



Review

Emerging and Established Technologies to Increase Nitrogen Use Efficiency of Cereals

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Abstract: Nitrogen (N) fertilizers are one of the most expensive inputs in agricultural settings. Additionally, the loss of N increases costs, contributes to soil acidification, and causes off-site pollution of the air, groundwater and waterways. This study reviews current knowledge about technologies for N fertilization with potential to increase N use efficiency and reduce its negative effects on the environment. Classic inorganic sources such as urea and ammonium sulfate are the major sources utilized, while controlled N release fertilizers have not been significantly adopted for cereals and oil crops. Microorganisms, with the exception of *Rhizobium* sp. in soybeans, are also not widely used nowadays (e.g., plant growth-promoting bacteria and cyanobacteria). The interest in implementing new N fertilization knowledge is stimulating the development of sensors to diagnose the N status and decision support systems for integrating several variables to optimize sources, rates and methods of application. Among potential new technologies we identified the incipient development of nanofertilizers, nutrient formulations to coat seeds, and recycled nutrients. Furthermore, increasing concern about the environmental consequences of N may facilitate the implementation of innovations outside the farm such as more effective regulations to guide N fertilization and methods to manufacture N fertilizers that are more energy-efficient and less CO₂ equivalent emitting.

Keywords: nitrogen use efficiency; nanofertilizers; recycled fertilizers; slow N released fertilizers

1. Introduction

Nitrogen (N) availability is the primary nutrient limitation for both the total food supply and protein content in food [1–3]. Nitrogen availability, uptake and translocation affects basic physiological functions associated with biomass production and grain yield [4,5]. Four major roles of N regarding the production of biomass and grain of cereals have been identified: (i) the establishment of photosynthetic capacity and photosynthetic activity [6–10]; (ii) the maintenance of photosynthetic activity [4,11–18]; (iii) the establishment and maintenance of sink capacity (the number and size of seeds) [16–18]; and (iv) diverse effects on the quality of crop products [19]. As a result of these effects, N is a fundamental

nutrient for agriculture and global food security, and N fertilizers are essential to achieve the production of food for a growing human population that this planet would not otherwise be able to support.

Nitrogen fertilizers are, however, expensive inputs in cereal cropping systems [20]. Therefore, the ultimate goal of a farmer is that the target crop takes up the applied N with the maximum efficiency. Fertilizer N recovery depends on the crop, environmental conditions, and management technology; it ranges from 35% to 65% for cereals around the world (Table 1). A global outlook of major crops show that barley has the highest efficiencies recovering the applied N, while rice show the lowest ones (Table 1). In addition, the global use of fertilizers is highly unbalanced: over-fertilization occurs in North America, Western Europe, China, and India, causing environmental pollution, while underutilization in Africa and parts of Latin America [21] causes so-called “soil mining”; *i.e.*, the depletion of nutrients from the soil. Within the same country, whether there is over- or sub-fertilization depends also on the crop and the region; for example, in Argentina, the N balance associated with wheat cropping is neutral while maize cropping is associated with a negative balance [22]. Switzerland, in contrast, is an example of how regulations contributed to change from over-fertilization to a neutral N balance [23], and maize in USA is another success story associated with an increased nitrogen use efficiency (NUE); maize grain yield increased significantly during the last two decades while fertilizer application rate stayed approximately constant. Fertilizer utilization comes at an environmental cost: the loss of N contributes to soil acidification, and causes off-site pollution of the air, groundwater and waterways. Detailed reviews about N losses and its environmental consequences exist elsewhere [24,25].

The essentiality of fertilizers to secure sufficient food and the need to reduce its environmental consequences, placed the focus on NUE. This goal calls for the development of new technologies. Here, we will review the current knowledge regarding technologies to supply N fertilizers while increasing NUE and controlling the environmental problems resulting from N fertilization. We consider NUE as defined by Good *et al.* [26]; *i.e.*, as the ratio between output (harvested organ) and N input (N supplied in fertilizers and/or residual N in the soil). The range of technologies and agronomic practices that will be reviewed here will have a main focus on cereal production.

Table 1. Outlook of agronomic efficiency and N recovery of major crops around the world.

