRFs, are less influenced by soil temperature, soil texture, and soil microbial activity in releasing nutrients. The authors referred to CRFs as products coated with macromolecule materials, capable of releasing nutrients with a dynamic that can match the crop nutrients demands with a single application at the beginning of the growing season (Figure 7), and that can be modified with the agronomic practice. As reported by Shaviv *et al.* (2001), '*The term controlled-release fertilizer became acceptable when applied to fertilizers in which the factors dominating the rate, pattern and duration of release are well known and controllable during CRFs preparation*'.

The major advantages related to the use of SRFs and CRFs are:

- *Enhanced nutrient-use efficiency.* The use of CRFs and SRFs allowed obtaining the same yield of CF's recommended rate upon reducing applied fertilizer by 20% to 30% (Trenkel, 2010). At the field scale, it has been demonstrated that similar rice and wheat yields could be obtained with SRF, and CRF applied at -20% N dose (Gil-Ortiz *et al*., 2020a, 2020b). The reduction in fertilizer application rate significantly enhances the efficiency of the fertilization practice compared to CF (urea).

- *Reduction of nutrients losses.* The reduction in the fertilizers dose compared to CF applied as well as the SRFs and CRFs formulations (coating, inhibitors, encapsulation of impermeable materials, *etc.*) prevents nutrients from being too quickly released in the soil, thus reducing the nutrients losses through runoff, leaching, and volatilization that can cause water contamination, eutrophication and an increase in GHG emissions.

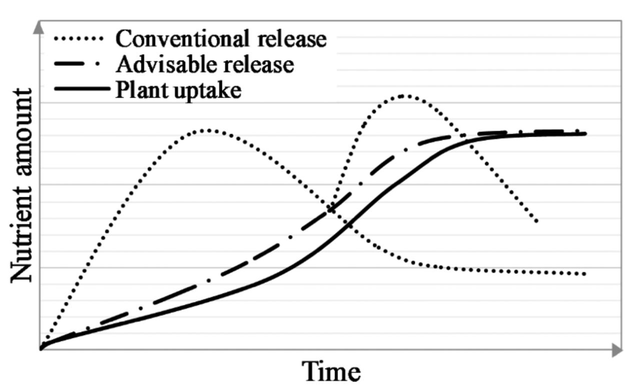

Figure 7. Nutrient release pattern of conventional fertilizer (dotted curves), advisable curve of nutrient release (dot-dashed curve) and crops nutrients demand (solid curve).

- *Reduction in the number of application and labour costs.* As compared to CFs that force farmers to apply extra doses of fertilizers split in more applications, the CRFs and SRFs reduce the extra costs in terms of labour and mechanical operations because they require a single application. Liu *et al.* (2014) showed that avoiding extra fertilizer applications in potato cultivation saves the farmer between 5 and 7 \$ acre^{-1} of broadcasting expense.

- *A step towards precision farming practices.* The CRFs, being less sensitive to soil and climatic conditions, allow a better prediction of nutrient release rate and duration, which can be adapted to each specific crop need. Many CRFs are produced with a specific formulation whose releasing curves can have linear and sigmoidal shapes. Their releasing pattern can be designed during the production process, enabling fertilization programs that best meet the crop's nutrient demand. CRFs may also be used in addition to CF to ensure a precision fertilization management of certain crops. An example of this practice is reported by Shoji (2005) for programmed fertilization of transplanted wetland rice. Furthermore, proper placement of the CRF increases fertilization efficiency while preventing injures to crops (Shoji, 2005). Using CRFs that allow controlling the releasing time (when), the position (where), and the rate of application (how) entail a precision fertilization management that reduces the production costs, reduces fertilizer-associated risks to crops and the environment, and enhances crops yield in accordance with the principles of precision farming.

- *Effects on agricultural soil.* The application of some CRFs such as the S coated may induce changes in soil pH that increase Fe and P bioavailability for some crops (Melia *et al*., 2017).

The major disadvantages related to the use of SRFs and CRFs are:

- *Cost.* Generally, SRFs and CRFs are more expensive than CF.
- *Drawback effects on agricultural soil*. As aforementioned, CRFs such as S-coated urea may acidify soils. This change in soil pH, besides favouring some elements' bioavailability, can also cause some nutrient disorders (*e.g*., Ca, Mg deficiency) that need to be addressed with a proper fertilization program (Melia *et al*., 2017).
- *Climatic impacts*. Despite both SRFs and CRFs being more resilient to soil and climatic conditions than CF, they may still be slightly affected by temperature changes, flooding conditions, microbial activity, and runoff. Moreover, the production of SRFs and CRFs also has a higher C footprint than that of CFs.

In the light of the above-reported considerations, one of the main questions underlying this review is how the expression 'smart fertilizers' is associated with CRFs and/or SRFs. Based on the literature review, we conclude that the slow release of nutrients is not enough to classify an enhanced fertilizer as 'smart' because they do not allow the control of rate, timing, and duration of the release. For this reason, only CRFs can be considered 'smart fertilizers'.

Bioactivation

The bioactivation is a mechanism used to make mineral nutrients soluble and available for plant uptake using the microorganisms' activity as a trigger. In the bioactivated fertilizers, the effective MO are carried on materials suitable for their immobilization and preservation such as alginate gels, synthetic gels (Sol-Gel), polyacrylamide, agar and agarose, polyurethane, vermiculite, and polysaccharides (Liu *et al*., 2008). The use of carrier materials protect the MO when applied to the soil and extend nutrient release over time compared to the CF. Bioactivation is usually referred to as fertilizers composed of mineral nutrients, carrier materials (such as those reported above), and MO (Klaic *et al*., 2018). These MO are used for their ability to transform nutrients from unavailable into plant-available forms. Klaic *et al.* (2018) reported that a starch matrix as a supporting substrate for *Aspergillus* spp. was able to solubilize up to 70% of the total available P from low soluble phosphate rocks. The authors referred to their fertilizer as a 'bioreactor granule' made of phosphate rock as mineral nutrients and gelatinized starch as carrier material to sustain growth and organic acid production of MO. *Aspergillus* spp. and *Penicillium* spp. were also used in a bioactivated fertilizer for the phosphate solubilization by Saber *et al.* (2009) and Schneider *et al.* (2010). Liu *et al.* (2008) studied the *Cellulosimicrobium cellulans* encapsulated in a Ca-alginate matrix blended with various supplemented materials and demonstrated the crucial role played by the type of capsules on the rate and number of cells release, determining the timing of bioactivation and nutrient release. The MO encapsulated in fertilizers granules can also be used to supply hormones and plant growth regulators (Badawi *et al*., 2011). Mijwel and Jassim (2018) reported that the fungus species *Glomus mosseae* and *Trichoderma harizanum* carried on peat moss induced a significant increase in chlorophyll percentage, vegetative dry weight, and N and P content in potato crop. The presence of fungi in organic matrix fertilizer also acted as antigens against plant pathogens, contributing to plant growth and yield. *T. harizanum* in particular, showed the capability to secrete some phytohormones similar to auxins, increase nutrients absorption, and resistance to phytopathogenic fungi, leading to an increase in plant growth and yield (Harman, 2000; Sofo *et al*., 2011).

Therefore, bioactivated fertilizers contain viable microorganisms able to colonize the rhizosphere and/or the root systems, increasing the nutrients availability to plants and producing plant biostimulants and preventing crop disease. Therefore, MOs supplied with bioactivated fertilizers could better integrate with the native soil microbial populations and plant microbiome and increase the nutrient availability concerning the crop nutrient demand and absorption rate, *i.e*., higher nutrient release in response to crop nutrient uptake.

Where we should go: a definition of smart fertilizers

One of the biggest tasks for modern agriculture production is improving the agronomic efficiency of fertilizers while reducing their cost and environmental impact. Many efforts have been made to develop innovative fertilizers that achieve these goals, as showed by the large number of papers found in our literature review (3968 papers). However, only a minority of them (126 papers) have been carried out on herbaceous crops in open field conditions. They mostly use self-made innovative fertilizers in short term experiments and adopt small size plots, with reduced potentials of industrial production scaling up. Consequently, data that can be easily transferred at real farm scale are still limited. Therefore, future research should increase the number of open field experiments on larger plot sizes with a multiple-year validation to evaluate these innovative fertilizers' effect in real conditions.

Among the results obtained from open field conditions, 90% of the studies tested composite materials that in 58% of the case studies concerned rice, maize, and wheat. Therefore, more open field experiments on different crops and with bioactivated and nanofertilizers are desirable, and further developing and testing other nutrients, especially P.

Based on the innovative fertilizers' operational mechanisms, bioactivation-based fertilizers can be considered true *smart fertilizers* because their mode of action is modulated by biological mechanisms and therefore result in nutrient release kinetics that mirrors the plants' nutrient needs. In addition to the nutritional effect and according to their physical structure and their organic or chemical compositions, smart fertilizers can also enhance plants' disease resistance and soil properties. Most of the analysed papers associate the 'smart' concept to the controlled and/or slow release of nutrients, using both terms as synonymous. Some others broadened the concept by including the controlled release of nutrients to reduce the environmental impact. In our opinion, smart fertilizers are those capable of synchronizing the nutrients release from fertilizers with the plant's nutritional needs. This implies that the nutrient carriers should respond to the physico-chemical changes that plants induce in the rhizosphere in the different phenological stages, not to changes in bulk soil properties such as temperature, moisture content, pH, Eh, and EC values. A significant step forward in this direction would be delivering nutrients at the surface of the plant root districts actively absorbing nutrients. Bio-nanotechnology can greatly contribute to producing fertilizing materials that release nutrients in response to plant secretion of specific molecules at different phenological stages or respond to the nutrient shortage. Among the most promising technologies, the synthesis of aptamers which are DNA or RNA molecules of different lengths and three-dimensional shapes, holds the potential to carry nutrients and deliver them to selected binding sites onto the root cell membranes (DeRosa *et al.,* 2010). The rationale of the use of aptamers is that the root exudation profile changes in response to the nutrient depletion in the rhizosphere (Dakora and Phillips, 2002), and that the root exudate profiles are different for different plants, thus making it possible to design plant 'tailored' fertilizers in the future. Nutrient starvation signalling molecules are generally simple sugars, single amino acids, low molecular weight organic acids, sugars, and phenolics. Aptamers capable of recognizing several of the signal molecules have been tested and promising results have been reported (*e.g.* Monreal *et al*., 2016), and this technology can still be improved as the knowledge on the root metabolome progresses. However, specific or non-specific adsorption of 'naked' DNA or RNA onto soil colloids may reduce their mobility at the soil/plant interface and reduce their uptake by plants. Moreover, active microorganisms may also bind and take up aptamers, thus immobilizing the nutrients into the soil microbial biomass. To overcame these potential shortcomings, aptamers may be embedded into polymeric films or microcapsules of SRFs, CRFs, and also included in bioactivated fertilizers, acting as antennas for target recognition sites and root exudates as signals; however, this technology is still in its infancy. Besides the laboratory scale evidence, knowledge must be gained at the field scale to test both the nutrient use efficiency and the overall sustainability and environmental toxicology and safety of these innovative biotechnologies.

Based on our critical analysis of the available literature, we conclude that *a fertilizer can be considered 'smart'* when *applied to the soil allows us to control the rate, timing, duration of nutrients release, and actively absorbing root traits.* Our new comprehensive proposed definition is the following: 'S*mart fertilizer is any single or composed (sub)nanomaterial, multi-component and/or bioformulation containing one or more nutrients that through physical, chemical, and/or biological processes, can adapt the timing of nutrient release to the plant nutrient demand, enhancing the agronomic yields and reducing the environmental impact at sustainable costs, when compared to conventional fertilizers*'.

References

Abalos D, Sanchez-Martin L, Garcia-Torres L, van Groenigen JW, Vallejo A. 2014. Management of irrigation frequency and nitrogen fertilization to mitigate GHG and NO emissions from drip-fertigated crops. Sci. Total Environ. 490:880-8.

Abd El-Azeim MM, Sherif MA, Hussien MS, Haddad SA. 2020. Temporal impacts of different fertilization systems on soil health under arid conditions of potato monocropping. J. Soil Sci. Plant Nutr. 20:322-34.

Abdelsalam NR, Fouda MM, Abdel-Megeed A, Ajarem J, Allam AA, El-Naggar ME. 2019. Assessment of silver nanoparticles decorated starch and commercial zinc nanoparticles with respect to their genotoxicity on onion. Int. J. Biol. Macromol 133:1008-18.

Adams C, Frantz J, Bugbee B. 2013. Macro-and micronutrient-release characteristics of three polymer-coated fertilizers: Theory and measurements. J. Soil Sci. Plant Nutr. 176:76-88.

Akhtar SS, Amby DB, Hegelund JN, Fimognari L, Großkinsky DK, Westergaard JC, Müller R, Moelbak L, Liu F, Roitsch T. 2020. Bacillus licheniformis FMCH001 increases water use efficiency via growth stimulation in both normal and drought conditions. Front. Plant Sci. 11:297.

Al-Antary TA, Kahlel A, Ghidan A, Asoufi H. 2020. Effects of nanotechnology liquid fertilizers on fruit set and pods of broad bean (Vicia faba L.). Fresen. Environ. Bull, 29:4794-98.

Al-Uthery HW, Al-Shami QM. 2019. Impact of fertigation of nano NPK fertilizers, nutrient use efficiency and distribution in soil of potato (Solanum tuberosum L.). Plant Arch. 19:1087-96.

Arora NK, Verma M, Mishra J. 2017. Rhizobial bioformulations: past, present and future. In: S. Mehnaz (ed.) Rhizotrophs: Plant growth promotion to bioremediation. Springer, Singapore, pp 69-99.

Azeem B, KuShaari K, Man ZB, Basit A, Thanh TH. 2014. Review on materials & methods to produce controlled release coated urea fertilizer. J. Control. Release, 181:11-21.

Babalola OO. 2010. Beneficial bacteria of agricultural importance. Biotechnol. Lett. 32:1559-1570.

Badawi FSF, Biomy AMM, Desoky AH. 2011. Peanut plant growth and yield as influenced by co-inoculation with Bradyrhizobium and some rhizo-microorganisms under sandy loam soil conditions. Ann. Agric. Sci. 56:17-25.

Bahadar H, Maqbool F, Niaz K, Abdollahi M. 2016. Toxicity of nanoparticles and an overview of current experimental models. Iran. Biomed. J. 20:1-11.

Beig B, Niazi MBK, Jahan Z, Hussain A, Zia MH, Mehran MT. 2020. Coating materials for slow release of nitrogen from urea fertilizer: a review. J. Plant Nutr. 43:1510-33.

Bernardo MP, Guimarães GG., Majaron VF, Ribeiro C. 2018. Controlled release of phosphate from layered double hydroxide structures: dynamics in soil and application as smart fertilizer. ACS Sustain. Chem. Eng. 6:5152-61.

Berruti A, Borriello R, Orgiazzi A, Barbera AC, Lumini E, Bianciotto V. 2014. Arbuscular mycorrhizal fungi and their value for ecosystem management. In: O. Grillo (ed.) Biodiversity: The Dynamic Balance of the Planet. InTech, Rijeta, Croacia, pp 159-91.

Bhattacharyya PN, Jha DK. 2012. Plant growth-promoting rhizobacteria (PGPR): emergence in agriculture. World J. Microbiol. Biotechnol. 28:1327-50.

Bi S, Barinelli V, Sobkowicz MJ. 2020. Degradable controlled release fertilizer composite prepared via extrusion: fabrication, characterization, and release mechanisms. Polymers 12:301.

Bilgili U, Açikgöz E. 2011. Effects of slow-release fertilizers on turf quality in a turf mixture. Turk. J. Field Crops 16:130-6.

Bley H, Gianello C, Santos LDS, Selau LPR. 2017. Nutrient release, plant nutrition, and potassium leaching from polymer-coated fertilizer. Rev. Bras. Ciênc. 41:e0160142.

Bock E, Wilderer PA, Freitag A. 1988. Growth of Nitrobacter in the absence of dissolved oxygen. Water Res. 22:245-50.

Bonfante P, Genre A. 2010. Mechanisms underlying beneficial plant–fungus interactions in mycorrhizal symbiosis. Nat. Commun. 1:1-11.

Bouwman AF, Boumans LJM, Batjes NH. 2002. Emissions of N_2O and NO from fertilized fields: Summary of available measurement data. Global Biogeochem. Cycles 16:1058.

Brahmaprakash GP, Sahu PK, Lavanya G, Gupta A, Nair SS, Gangaraddi V. 2020. Role of additives in improving efficiency of bioformulation for plant growth and development. Front. Soil Environ. Microbiol. 1:1-10.