Crop	Agronomic Efficiency (kg grain/kg N)	N Recovery %	Reference
Barley	9	63	Delogu <i>et al.</i> [27]
Maize	20–50	37	Rimski-Korsakov <i>et al.</i> [28]
Oilseed rape	17	50	Rathke <i>et al.</i> [29]
Rice	10–30	30–40	Cassman <i>et al.</i> [20]
Grain sorghum	5–12	55–65	Varvel and Peterson [30]
Soybean	14	50	Varvel and Peterson [31]
Sunflower	22	51	Scheiner <i>et al.</i> [32]
Wheat	33	35–45	Cassman <i>et al.</i> [20]

2. Literature Review

2.1. Classic Fertilizer Sources

Organic fertilizers were the most popular N sources in the past. Their N content ranges between 1% and 3% and, as a consequence of their low N content, these sources must be applied at high rates (several tons per hectare). Manufactured fertilizers became important sources of N only in the last century. From 1860 to the early 1990s, anthropogenic N production globally increased from 15 to 156 Tg·Nyr⁻¹ [33]. Table 2 shows the main N sources used in the production of cereals [34,35].

Table 2. Nitrogen sources and their composition.

Source	Nitrogen Content (%)
Anhydrous ammonia	82
Aqua ammonia	20–25
Ammonium nitrate	33.5–34
Ammonium nitrate sulfate	26
Ammonium nitrate/lime	20.5
Ammonium sulfate	21
Ammonium thiosulfate	12
Urea-ammonium nitrate solution	28–32
Ammonium chloride	26
Urea	46
Monoammonium phosphate	10–11
Diammonium phosphate	18
Sodium nitrate	16
Potassium nitrate	13
Calcium nitrate	15.5
Calcium ammonium nitrate	21–27
Sulfur-coated urea	39
Urea-formaldehyde	38

Among inorganic fertilizers, anhydrous ammonia contains the highest concentration of N (>80%, Table 2), which constitutes the major advantage of using this source. In addition, it has a low cost in several countries. As it is a gas and must be pressurized for storage and handled as a liquid, it requires specialized equipment for storage, handling, and application. In addition, the effect on soil pH produced by this source might require lime to maintain a desired soil pH. This later effect is not exclusively from anhydrous ammonia but from all ammoniacal sources.

Aqua ammonia (ammonium hydroxide) is composed of 25% to 29% of NH_3 by weight. Transportation limits aqua NH_3 production to small, local, and fluid fertilizer plants and since ammonia volatilizes quickly at temperatures above 10°C , it is usually injected into soil depths of 50 to 100 mm or applied on the surface and incorporated immediately with temperatures over 10°C .

Ammonium nitrate (NH_4NO_3), from an agronomic point of view, is an excellent fertilizer because it combines two different N forms. It was reported that it allows improving the baking quality of wheat [36]. However, its low N content compared to other sources makes the transportation, storage, and application more expensive per unit of N. Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) is a source of both N and S that can be advantageous for acid-requiring crops (e.g., rice) and in high-pH soils (while it is undesirable in acidic soils). The main disadvantage of ammonium sulfate is its relatively low N content (21% N) compared to other sources. However, ammonium sulfate is popular in many parts of the world, particularly in some rice-producing areas. Monoammonium ($\text{NH}_4\text{H}_2\text{PO}_4$) and diammonium ($(\text{NH}_4)_2\text{HPO}_4$) phosphates are more important P sources than N sources due to their relative low N concentration. The advantage of these globally popular fertilizers resides in their dual nutrient composition. Ammonium chloride (NH_4Cl) is a low N source highly used for rice in Japan, China, India, and Southeast Asia. Ammonium chloride is a suitable N source for chloride (Cl^-) responsive crops (e.g., cereals or coconut). Ammonium chloride, like ammonium sulfate, is undesirable in acid soils because it increases acidity and its use is limited to chloride-tolerant crops [35]. Ammonium bicarbonate (NH_4HCO_3) is a source with low N content (19% N) that has been used almost exclusively in China [35].