Bryant RJ, Anders M, McClung A. 2012. Impact of production practices on physicochemical properties of rice grain quality. J. Sci. Food Agric. 92:564-69.

Bunquin MAB, Tandy, S, Beebout, SJ, Schulin, R 2017. Influence of soil properties on zinc solubility dynamics under different redox conditions in non–calcareous soils. Pedosphere 27:96-105.

Byrne MP, Tobin JT, Forrestal PJ, Danaher M, Nkwonta CG, Richards K, Cummins E, Hogan AS, O'Callaghan TF. 2020. Urease and nitrification inhibitors—As mitigation tools for greenhouse gas emissions in sustainable dairy systems: a review. Sustainability 12:6018.

Cakmak I. 2000. Tansley Review No. 111: possible roles of zinc in protecting plant cells from damage by reactive oxygen species. New Phytol. 146:185-205.

Calabi-Floody M, Medina J, Rumpel C, Condron LM, Hernandez M, Dumont M, de la Luz Mora M. 2018. Smart fertilizers as a strategy for sustainable agriculture. Adv. Agron. 147:119-57.

Calabi-Floody M, Medina J, Suazo J, Ordiqueo M, Aponte H, Mora MDLL, Rumpel C. 2019. Optimization of wheat straw co-composting for carrier material development. Waste Manage. 98:37-49.

Callahan BP, Yuan Y, Wolfenden R. 2005. The burden borne by urease. J. Am. Chem. Soc. 127:10828-9.

Cameron KC, Di HJ, Moir JL. 2013. Nitrogen losses from the soil/plant system: a review. Ann. Appl. Biol. 162:145-73.

Cantarella H, Otto R, Soares JR, de Brito Silva AG. 2018. Agronomic efficiency of NBPT as a urease inhibitor: A review. J. Adv. Res. 13:19-27.

Carreres R, Sendra J, Ballesteros R, Valiente EF, Quesada A, Carrasco D, Leganés F, de la Cuadra JG. 2003. Assessment of slow release fertilizers and nitrification inhibitors in flooded rice. Biol. Fertil. Soils 39:80-7.

Cazzato E, Tufarelli V, Ceci E, Stellacci AM, Laudadio V. 2012. Quality, yield and nitrogen fixation of faba bean seeds as affected by sulphur fertilization. Acta Agr. Scand. B-S P 62:732-8.

Chen D, Freney JR, Rochester I, Constable GA, Mosier AR, Chalk PM. 2008b. Evaluation of a polyolefin coated urea (Meister) as a fertilizer for irrigated cotton. Nutr. Cycling Agroecosyst. 81:245-54.

Chen D, Suter H, Islam A, Edis R, Freney JR, Walker CN. 2008a. Prospects of improving efficiency of fertiliser nitrogen in Australian agriculture: a review of enhanced efficiency fertilisers. Soil Res. 46:289-301.

Chen J, Lü S, Zhang Z, Zhao X, Li X, Ning P, Liu M. 2018. Environmentally friendly fertilizers: A review of materials used and their effects on the environment. Sci. Total Environ. 613:829-39.

Chhipa H. 2017. Nanofertilizers and nanopesticides for agriculture. Environ. Chem. Lett. 15:15-22.

Cordell D, White S. 2014. Life's bottleneck: sustaining the world's phosphorus for a food secure future. Annu. Rev. Environ. Resour. 39:161-88.

Crosera M, Bovenzi M, Maina G, Adami G, Zanette C, Florio C, Larese FF. 2009. Nanoparticle dermal absorption and toxicity: a review of the literature. Int. Arch. Occup. Environ. Health 82:1043-55.

Cruchaga S, Artola E, Lasa B, Ariz I, Irigoyen I, Moran JF, Aparicio-Tejo PM. 2011. Short term physiological implications of NBPT application on the N metabolism of Pisum sativum and Spinacea oleracea. J. Plant Physiol. 168:329-36.

Cunliffe M, Kertesz MA. 2006. Effect of Sphingobium yanoikuyae B1 inoculation on bacterial community dynamics and polycyclic aromatic hydrocarbon degradation in aged and freshly PAH-contaminated soils. Environ. Pollut. 144:228-37.

da Cruz DF, Bortoletto-Santos R, Guimarães GGF, Polito WL, Ribeiro C. 2017. Role of polymeric coating on the phosphate availability as a fertilizer: insight from phosphate release by castor polyurethane coatings. J. Agric. Food Chem. 65:5890-5.

Dakora FD, Phillips DA. 2002. Root exudates as mediators of mineral acquisition in low-nutrient environments. Plant Soil 245:35-47.

Danaher M, Jordan K. 2013. Identification of existing and emerging chemical residue contamination concerns in milk. Irish J. Agr. Food Res. 52:173-83.

Dankers AC, Kuper CF, Boumeester AJ, Fabriek BO, Kooter IM, Gröllers-Mulderij M, Peter Tromp P, Nelissen I, Zondervan-Van Den Beuken EK, Vandebriel RJ. 2018. A practical approach to assess inhalation toxicity of metal oxide nanoparticles in vitro. J. Appl. Toxicol. 38:160-71.

Delavaux CS, Smith-Ramesh LM, Kuebbing SE. 2017. Beyond nutrients: a meta-analysis of the diverse effects of arbuscular mycorrhizal fungi on plants and soils. Ecology 98:2111-9.

DeRosa MC, Monreal C, Schnitzer M, Walsh R, Sultan Y. 2010. Nanotechnology in fertilizers. Nat. Nanotechnol. 5:91.

Devassine M, Henry F, Guerin P, Briand X. 2002. Coating of fertilizers by degradable polymers. Int. J. Pharm. 242:399-404.

Dewdar M, Abbas M, Hassanin A, Aleem H. 2018. Effect of nano micronutrients and nitrogen foliar applications on sugar beet (Beta vulgaris L.) of quantity and quality traits in marginal soils in Egypt. Int. J. Curr. Microbiol. Appl. Sci. 7:4490-8.

Diez JA, Caballero R, Bustos A, Roman R, Cartagena MC, Vallejo A. 1996. Control of nitrate pollution by application of controlled release fertilizer (CRF), compost and an optimized irrigation system. Fertil. Res. 43:191–5.

Diez JA, Caballero R, Roman R, Tarquis A, Cartagena MC, Vallejo A. 2000. Integrated fertilizer and irrigation management to reduce nitrate leaching in Central Spain. J. Environ. Qual. 29:1539-47.

Dimkpa CO, Bindraban PS. 2017. Nanofertilizers: new products for the industry? J. Agric. Food Chem. 66:6462-73.

Donida MW, Rocha SC. 2002. Coating of urea with an aqueous polymeric suspension in a two-dimensional spouted bed. Dry. Technol. 20:685-704.

Drury CF, Reynolds WD, Yang XM, McLaughlin NB, Welacky TW, Calder W, Grant CA. 2012. Nitrogen source, application time, and tillage effects on soil nitrous oxide emissions and corn grain yields. Soil Sci. Soc. Am. J. 76:1268-79.

El-Kereti MA, El-feky SA, Khater MS, Osman YA, El-sherbini EA. 2013. ZnO nanofertilizer and He Ne laser irradiation for promoting growth and yield of sweet basil plant. Recent Pat. Food Nutr. Agric. 5:169-81.

Erisman JW, Schaap M. 2004. The need for ammonia abatement with respect to secondary PM reductions in Europe. Environ. Pollut. 129:159-63.

Etesami H, Emami S, Alikhani HA. 2017. Potassium solubilizing bacteria (KSB): Mechanisms, promotion of plant growth, and future prospects - a review. J. Soil Sci. Plant Nutr. 17:897-911.

Feng C, Lü S, Gao C, Wang X, Xu X, Bai X, Gao N, Liu M, Wu L. 2015. 'Smart' fertilizer with temperature-and pH-responsive behaviour via surface-initiated polymerization for controlled release of nutrients. ACS Sustain. Chem. Eng. 3:3157-66.

Follmer C. 2008. Insights into the role and structure of plant ureases. Phytochemistry 69:18-28.

Fu J, Wang C, Chen X, Huang Z, Chen D. 2018. Classification research and types of slow controlled release fertilizers (SRFs) used-a review. Commun. Soil Sci. Plant Anal. 49:2219-30.

Gaind S, Nain L. 2015. Soil–phosphorus mobilization potential of phytate mineralizing fungi. J. Plant Nutr. 38:2159-75.

Geiser M, Jeannet N, Fierz M, Burtscher H. 2017. Evaluating adverse effects of inhaled nanoparticles by realistic in vitro technology. Nanomaterials 7:49.

Gil-Ortiz R, Naranjo MÁ, Ruiz-Navarro A, Atares S, García C, Zotarelli L, San Bautista A, Vicente O. 2020a. Enhanced agronomic efficiency using a new controlled-released, polymeric-coated nitrogen fertilizer in rice. Plants 9:1183.

Gil-Ortiz R, Naranjo MÁ, Ruiz-Navarro A, Caballero-Molada M, Atares S, García C, Vicente O. 2020b. New eco-friendly polymeric-coated urea fertilizers enhanced crop yield in wheat. Agronomy 10:438.

Giroto AS, Fidélis SC, Ribeiro C. 2015. Controlled release from hydroxyapatite nanoparticles incorporated into biodegradable, soluble host matrixes. RSC Adv. 5:104179-86.

Giroto AS, Guimarães GGF, Ribeiro C. 2018. A novel, simple route to produce urea: urea–formaldehyde composites for controlled release of fertilizers. J. Polym. Environ. 26:2448-58.

Godfray HCJ, Beddington JR, Crute IR, Haddad L, Lawrence D, Muir JF, Pretty J, Robinson S, Thomas SM, Toulmin C. 2010. Food security: the challenge of feeding 9 billion people. Science 327:812–8

Golden BR, Slaton NA, Norman RJ, Wilson CE, DeLong RE. 2009. Evaluation of polymer-coated urea for direct-seeded,

delayed-flood rice production. Soil Sci. Soc. Am. J. 73:375-83.
Gomiero T. 2016. Soil degradation, land scarcity and food security: Reviewing a complex challenge. Sustainability 8:281.
Gontia-Mishra I, Sapre S, Tiwari S. 2017. Zinc solubilizing bacteria from the rhizosphere of rice as prospective modulator of zinc biofortification in rice. Rhizosphere 3:185-90.
Goswami M, Suresh DEKA. 2020. Plant growth-promoting rhizobacteria—alleviators of abiotic stresses in soil: A review. Pedosphere 30:40-61.
Gough EC, Owen KJ, Zwart RS, Thompson JP. 2020. A systematic review of the effects of arbuscular mycorrhizal fungi on root-lesion nematodes, Pratylenchus spp. Front. Plant Sci. 11:923.
Gray EJ, Smith DL. 2005. Intracellular and extracellular PGPR: commonalities and distinctions in the plant–bacterium signalling processes. Soil Biol. Biochem. 37:395-412.
Guardia G, Cangani MT, Andreu G, Sanz-Cobena A, García-Marco S, Álvarez JM, Recio-Huetos J, Vallejo A. 2017. Effect of inhibitors and fertigation strategies on GHG emissions, NO fluxes and yield in irrigated maize. Field Crops Res. 204:135-45.
Guardia G, Marsden KA, Vallejo A, Jones DL, Chadwick DR. 2018. Determining the influence of environmental and edaphic factors on the fate of the nitrification inhibitors DCD and DMPP in soil. Sci. Total Environ. 624:1202-12.
Guimarães GG, Klaic R, Giroto AS, Majaron VF, Avansi Jr W, Farinas CS, Ribeiro C. 2018. Smart fertilization based on sulfur–phosphate composites: synergy among materials in a structure with multiple fertilization roles. ACS Sustain. Chem. Eng. 6:12187-96.
Guo YP, Wang HJ, Guo YJ, Guo LH, Chu LF, Guo CX. 2011. Fabrication and characterization of hierarchical ZSM-5 zeolites by using organosilanes as additives. Chem. Eng. J 166:391-400.
Haderlein L, Jensen TL, Dowbenko RE, Blaylock AD. 2001. Controlled release urea as a nitrogen source for spring wheat in western Canada: Yield, grain N content, and N use efficiency. Sci. World J. 1:114-21.
Halvorson AD, Del Grosso SJ, Stewart CE. 2016. Manure and inorganic nitrogen affect trace gas emissions under semi-arid irrigated corn. J. Environ. Qual. 45:906-14.
Halvorson AD, Del Grosso SJ. 2013. Nitrogen placement and source effects on nitrous oxide emissions and yields of irrigated corn. J. Environ. Qual. 42:312-22.
Han Y, Chen S, Yang M, Zou H, Zhang Y. 2020. Inorganic matter modified water-based copolymer prepared by chitosan-starch-CMC-Na-PVAL as an environment-friendly coating material. Carbohydr. Polym. 234:115925.
Harder Nielsen T, Bonde TA, Sørensen J. 1998. Significance of microbial urea turnover in N cycling of three Danish agricultural soils. FEMS Microbiol. Ecol. 25:147-57.
Harman GE. 2000. Myths and dogmas of biocontrol changes in perceptions derived from research on Trichoderma harzinum T-22. Plant Dis. 84:377-93.
Henke CR. 2000. Making a place for science: The field trial. Soc. Stud. Sci. 30:483-511.
Hergert GR, Ferguson C, Wortmann C, Shapiro C, Shaver T. 2011. Enhanced efficiency fertilizers: will they enhance my fertilizer efficiency. Proceedings of the 3rd Annual Crop Production Clinics, University of Nebraska-Lincoln Extension, United States.
Hoefler R, González-Barrios P, Bhatta M, Nunes JAR, Berro I, Nalin RS, Borges A, Covarrubias E, Diaz-Garcia L, Quincke M, Gutierrez L. 2020. Do spatial designs outperform classic experimental designs? J. Agric. Biol. Environ. Stat. 25:523-52.
Hou P, Li G, Wang S, Jin X, Yang Y, Chen X, Ding C, Liu Z, Ding Y. 2013. Methane emissions from rice fields under continuous straw return in the middle-lower reaches of the Yangtze River. J. Environ. Sci. 25:1874-81.
Hric P, Jančovič J, Kovár P, Vozár Ľ. 2016. The effect of varying speed release of nutrients from fertilizers on growth-production process of turf. Acta Univ. Agric. Silvic. Mendel. Brun. 64:441-7.
Hu F, Zhao C, Feng F, Chai Q, Mu Y, Zhang Y. 2017. Improving N management through intercropping alleviates the inhibitory effect of mineral N on nodulation in pea. Plant Soil 412:235-51.
Hu XK, Su F, Ju XT, Gao B, Oenema O, Christie P, Huang BX, Jiang RF, Zhang FS. 2013. Greenhouse gas emissions from a wheat–maize double cropping system with different nitrogen fertilization regimes. Environ. Pollut. 176:198-207.
Hummel Jr NW, Waddington DV. 1984. Sulfur-coated urea for turfgrass fertilization. Soil Sci. Soc. Am. J. 48:191-5.
Ibrahim KA, Naz MY, Shukrullah S, Sulaiman SA, Ghaffar A, AbdEl-Salam NM. 2020. Nitrogen pollution impact and remediation through low cost starch based biodegradable polymers. Sci. Rep. 10: 5927.
Irfan SA, Razali R, KuShaari K, Mansor N, Azeem B, Versypt ANF. 2018. A review of mathematical modeling and simulation of controlled-release fertilizers. J. Control. Release 271:45-54.
Jahangirian H, Rafiee-Moghaddam R, Jahangirian N, Nikpey B, Jahangirian S, Bassous N, Saleh B, Kalantari K, Webster TJ. 2020. Green synthesis of zeolite/Fe_2O_3 nanocomposites: toxicity & cell proliferation assays and application as a smart iron nanofertilizer. International Journal of Nanomedicine, 15:1005-20.
Jang JR, Hong EM, Song I, Kang MS, Cho JY, Cho YK. 2016. Impact of Different Fertilizer Types on Nutrient Pollutant Loads from Rice Paddy Fields in South Korea. Irrig. Drain. 65:105-11.
Jarosiewicz A, Tomaszewska M. 2003. Controlled-release NPK fertilizer encapsulated by polymeric membranes. J. Agric. Food Chem. 51:413-7.
Jha Y. 2017. Potassium mobilizing bacteria: enhance potassium intake in paddy to regulates membrane permeability and accumulate carbohydrates under salinity stress. Braz. J. Biol. Sci. 4:333-44.
Ji Y, Liu G, Ma J, Zhang G, Xu H, Yagi K. 2013. Effect of controlled-release fertilizer on mitigation of N_2O emission from paddy field in South China: a multi-year field observation. Plant Soil 371:473-86.
Jiao X, Liang W, Chen L, Zhang H, Li Q, Wang P, Wen D. 2005. Effects of slow-release urea fertilizers on urease activity, microbial biomass, and nematode communities in an aquic brown soil. Sci. China Life Sci. 48:26.
Kabala C, Karczewska A, Gałka B, Cuske M, Sowiński J. 2017. Seasonal dynamics of nitrate and ammonium ion concentrations in soil solutions collected using MacroRhizon suction cups. Environ. Monit. Assess. 189:304.
Kah M, Kookana RS, Gogos A, Bucheli TD. 2018. A critical evaluation of nanopesticides and nanofertilizers against their conventional analogues. Nat. Nanotechnol. 13:677-84.
Kalia A, Sharma SP, Kaur H. 2019. Nanoscale fertilizers: har-

nessing boons for enhanced nutrient use efficiency and crop productivity. In: K.A. Abd-Elsalam, R. Prasad, (eds.) Nanobiotechnology Applications in Plant Protection. Springer, Cham, Switzerland, pp 191-208.