Urea ($\text{CO}(\text{NH}_2)_2$) is the most widely used N source worldwide [37]. Favorable characteristics of manufacturing, costs, handling, storage, and transport make urea a very competitive N source. Some of the disadvantages of urea are that its use is associated to significant ammonia volatilization losses [38] and it contains biuret, which is a phytotoxic compound that affects sensitive crops (e.g., citrus, and pineapple). Free NH_3 released from urea hydrolysis also has toxic effects on germinating

seedlings during the emergence stage. Urea-ammonium nitrate solutions (UAN) are produced from urea and ammonium nitrate and are also popular N solution fertilizers. One of the major drawbacks of UAN solutions is the tendency to salt-out during cold weather.

Nitrate salts such as sodium nitrate (NaNO_3), potassium nitrate (KNO_3), and calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) are additional N sources available as fertilizers. Sodium nitrate, NaNO_3 (16% N), was in the past a major source of N in Chile, while KNO_3 (13% N) is common in horticultural crops such as tomatoes, potatoes, tobacco, leaf vegetables, citrus fruits, peaches, and other crops. Calcium nitrate ($\text{Ca}(\text{NO}_3)_2$, 15% N, 19% Ca) is a common fertilizer for winter vegetable production and for foliar sprays for celery, tomatoes, and apples.

2.2. Controlled and Slow N Release Fertilizers

Controlled-release and slow N release fertilizers that minimize losses through volatilization and leaching were identified as promising tools to mitigate the negative effects of nitrous oxide (N_2O) and methane emissions (CH_4) on global climate [39] and also sources that increase the recovery of applied N fertilizer [40]. These fertilizers release soluble N (NH_4 and/or NO_3) over several weeks or months and they increase the amount of fertilizer recovered by improving the synchronization between N availability and crop demand. Most products involve nitrification and urease inhibition and/or low water solubility compounds that undergo chemical and/or microbial decomposition to release N. However, the precise rate of release cannot be controlled. In such sense, some authors have distinguished controlled-release from slow-release fertilizers because they release nutrients by physical processes such as diffusion. Slow N release fertilizers, in contrast, are those that release nutrients by chemical or biochemical processes (e.g., aldehydes) [41,42]. The main disadvantage of slow release fertilizers is the cost, which can be four to eight times the cost of conventional fertilizers (e.g., urea). Therefore, they are primarily used in turfgrass, landscaping, ornamental, vegetable crops, greenhouse crops, and in transplantation of coniferous seedlings.

Urease inhibitors have been commercially used in some countries with some degree of success [43]. Shoji *et al.* [44] showed in a field experiment that the use of a controlled release fertilizer (dicyandiamide and polyolefin coated urea) instead of conventional N sources (UAN and ammonium polyphosphate) increased potato tuber yields and N use efficiency by 17% and 58%, respectively. Additionally, Delgado and Mosier [45] reported that urea-dicyandiamide (DCD) significantly reduced the emissions of N_2O and N losses to the environment. The principal purpose of using nitrification inhibitors is to keep the N fertilizer in the NH_4 form for a longer period. Nitrification inhibitors also may reduce denitrification N losses by decreasing the amount of NO_3^- available for denitrification. Although nitrification inhibitors were originally developed to minimize N losses, they have also been proposed as a mean of altering the predominant form of N in the soil. Coarse textured soils with low soil organic matter are generally the most responsive to nitrification inhibitors [46]. However, the management of nitrification inhibitors is complex because it is difficult to predict when and how much N will be lost, while conditions favorable for NO_3^- leaching may develop after the inhibitor has degraded. In addition, a consistent yield increase from the use of nitrification inhibitors was not always observed [47]. Sulfur-coated urea has the greatest suitability where multiple applications of N during the growing season are needed, particularly on sandy soils under high rainfall or irrigation. It is advantageous to be used on sugarcane, pineapple, grass forages, turf, ornamentals, fruits such as cranberries and strawberries, and rice under intermittent or delayed flooding. Urea and organic compounds that inhibit the microbial activity and hydrolysis of urea rely on microbial decomposition as the primary mechanism of N release [48].

Urea-triazone is a controlled-release N compound predominantly used for foliar applications that exhibits excellent absorption properties with no toxicity to plants. Polymer-coated fertilizers (PCFs), on the other hand, are the most advanced products in controlling N release and improving nutrient efficiency. Because most polymer-coated products release by diffusion through a semipermeable membrane, the rate of release can be altered by composition of the coating and the coating thickness.