Khan MS, Zaidi A, Wani PA. 2009. Role of phosphate-solubilizing microorganisms in sustainable agriculture-a review. Agron. Sustain. Dev. 27:29-43.

Kandil EE, Abdelsalam NR, Aziz AAAE, Ali HM, Siddiqui MH. 2020. Efficacy of nanofertilizer, fulvic acid and boron fertilizer on sugar beet (Beta vulgaris L.) yield and quality. Sugar Tech 22:782–91.

Kang SM, Waqas M, Shahzad R, You YH, Asaf S, Khan MA, Lee KE, Joo GJ, Kim SJ, Lee IJ. 2017. Isolation and characterization of a novel silicate-solubilizing bacterial strain Burkholderia eburnea CS4-2 that promotes growth of japonica rice (Oryza sativa L. cv. Dongjin). J. Soil Sci. Plant Nutr. 63:233-41.

Kiss S, Simihăian M. 2002. Effect of soil urease inhibitors on germination, growth, and yield of plants. In: S. Kiss, M. Simihăian (eds.) Improving efficiency of urea fertilizers by inhibition of soil urease activity. Springer, Dordrecht, pp 251-319.

Klaic R, Giroto AS, Guimarães GG, Plotegher F, Ribeiro C, Zangirolami TC, Farinas CS. 2018. Nanocomposite of starch-phosphate rock bioactivated for environmentally-friendly fertilization. Miner. Eng. 128:230-7.

Kloepper JW, Schroth MN. 1978. Plant growth-promoting rhizobacteria on radishes. Proceedings of the 4th International Conference on Plant Pathogenic Bacteria, Gilbert-Clarey, Tours, France, pp. 879–82.

Knight EC, Guertal EA, Wood CW. 2007. Mowing and nitrogen source effects on ammonia volatilization from turfgrass. Crop Sci. 47:1628-34.

Knijnenburg JT, Hilty FM, Oelofse J, Buitendag R, Zimmermann MB, Cakmak I, Grobler AF. 2018. Nano- and Pheroid technologies for development of foliar iron fertilizers and iron biofortification of soybean grown in South Africa. Chem. Biol. Technol. Agric. 5:26.

Kudoyarova GR, Vysotskaya LB, Arkhipova TN, Kuzmina LY, Galimsyanova NF, Sidorova LV, Gabbasova IM, Melentiev AI, Veselov SY. 2017. Effect of auxin producing and phosphate solubilizing bacteria on mobility of soil phosphorus, growth rate, and P acquisition by wheat plants. Acta Physiol. Plant. 39:253.

Kumar D, Devakumar C, Kumar R, Das A, Panneerselvam P, Shivay YS. 2010. Effect of neem-oil coated prilled urea with varying thickness of neem-oil coating and nitrogen rates on productivity and nitrogen-use efficiency of lowland irrigated rice under Indo-Gangetic plains. J. Plant Nutr. 33:1939-59.

Kumar M, Bauddh K, Sainger M, Sainger PA, Singh RP. 2015. Enhancing efficacy of Azotobacter and Bacillus by entrapping in organic matrix for rice cultivation. Agroecol. Sustain. Food Syst. 39:907-23.

Kumar S, Bauddh K, Barman SC, Singh RP. 2014. Organic matrix entrapped bio-fertilizers increase growth, productivity, and yield of Triticum aestivum L. and transport of NO_3^-, NO_2^-, NH_4^+ and PO_4^{-3} from soil to plant leaves. J. Agr. Sci. Tech. 16:315-29.

Kumar V. 2014. Characterization, bio-formulation development and shelf-life studies of locally isolated bio-fertilizer strains. Oct. Jour. Env. Res. 2:32-37.

Latef AAHA, Hashem A, Rasool S, Abd Allah EF, Alqarawi AA, Egamberdieva D, Jan S, Anjum NA Ahmad P. 2016. Arbuscular mycorrhizal symbiosis and abiotic stress in plants: a review. J. Plant Biol. 59:407-26.

Lemaire G, Ciampitti I. 2020. Crop mass and N status as prerequisite covariables for unraveling nitrogen use efficiency across genotype-by-environment-by-management scenarios: a review. Plants 9:1309.

León-Silva S, Arrieta-Cortes R, Fernández-Luqueño F, López-Valdez F. 2018. Design and production of nanofertilizers. In: F. López-Valdez, F. Fernández-Luqueño (eds.) Agricultural Nanobiotechnology. Springer, Cham, Switzerland, pp 17-31.

Li M, Yang JT, Yan LY, Shi Y. 2014. The effects of different amounts of controlled release fertilizer on the root growth and the filling rate in winter wheat. Adv. J. Food Sci. Technol. 6:358-61.

Li P, Lu J, Hou W, Pan Y, Wang Y, Khan MR, Ren T, Cong R, Li, X. 2017. Reducing nitrogen losses through ammonia volatilization and surface runoff to improve apparent nitrogen recovery of double cropping of late rice using controlled release urea. Environ. Sci. Pollut. Res. 24:11722-33.

Li Z, Liu Z, Zhang M, Li C, Li YC, Wan Y, Martin CG. 2020. Long-term effects of controlled-release potassium chloride on soil available potassium, nutrient absorption and yield of maize plants. Soil Till. Res. 196:104438.

Lin D, Xing B. 2007. Phytotoxicity of nanoparticles: inhibition of seed germination and root growth. Environ. Pollut. 150:243-50.

Liu CH, Wu JY, Chang JS. 2008. Diffusion characteristics and controlled release of bacterial fertilizers from modified calcium alginate capsules. Bioresour. Technol. 99:1904-10.

Liu G, Zotarelli L, Li Y, Dinkins D, Wang Q, Ozores-Hampton M. 2014. Controlled-release and slow-release fertilizers as nutrient management tools. USA: US Department of Agriculture, UF/IFAS Extension Service, University of Florida, IFAS.

Liu X, Chen L, Hua Z, Mei S, Wang P, Wang S. 2020. Comparing ammonia volatilization between conventional and slow-release nitrogen fertilizers in paddy fields in the Taihu Lake region. Environ. Sci. Pollut. Res. 27:8386-94.

Lu P, Zhang M, Li C, Liu Z. 2012. Effect of acid-modified clay on the microstructure and performance of starch films. Polym. Plast. Technol. Eng. 51:1340-5.

Liu R, Lal R. 2015. Potentials of engineered nanoparticles as fertilizers for increasing agronomic productions. Sci. Total Environ. 514:131-9.

Lü S, Feng C, Gao C, Wang X, Xu X, Bai X, Gao N, Liu M. 2016. Multifunctional environmental smart fertilizer based on L-aspartic acid for sustained nutrient release. J. Agr. Food Chem. 64:4965-74.

Ma Y. 2019. Seed coating with beneficial microorganisms for precision agriculture. Biotechnol. Adv. 37:107423.

Mącik M, Gryta A, Frąc M. 2020. Biofertilizers in agriculture: An overview on concepts, strategies and effects on soil microorganisms. Adv. Agron. 162:31-87.

Maheshwari DK, Dubey RC, Agarwal M, Dheeman S, Aeron A, Bajpai VK. 2015. Carrier based formulations of biocoenotic consortia of disease suppressive Pseudomonas aeruginosa KRP1 and Bacillus licheniformis KRB1. Ecol. Eng. 81:2727.

Majeed Z, Ramli NK, Mansor N, Man Z. 2015. A comprehensive review on biodegradable polymers and their blends used in controlled-release fertilizer processes. Rev. Chem.

Eng. 31:69-95.
Malusá E, Sas-Paszt L, Ciesielska J. 2012. Technologies for beneficial microorganisms inocula used as biofertilizers. Sci. World J. 2012:491206
Mandlik R, Thakral V, Raturi G, Shinde S, Nikolić M, Tripathi DK, Sonah H, Deshmukh R. 2020. Significance of silicon uptake, transport, and deposition in plants. J. Exp. Bot. 71:6703-18.
Marchiol L. 2019. Nanofertilisers. An outlook of crop nutrition in the fourth agricultural revolution. Ital. J. Agron. 14:183-90.
Master Y, Laughlin RJ, Shavit U, Stevens RJ, Shaviv A. 2003. Gaseous nitrogen emissions and mineral nitrogen transformations as affected by reclaimed effluent application. J. Environ. Qual. 32:1204-11.
Mastronardi E, Tsae P, Zhang X, Monreal C, DeRosa MC. 2015. Strategic role of nanotechnology in fertilizers: potential and limitations. In: M. Rai, C. Ribeiro, L. Mattoso, N. Duran (eds.) Nanotechnologies in food and agriculture. Springer, Switzerland, Cham, pp 25-67.
Mehmood U, Inam-ul-Haq M, Saeed M, Altaf A, Azam F, Hayat S. 2018. A brief review on plant growth promoting rhizobacteria (PGPR): a key role in plant growth promotion. Plant Prot. 2:77-82.
Melia PM, Cundy AB, Sohi SP, Hooda PS, Busquets R. 2017. Trends in the recovery of phosphorus in bioavailable forms from wastewater. Chemosphere 186:381-95.
Menéndez S, Barrena I, Setien I, González-Murua C, Estavillo JM. 2012. Efficiency of nitrification inhibitor DMPP to reduce nitrous oxide emissions under different temperature and moisture conditions. Soil Biol. Biochem. 53:82-9.
Menezes-Blackburn D, Jorquera M, Gianfreda L, Rao M, Greiner R, Garrido E, Mora ML. 2011. Activity stabilization of Aspergillus niger and Escherichia coli phytases immobilized on allophanic synthetic compounds and montmorillonite nanoclays. Bioresour. Technol. 102:9360-7.
Menezes-Blackburn D, Jorquera MA, Gianfreda L, Greiner R, de la Luz Mora M. 2014. A novel phosphorus biofertilization strategy using cattle manure treated with phytase–nanoclay complexes. Biol. Fertil. Soils 50:583-92.
Mérigout P, Lelandais M, Bitton F, Renou J-P, Briand X, Meyer C, Daniel-Vedele F. 2008. Physiological and transcriptomic aspects of urea uptake and assimilation in Arabidopsis plants. Plant Physiol. 147:1225-38.
Mesias VSD, Agu ABS, Benablo PJL, Chen CH, Penaloza Jr DP. 2019. Coated NPK fertilizer based on citric acid-crosslinked chitosan/alginate encapsulant. J. Ecol. Eng. 20:1-12.
Metz B, Davidson OR, Bosch PR, Dave R, Meyer LA. 2007. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, 2007 Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
Mijwel AK, Jassim HM. 2018. Effect of organic remnants compost and bioactiv fertilizer on growth and yield of potato. Plant Arch. 18:2389-97.
Mira AB, Cantarella H, Souza-Netto GJM, Moreira LA, Kamogawa MY, Otto R. 2017. Optimizing urease inhibitor usage to reduce ammonia emission following urea application over crop residues. Agric. Ecosyst. Environ. 248:105-12.
Modolo LV, da-Silva CJ, Brandão DS, Chaves IS. 2018. A mini review on what we have learned about urease inhibitors of agricultural interest since mid-2000s. J. Adv. Res. 13:29-37.
Modolo LV, de Souza AX, Horta LP, Araujo DP, de Fatima A. 2015. An overview on the potential of natural products as ureases inhibitors: A review. J. Adv. Res. 6:35-44.
Mohammad Ghasemi V, Siavash Moghaddam S, Rahimi A, Pourakbar L, Popović-Djordjević J. 2020. Winter cultivation and nano fertilizers improve yield components and antioxidant traits of Dragon's Head (Lallemantia iberica (MB) Fischer & Meyer). Plants 9:252.
Mohanty S, Swain CK, Sethi SK, Dalai PC, Bhattachrayya P, Kumar A, Tripathi R, Shahid M, Panda BB, Kumar U, Lal B, Gautam P, Munda S, Nayak AK 2017. Crop establishment and nitrogen management affect greenhouse gas emission and biological activity in tropical rice production. Ecol. Eng. 104:80-98.
Monreal CM, DeRosa M, Mallubhotla SC, Bindraban PS, Dimkpa C. 2016.Nanotechnologies for increasing the crop use efficiency of fertilizer-micronutrients. Biol. Fertil. Soils 52:423-37.
Nash P, Nelson K, Motavalli P. 2015. Reducing nitrogen loss with managed drainage and polymer-coated urea. J. Environ. Qual. 44:256-64.
Nassal D, Spohn M, Eltlbany N, Jacquiod S, Smalla K, Marhan S, Kandeler E. 2018. Effects of phosphorus-mobilizing bacteria on tomato growth and soil microbial activity. Plant Soil 427:17-37.
Naz MY, Sulaiman SA. 2016. Slow release coating remedy for nitrogen loss from conventional urea: a review. J. Control. Release 225:109-20.
Nazari M, Smith DL. 2020. A PGPR-Produced bacteriocin for sustainable agriculture: a review of thuricin 17 characteristics and applications. Front Plant Sci. 11:916.
Nisar S, Shehzad MR, Rafiq M, Kousar S, Abdul H. 2017. Production of clay polymers for fertilizer coating. Int. J. Chem. Biochem. Sci. 12:122-9.
Nogueira V, Lopes I, Rocha-Santos T, Santos AL, Rasteiro GM, Antunes F, Gonçalves F, Soares AMVM, Cunha A, Almeida A, Gomes NNCM, Pereira R. 2012. Impact of organic and inorganic nanomaterials in the soil microbial community structure. Sci. Total Environ. 424:344-50
Norton JM, Ouyang Y. 2019. Controls and adaptive management of nitrification in agricultural soils. Front. Microbiol. 10:1931.
Pahl-Wostl C. 2009. A conceptual framework for analysing adaptive capacity and multi-level learningprocesses in resource governance regimes. Glob. Environ. Change19:354-65
Pampana S, Masoni A, Mariotti M, Ercoli L, Arduini I. 2018. Nitrogen fixation of grain legumes differs in response to nitrogen fertilisation. Exp. Agric. 54:66.
Parihar M, Rakshit A., Meena VS, Gupta VK, Rana K, Choudhary M., Tiwari G, Mishra PK, Pattanayak A, Bisht JK, Jatav SS, Khati P., Jatav HS. 2020. The potential of arbuscular mycorrhizal fungi in C cycling: a review. Arch. Microbiol. 202:1581-96.
Parniske M. 2008. Arbuscular mycorrhiza: the mother of plant root endosymbioses. Nat. Rev. Microbiol. 6:763-75.
Pohshna C, Mailapalli DR, Laha T. 2020. Synthesis of Nanofertilizers by Planetary Ball Milling. In: E. Lichtfouse (ed.) Sustainable agriculture reviews. Springer, Cham, Switzerland, pp 75-112.
Pollock KM. 1988. Grass establishment and performance on a high country soil fertilised with nitrogen. New Zealand J.

Agric. Res. 32:7-15.

Porcel R, Aroca R, Ruiz-Lozano JM. 2012. Salinity stress alleviation using arbuscular mycorrhizal fungi. A review. Agron. Sustain. Dev. 32:181-200.

Prasad R, Pandey R, Barman I. 2016. Engineering tailored nanoparticles with microbes: quo vadis? WIREs Nanomed. Nanobiotechnol. 8:316-30.

Premanandh J. 2011. Factors affecting food security and contribution of modern technologies in food sustainability. J. Sci. Food Agric. 91:2707-14.

Pulat M, Yoltay N. 2016. Smart fertilizers: preparation and characterization of gelatin-based hydrogels for controlled release of MAP and AN fertilizers. Agrochimica 60:249-61.