For example, it is possible to alter the rate in which polymer-coated urea release N in time intervals that spanned from 20 to 90 days [44]. Due to the relatively high cost of these products, their use has been restricted mostly to high-value products [41].

2.3. Microorganisms Used for Crop N Nutrition

Several microorganisms are currently used in agriculture, and many others show potential to be used in the future. There are indications that microbial inoculants could be integrated into fertilization programs and could potentially reduce nutrient inputs [49]. There are, however, still doubts about the beneficial effect, effectiveness, negative interactions and potential risks, especially concerning the stability of the inoculants over time and under varying climatic conditions.

Microorganisms of the genus *Rhizobium* sp. are currently used worldwide, since they fix N₂ in symbiosis with leguminous crops. The inoculation of soybean with the optimal species/strain has a significant impact on the yield and quality [50,51]. A positive response to inoculation depends on limited N availability and that the inoculant bacteria is present in a higher concentration and has greater capacity to compete than native populations. Interactions between *Rhizobium* sp. and vesicular-arbuscular mycorrhizas (VAM) in the rhizosphere of leguminous crops were reported to increase N uptake due to an increased availability of P [52] and higher C translocation to the N fixing nodules [53,54].

Several experiments in different environments suggest that *Azospirillum* sp. inoculation may increase yield of certain cereals [55,56]. *Azospirillum* sp. have been proven to fix effectively N₂, however the beneficial effects of inoculation have been mainly attributed to increased root development and thus to increased rates of water and mineral uptake. A slight yield increase of the inoculated plants over the control suggests that these inoculations combined with an integrated management strategy, might be suitable for low input systems [57].

The group of rhizospheric microorganisms known as plant growth-promoting bacteria (PGPB) include bacterial genres as *Azospirillum*, *Azotobacter*, *Pseudomonas*, *Acetobacter*, *Serratia*, *Bacillus*, and *Burkholderia*. PGPB have shown potential to promote vegetative growth when they are used to inoculate row or horticultural crops [58,59]. These microorganisms can have direct effects on plants like the production of growth regulators that are absorbed by the plant and stimulate the uptake of nutrients [60,61]. The indirect effects that PGPB has on plants are attributed to the prevention of the plant's being colonized by phytopathogens. Field grown wheat inoculated with three species of *Bacillus* sp. consistently increased wheat grain quality and the use efficiency of the applied fertilizer [62]. Several reports show positive effects on growth and nodulation of leguminous crops when they were co-inoculated with *Rhizobium* sp. and PGPB [63–65]. One explanation for the contrasting results is that the expected grain yield increases by PGPBs are usually below 5%, a threshold not easy to detect with conventionally designed field experiments. There are, however, commercial inoculants available for beans, lentils, and wheat that contain the fungus *Penicillium bilaii*, which increase the uptake of nutrients [66]. The use of those inoculants that are effective will help to develop novel management strategies for sustainable agriculture [67].

The potential of phyllospheric microorganisms to enhance N nutrition is still not clear. Nevertheless, certain phyllospheric microorganisms could play a role in plant nutrition; e.g., the cyanobacteria *Scytonema javanicum* and *Scytonema hofmanni* have shown the capacity to influence the ability of legumes to fix N and to uptake NH₃ on leaf surfaces [68,69]. With advances in molecular and biochemical techniques, the research on how management practices impact soil activity has been expanded and developments increasing NUE are to be expected.

2.4. New Potential N Sources

Biomethanation is used as a technique to produce biofuel from biomass. Fermented residues left after biomethanation processes can be used for liquid fertilizer production and as raw materials for compost. The use of fertilizers derived from biomethanation has expanded in the last years.

In Germany, for example, more than 4000 farm anaerobic bioreactors produce 390,000 t of N [70]. This N is suitable for cereals and vegetables [71] and is usually applied as liquid fertilizer [72].

Nanofertilizers (1–100 nm), on the other hand, are highly reactive due to their small size and large surface area, compared to bulk materials. As a consequence, the positive effects of nanofertilizers on crop growth may occur at lower doses than with the same nutrient supplied in its bulk form. Although research on how they can be exploited in specific crops is incipient, recent results and patent requests suggest potential useful benefits [73–76]. Concerning N, it is possible to hypothesize that as N sources that are highly soluble in water, N nanofertilizers once applied would be transformed in highly dynamic forms and that this characteristic would make N nanofertilizers particularly suitable to correct rapidly severe N deficiencies. Recent research suggests that their nano-dimensions allow their uptake through stomatal openings and the base of trichomes [77]. As with most new technologies, nanotechnology involves certain risks since it could have undesirable effects on non-target organisms such as plants and plant or soil microbes; thus, research for the development of nanofertilizers should be accompanied with studies addressing the environmental consequences of its use.