Qiao J, Yu X, Liang X, Liu Y, Borriss R, Liu Y. 2017. Addition of plant-growth-promoting Bacillus subtilis PTS-394 on tomato rhizosphere has no durable impact on composition of root microbiome. BMC Microbiol. 17:131.

Rai A, Kumar S, Bauddh K, Singh N, Singh RP. 2017. Improvement in growth and alkaloid content of Rauwolfia serpentina on application of organic matrix entrapped biofertilizers (Azotobacter chroococcum, Azospirillum brasilense and Pseudomonas putida). J. Plant Nutr. 40:2237-47.

Rajan M, Shahena S, Chandran V, Mathew L. 2021. Controlled release of fertilizers—concept, reality, and mechanism. In: F.B. Lewu, T. Volova, S. Thomas, K.R. Rakhimol (eds.) Controlled release fertilizers for sustainable agriculture. Academic Press, pp 41-56.

Raliya R, Saharan V, Dimkpa C, Biswas P. 2017. Nanofertilizer for precision and sustainable agriculture: current state and future perspectives. J. Agric. Food Chem. 66:6487-503.

Ramesh A, Sharma SK, Joshi OP, Khan IR. 2011. Phytase, phosphatase activity and P-nutrition of soybean as influenced by inoculation of Bacillus. Indian J. Microbiol. 51:94-9.

Ramli RA. 2019. Slow release fertilizer hydrogels: a review. Polym. Chem. 10:6073-90.

Rao JK, Thompson JA, Sastry PVSS, Giller KE, Day JM. 1987. Measurement of N_2-fixation in field-grown pigeonpea [Cajanus cajan (L.) Millsp.] using ^{15}N-labelled fertilizer. Plant Soil 101:107-13.

Rawluk CDL, Grant CA, Racz GJ. 2001. Ammonia volatilization from soils fertilized with urea and varying rates of urease inhibitor NBPT. Can. J. Soil Sci. 81:239-46.

Real-Guerra R, Stanisçuaski F, Carlini CR. 2013. Soybean urease: over a hundred years of knowledge. In: J.E. Board (ed.), A comprehensive survey of international soybean research – Genetics, physiology, agronomy and nitrogen relationships, InTech, Croatia, pp 317-40.

Reay DS, Davidson EA, Smith KA, Smith P, Melillo JM, Dentener F, Crutzen PJ. 2012. Global agriculture and nitrous oxide emissions. Nat Clim Change 2:410–6

Rindt DW, Blouin GM, Getsinger JG. 1968. Sulfur coating on nitrogen fertilizer to reduce dissolution rate. J. Agric. Food Chem. 16:773-8.

Robbins J. 2005. Slow-release fertilizers as tools. IFA International Workshop on Enhanced-Efficiency Fertilizers. Frankfurt, Germany, 28–39 June 2005.

Rodrigues JM, Lasa B, Aparicio-Tejo PM, González-Murua C, Marino D. 2018. 3, 4-Dimethylpyrazole phosphate and 2-(N-3, 4-dimethyl-1H-pyrazol-1-yl) succinic acid isomeric mixture nitrification inhibitors: quantification in plant tissues and toxicity assays. Sci. Total Environ. 624:1180-6.

Saber WIA, Ghanem KM, El-Hersh MS. 2009. Rock phosphate solubilization by two isolates of Aspergillus niger and Penicillium sp. and their promotion to mung bean plants. Res. J. Microbiol. 4:235-50.

Sahai P, Sinha VB, Dutta R. 2019. Bioformulation and nanotechnology in pesticide and fertilizer delivery system for eco-friendly agriculture: a review. Sci. Agric. 3:2-10.

Saleh K, Steinmetz D, Hemati M. 2003. Experimental study and modeling of fluidized bed coating and agglomeration. Powder Technol. 130:116-23.

Sanderson KR, Fillmore SAE. 2012. Slow-release nitrogen fertilizer in carrot production on Prince Edward Island. Can. J. Plant Sci. 92:1223-8.

Santi LP, Goenadi DH. 2017. Solubilization of silicatefrom quartz mineral by potential silicate solubilizing bacteria. Menara Perkebunan 85:95-104.

Saranya K, Krishnan PS, Kumutha K, French J. 2011. Potential for biochar as an alternate carrier to lignite for the preparation of biofertilizers in India. Int. J. Agric. Environ. Biotechnol. 4:167-72.

Sarkar S, Datta SC, Biswas DR. 2014. Synthesis and characterization of nanoclay–polymer composites from soil clay with respect to their water-holding capacities and nutrient-release behaviour. J. Appl. Polym. Sci. 131:39951.

Sattar A, Naveed M, Ali M, Zahir ZA, Nadeem SM, Yaseen M, Meena VS, Farooq M, Singh R, Rahman M, Meena HN. 2019. Perspectives of potassium solubilizing microbes in sustainable food production system: A review. Appl. Soil Ecol. 133:146-59.

Schneider KD, Van Straaten P, De Orduña RM, Glasauer S, Trevors J, Fallow D, Smith PS. 2010. Comparing phosphorus mobilization strategies using Aspergillus niger for the mineral dissolution of three phosphate rocks. J. Appl. Microbiol. 108:366-74.

Scott N, Chen H. 2013. Nanoscale science and engineering for agriculture and food systems. Ind. Biotechnol. 9:17-8.

Senna AM, Botaro VR. 2017. Biodegradable hydrogel derived from cellulose acetate and EDTA as a reduction substrate of leaching NPK compound fertilizer and water retention in soil. J. Control. Release 260:194-201.

Shan L, He Y, Chen J, Huang Q, Lian X, Wang H, Liu Y. 2015b. Nitrogen surface runoff losses from a Chinese cabbage field under different nitrogen treatments in the Taihu Lake Basin, China. Agric. Water Manag. 159:255-63.

Shan L, He Y, Chen J, Huang Q, Wang H. 2015a. Ammonia volatilization from a Chinese cabbage field under different nitrogen treatments in the Taihu Lake Basin, China. J. Environ. Sci. 38:14-23.

Shaviv A, Mikkelsen RL. 1993. Controlled-release fertilizers to increase efficiency of nutrient use and minimize environmental degradation-A review. Fert. Res. 35:1-12.

Shaviv A, Raban S, Zaidel E. 2001. Modeling controlled nutrient release from polymer coated fertilizers: Diffusion release from single granules. Environ. Sci. Technol. 37:2251-6.

Shaviv A. 2000. Advances in controlled release fertilizers. Adv. Agron. 71:1-49.

Shen Y, Zhou J, Du C. 2019. Development of a polyacrylate/silica nanoparticle hybrid emulsion for delaying nutrient release in coated controlled-release urea. Coatings 9:88.

Shi N, Zhang Y, Li Y, Luo J, Gao X, Jing Y, Bo L. 2018. Water pollution risk from nitrate migration in the soil profile as affected by fertilization in a wheat-maize rotation system.