There is evidence that certain nutrients might be required to facilitate seed germination, especially those needed for early-required amino acids [78]. This suggests that coating seeds with nutrients could be a promising technique to improve N nutrition. Seeds can be coated with nutrients to allow better early contact between the emerging radicle and nutrients released from the coating formulation. Seed coating with N alone demonstrated greater efficacy than N combined with P. However, coating with P enhanced P uptake by the plant [79].

After nutrients are used by crops and consumed by humans, animals, or through industrial processes to produce energy or any other good, the waste ends up in the environment. Recapturing of nutrients either directly lost from the field or after consumption by humans and animals should become a more integral part of fertilizer production. Recycling these nutrients reduces overall losses and helps to recapture nutrients for plant uptake [49].

2.5. Methods of Applying N Fertilizers

The 4R nutrient management principles (right source, right rate, right time, and right placement) summarize the best management principles to achieve high NUE [80].

A 50% reduction in the N fertilizer rate in China showed that the groundwater N pollution could decrease by 17% with less than 5% decrease in crop production [81]. Thus, N rate has a strong impact on NUE. In general, the N source determines which method is more suitable for applying the fertilizer. In many cases, also the timing of application, as a consequence of the crop growth stage, determines the preferable application method [82,83]. Differences in plant N uptake dynamics due to the physiology of the plant species and the environmental conditions and the possibility to fractionate N application to meet N demand also orientates decisions on the application method. Some application methods may be more suitable than others or not suitable at all, depending on the timing of application. Finally, the potential methods and N sources that can be used are restricted to those that do not damage the crop. Table 3 shows methods of applying mineral N fertilizers and their corresponding N sources and timing of application. Boswell *et al.* [84] and Peterson and Fryre [83] identified source, rate, placement, and timing as the management factors that influence the N fertilizer recovery efficiency the most.

Table 3. Examples of methods of N fertilizer application as related to N source and timing.

Time of Application	N Source	Method of Application
Pre-sowing	Urea	Incorporated
	Ammonium nitrate Anhydrous ammonia N solution	Broadcast on the surface Subsurface injection Sprayed or dripped on the surface
At sowing or pre-emergence	All sources	In the row with the seed
	All sources Anhydrous ammonia N solution	Banded beside seed Subsurface injection Sprayed or dripped on the surface
Post-emergence	All sources	In the inter-row (side-dress) in bands
	Anhydrous ammonia Anhydrous ammonia N solution	In the inter-row (side-dress), subsurface injection Subsurface injection Foliar, sprayed on the leaves

Nitrogen use efficiency increases significantly by synchronizing, as much as possible, N availability with N demand. Therefore, timing the N application to match the maximum uptake by the crop is fundamental to maximizing uptake by the crop and minimizing N losses [85–88]. A precise synchronization of N application is especially important in environments prone to N leaching such as, for example, sandy soils.

Antagonism among nutrients and unsuitable pH levels, occur mainly in the soil, thus foliar applications allow for circumventing the restricted availability through the root. Foliar applications could also increase nutritional quality [89,90] and may allow exploiting synergistic effects; a mix of N, P, K, Fe, Cu and Mn enhanced the nutrient content in seeds and increased yield of maize by 50% as compared to the basal application of NPK alone [91]. Due to the limited quantity of nutrients that can be delivered this way, foliar applications cannot replace basal broadcast but can be used in addition to them.

The delivery of nutrients through irrigation, *i.e.*, fertigation, is a strategy that can be integrated into fertilizer regimes and used to adjust application rates to crop demand and, as a consequence, improve nutrient uptake efficiency [92].

Table 4 summarizes management practices that affect nitrogen nutrition.

Table 4. Management practices that affect nitrogen use efficiency from Rathke *et al.* [29].

Management Practice	Goal(s) as Related to N Nutrition
Crop and crop rotation	Increased uptake and utilization of soil available N by using N efficient crops.
	Reduction of N losses by minimizing fallow frequency and accessing deeper N pools with deep rooted crops.
	Increased N supply from mineralizable N.
	Increased N demand by reducing the incidence of pest and diseases.
Cover and inter-cropping	Reduction of N losses by minimizing fallow frequency and accessing deeper N pools with deep rooted crops. Increased N supply from mineralizable N.
Management of crop residues	Control of N mineralization.
Genotype	Increased uptake and utilization of soil available N by using N efficient genotypes.
Irrigation and crop protection	Increased uptake and utilization of soil available N by maximizing crop N demand and use.

Table 4. Cont.

Management Practice	Goal(s) as Related to N Nutrition
Adequate nutrition of other nutrients	Increased uptake and utilization of soil available N by maximizing crop N demand and use.
Accurate prediction of N need	Increased uptake and utilization of soil available N by avoiding over/under application of N fertilizer.
N source	Avoidance of N losses caused by specific N transformations in the soil. Increased N physiological efficiency (yield/N uptake) due to the metabolism of N forms (NO ₃ /NH ₄)
Timing of N application	Reduction of N losses and increased N agronomic efficiency (yield/N supply)
N application method (placement)	Reduction of N losses and immobilization. Improved spatial availability of soil mineral N.
Timing, intensity, and depth of tillage	Control of soil mineral N.

2.6. Technologies to Diagnose Crop N Status

Numerous factors influence crop N requirements, and low NUE occurs when the applied N exceeds potential demand. Since precision agriculture allows for the maximizing of NUE, the improvement of methods to diagnose N status of crops is an area of active research today.

The response of crops to N is not linear and depends on several factors. For example, under controlled conditions, the efficiency of different types of N fertilizers in cereals is nearly identical, but differences arise in the field as a result of interactions between N sources and environmental conditions (e.g., precipitation and temperature). Soil properties dictate to a large degree the responses of crops to nutrient applications; for example, pH can determine the extent to which a nutrient is available to plants [93], and crop response is affected by the scarcity of other nutrients such as phosphorus and potassium. Similarly, the crop rotation can change the dynamics of N, modifying the expected response to the N fertilizer; for example, cover crops were shown to increase the availability of N for the subsequent crop [94] and the duration of fallow periods affects the mineralization and water accumulation in the soil profile. In legumes, there is an additional source of N resulting from the symbiotic association with species of the genus *Bradyrhizobium* [95]. Furthermore, the type, timing, intensity, and depth of tillage has been reported to affect the response to N fertilization [96,97]. The crop choice also influences N fertilization and losses; Delogu *et al.* [27] showed that reduced N requirement of barley compared to wheat, makes barley a better choice to reduce ground-water pollution due to nitrate leaching in winter and early spring. Thus, N diagnose should integrate several sources of information and consider in-season dynamics to deliver correct N recommendations. Soil analysis of nitrate and ammonium at the start of the growing season is a widespread method to diagnose N availability in many parts of the world [98], even though results can be inconsistent due to environmental conditions and limitations on the number of samples taken.

The improvement of methods to diagnose N status is one of the areas of most active research in the field of N fertilization and management. Estimating crop N status during growth can be useful to adjust fertilizer levels during the growing season. Table 5 summarizes the current methods used to diagnose crop N needs during growth as identified by Muñoz-Huerta [99]. Sap nitrate tests [98,100], despite having high accuracy, are not widely applied in farms nowadays, possibly due to the effort required in sampling, preservation, extraction, dilution, and measurement [101]. In contrast, optical sensors, which do not destruct plant tissue, produce readings with generally high correlation with crop N status. Readings from passive ground-based sensors may be affected by soil and light conditions. Due to chlorophyll saturation, chlorophyll sensors fail to detect over-fertilization and lack the sensitivity to distinguish between different N treatments [102]. However, reliable correlation between reflectance and plant N concentration was obtained in the region of the spectrum between 480 and 870 nm [103], and analytical procedures that take into consideration at least two spectral indices, rather than one,

have demonstrated capacity to better diagnose leaf N concentration [104]. Such is the case of the Dualex sensor that measures flavonol, anthocyanin and Chlorophyll simultaneously [105].