Agric. Water Manag. 210:124-9.
Shitole AV, Gade RM, Bandgar MS, Wavare SH, Belkar YK. 2014. Utilization of spent mushroom substrate as carrier for biocontrol agent and biofertilizer. Bioscan 9:271-5.
Shoji S. 2005. Innovative use of controlled availability fertilizers with high performance for intensive agriculture and environmental conservation. Sci. China Life Sci. 48:912-20.
Shrivastava M, Srivastava PC, D'Souza SF. 2018. Phosphate-solubilizing microbes: diversity and phosphates solubilization mechanism. In: V. Meena (ed.) Role of rhizospheric microbes in soil. Springer, Singapore pp 137-165.
Silva AG, Sequeira CH, Sermarini RA., Otto R. 2017. Urease inhibitor NBPT on ammonia volatilization and crop productivity: A meta-analysis. Agron. J. 109:1-13.
Singh B, Satyanarayana T. 2012. Plant growth promotion by phytases and phytase-producing microbes due to amelioration in phosphorus availability. In: T. Satyanarayana, B.N. Johri, A. Prakash (eds.) Microorganisms in sustainable agriculture and biotechnology. Springer, Dordrecht pp 3-15.
Sivasakthi S, Usharani G, Saranraj P. 2014. Biocontrol potentiality of plant growth promoting bacteria (PGPR)-Pseudomonas fluorescens and Bacillus subtilis: a review. Afr. J. Agric. Res. 9:1265-77.
Sofo A, Scopa A, Manfra M, De Nisco M, Tenore G, Troisi J, Di Fiori R, Novellino E. 2011. Trichoderma harzianum strain T-22 induces changes in phytohormone levels in cherry rootstocks (Prunus cerasus × P. canescens). Plant Growth Regul. 65:421-5.
Souza CF, Faez R, Bacalhau FB, Bacarin MF, Pereira TS. 2017. In situ monitoring of a controlled release of fertilizers in lettuce crop. Eng. Agríc. 37:656-64.
Steiner C, Garcia M, Zech W. 2009 Effects of charcoal as slow release nutrient carrier on n-p-k dynamics and soil microbial population: pot experiments with ferralsol substrate. In: W.I. Woods, W.G. Teixeira, J. Lehmann, C. Steiner, A. WinklerPrins, L. Rebellato (eds.) Amazonian Dark Earths: Wim Sombroek's Vision. Springer, Berlin, pp 325-38.
Suganya A, Saravanan A, Manivannan N. 2020. Role of zinc nutrition for increasing zinc availability, uptake, yield, and quality of maize (Zea mays L.) grains: An overview. Commun. Soil Sci. Plant Anal. 51:2001-21.
Sun H, Zhang H, Min J, Feng Y, Shi W. 2016. Controlled-release fertilizer, floating duckweed, and biochar affect ammonia volatilization and nitrous oxide emission from rice paddy fields irrigated with nitrogen-rich wastewater. Paddy Water Environ. 14:105-11.
Sun H, Zhou S, Zhang J, Zhang X, Wang C. 2020. Year-to-year climate variability affects methane emission from paddy fields under irrigated conditions. Environ. Sci. Pollut. Res. 27:14780–9.
Surendhiran D, Cui H, Lin L. 2020. Mode of transfer, toxicity and negative impacts of engineered nanoparticles on environment, human and animal health. In: C.M. Hussain (ed.) The ELSI handbook of nanotechnology, pp 165-204.
Suresh BG, Kumari S, Singh AK, Singla A, Paul A, Masih S, Masih H. 2018. Bio-formulation of halotolerant phosphate solubilizing Enterobacter cloacae HFZ-H4 strain to screen different carrier materials and their shelf life Study. Int. J. Curr. Microbiol. App. Sci 7:2373-80.
Taghizadeh Y, Jalilian J, Moghaddam SS. 2019. Do Fertilizers and Irrigation Disruption Change Some Physiological Traits of Safflower? J. Plant Growth Regul. 38:1439-48.
Taimooz SH. 2018. Behavior of some nanomaterials in improving the growth of onion plant, Allium cepa and its effect on Pythium aphanidermatum. Plant Arch. 18:857-62.
Tao S, Liu J, Jin K, Qiu X, Zhang Y, Ren X, Hu S. 2011. Preparation and characterization of triple polymer-coated controlled-release urea with water-retention property and enhanced durability. J. Appl. Polym. Sci. 120:2103-11.
Tewari S, Sharma S. 2020. Rhizobial exopolysaccharides as supplement for enhancing nodulation and growth attributes of Cajanus cajan under multi-stress conditions: A study from lab to field. Soil Till. Res. 198:104545.
Thompson H. 2012. Food science deserves a place at the table – US agricultural research chief aims to raise the profile of farming and nutrition science. Nature, Available online: https://www.nature.com/news/food-science-deserves-a-place-at-the-table-1.10963 (accessed on 23 Novembre 2020).
Tilman D, Socolow, R, Foley, J A, Hill, J, Larson, E, Lynd, L, Pacala S, Reilly J, Searchinger T, Somerville C, Williams R. 2009. Beneficial biofuels—the food, energy, and environment trilemma. Science 325:270-1.
Timilsena YP, Adhikari R, Casey P, Muster T, Gill H, Adhikari B. 2015. Enhanced efficiency fertilisers: a review of formulation and nutrient release patterns. J. Sci. Food Agric. 95:1131-42.
Treinyte J, Grazuleviciene V, Paleckiene R, Ostrauskaite J, Cesoniene L. 2018. Biodegradable polymer composites as coating materials for granular fertilizers. J. Polym. Environ. 26:543-54.
Trenkel ME. 1997. Controlled-release and stabilized fertilizers in agriculture. Paris: International Fertilizer Industry Association.
Trenkel ME. 2010. Slow-and controlled-release and stabilized fertilizers: An option for enhancing nutrient use efficiency in agriculture in agriculture. Paris: International Fertilizer Industry Association (IFA).
Vejan P, Abdullah R, Khadiran T, Ismail S, Nasrulhaq Boyce A. 2016. Role of plant growth promoting rhizobacteria in agricultural sustainability—a review. Molecules 21:573.
Vempati RK, Hegde RS, Sloan JJ. 2011. U.S. Patent No. 8,034,147. Washington, DC: U.S. Patent and Trademark Office.
Vidyalakshmi R, Paranthaman R, Bhakyaraj R. 2009. Sulphur oxidizing bacteria and pulse nutrition - A review. World J. Agric. Sci. 5:270-8.
Wang J, Zhao Y, Zhang J, Zhao W, Müller C, Cai Z. 2017. Nitrification is the key process determining N use efficiency in paddy soils. J. Plant Nutr. Soil Sci. 180:648-58.
Wang Z, Xie X, Zhao J, Liu X, Feng W, White JC, Xing B. 2012. Xylem-and phloem-based transport of CuO nanoparticles in maize (Zea mays L.). Environ. Sci. Technol. 46:4434-41.
Xie L, Liu M, Ni B, Wang Y. 2012. New environment-friendly use of wheat straw in slow-release fertilizer formulations with the function of superabsorbent. Ind. Eng. Chem. Res. 51:3855-62.
Xie L, Liu M, Ni B, Zhang X, Wang Y. 2011. Slow-release nitrogen and boron fertilizer from a functional superabsorbent formulation based on wheat straw and attapulgite. Chem. Eng. J. 167:342-8.
Yang G, Ji H, Liu H, Zhang Y, Chen L, Zheng J, Guo Z, Sheng J. 2020. Assessment of productivity, nutrient uptake and economic benefits of rice under different nitrogen manage-

ment strategies. PeerJ 8:e9596.
Yang S, Peng S, Xu J, He Y, Wang Y. 2015. Effects of water saving irrigation and controlled release nitrogen fertilizer managements on nitrogen losses from paddy fields. Paddy Water Environ. 13:71-80
Yang Y, He C, Huang L, Ban Y, Tang M. 2017. The effects of arbuscular mycorrhizal fungi on glomalin-related soil protein distribution, aggregate stability and their relationships with soil properties at different soil depths in lead-zinc contaminated area. PloS one 12:e0182264.
Ye Y, Liang X, Chen Y, Liu J, Gu J, Guo R, Li L. 2013. Alternate wetting and drying irrigation and controlled-release nitrogen fertilizer in late-season rice. Effects on dry matter accumulation, yield, water and nitrogen use. Field Crop. Res. 144:212-24.
Zanin L, Tomasi N, Zamboni A, Varanini Z, Pinton R. 2015. The urease inhibitor NBPT negatively affects DUR3-mediated uptake and assimilation of urea in maize roots. Front. Plant Sci. 6:1007.
Zhang J, Chen H, Wang A. 2006. Study on superabsorbent composite. IV. Effects of organification degree of attapulgite on swelling behaviors of polyacrylamide/organo-attapulgite composites. Eur. Polym. J. 42:101-8.
Zhang S, Yang Y, Gao B, Wan Y, Li YC, Zhao C. 2016. Bio-based interpenetrating network polymer composites from locust sawdust as coating material for environmentally friendly controlled-release urea fertilizers. J. Agric. Food Chem. 64:5692-700.
Zhao B, Dong S, Zhang J, Liu P. 2013. Effects of controlled-release fertiliser on nitrogen use efficiency in summer maize. PLoS One 8:e70569.
Zhou T, Wang Y, Huang S, Zhao Y. 2018. Synthesis composite hydrogels from inorganic-organic hybrids based on leftover rice for environment-friendly controlled-release urea fertilizers. Sci. Total Environ. 615:422-30.
Zulfiqar F, Navarro M, Ashraf M, Akram NA, Munné-Bosch S. 2019. Nanofertilizer use for sustainable agriculture: advantages and limitations. Plant Sci. 289:110270.
Zvomuya F, Rosen CJ. 2001. Evaluation of polyolefin-coated urea for potato production on a sandy soil. HortScience 36:1057-60.