Satellite images currently offer the possibility to cover large areas at affordable prices or for free. Initial attempts to use satellite data were limited due to drawbacks such as: (a) high cost of images; (b) interference by weather conditions (e.g., clouds); (c) slow and time-consuming image pre-processing; (d) delays between image capture and the availability of usable data [106,107]; and (e) overly spaced coverage. The high cost of images is not a limitation anymore since there have been significant reductions in their price or have become available for free. In addition, the replacement of older satellites by a new generation of satellites that can obtain images at higher resolutions is taking place. These satellites are also enlarging the constellation of satellites that screen fields, making possible to overcome other initial limitations such as overly spaced coverage. Similarly, more accurate N deficiency detection could be achieved in the near future by advances in the development of light and portable hyperspectral sensors [99].

With unmanned aerial vehicles becoming more affordable, research efforts are being allocated to developing sensors for drones. Indices for assessing maize N status based on airborne measurements were found to be as reliable as measurements taken on the ground; field level readings with a chlorophyll meter (SPAD), red edge optical reflectance (R_{750}/R_{710}), and solar-induced fluorescence retrieval (SIF760) had the lowest error rates when distinguishing N-sufficient from N-deficient treatments [108,109]. Several indices based on waveband combinations of canopy reflectance have also been used: the normalized vegetation index (NDVI), the ration vegetation index (RVI), and other indices, calculated predominantly with red, green and near-infrared reflectance data of a crop canopy [110]. As hyperspectral sensors become more affordable [111], spectral indices based on differences (NDVI, green NDVI, red NDVI, red and green vegetation index (RGVI)) or ratios (red vegetation index (RVI), green vegetation index [GVI], red and green vegetation index) are calculated from averaged crop canopy reflectance readings at green (520–600 nm), red (630–690 nm), and near infrared reflectance (NIR; 760–900 nm), bandwidths e.g., [112]. Commercial reflectance sensors applied to estimate crop N status can be classified as passive or active, depending whether the energy source is the sun or an artificial source. Passive crop canopy reflectance sensors measure crop canopy reflectance generated by sunlight. A positive linear relationship between RVI and N uptake in winter wheat was demonstrated, as well as independence from growth stages and crop varieties. As a result, a major advantage of the RVI is that can also determine the N status in fields with high levels of N availability [112].

Table 5. Methods to assess N status of crops during growth.

Type of Method	Level of Analysis	Method	Reference
Destructive	Tissue assessment	Kjeldahl wet digestion Dumas combustion Nitrate ion-selective electrodes	Tomkiewicz and Piskier [113]
Non-Destructive	Leaf assessment	Leaf-light transmittance (chlorophyll meter, SPAD) Polyphenols-dualex (Chlorophyll fluorescence) Multiplex (Chlorophyll fluorescence)	Miao <i>et al.</i> [108] Goffart <i>et al.</i> [114] Fernandez-Jaramillo <i>et al.</i> [115]
	Canopy assessment	Satellite or aerial assessment (normalized vegetation index (NDVI), spectrometry) Passive sensors (Greenseeker [®] , Yara-N-sensor [®] , N-tester [®] , Crop circle, digital imaging) Active sensors (FieldSpec-spectroradiometer, CropScan)	Muñoz-Huerta [99] Muñoz-Huerta [99]

2.7. Decision Support Systems

Robust decision support tools were developed to help determine N fertilizer recommendations [116]. Crop simulation models have proven to be useful also to decide N applications that match crop needs [117]. The complexity associated with the fate of the applied N fertilizer, and the absorption and use of N by the crop, makes N fertilizer management complex and uncertain. Decision support systems are therefore fundamental in developing scenarios that predict potential consequences of N management practices, not only in agronomical and environmental terms but also in the context of financial constraints or opportunities.

2.8. Outside-Farm Technologies

Although, this review focuses on agronomical technologies, many precision conservation technologies with potential to control N environmental problems can be implemented outside the farm. Constructed wetlands [118] and buffer zones [119] allow for significant reduction of the environmental problems that result from N fertilization, especially offsite pollution of water and waterways. There are tools under development to estimate potential N savings. These N savings may be traded in future water and air quality markets [120]. Technological innovation can have a large impact, also enhancing efficiency and emission reduction, particularly at the beginning of the N fertilizer chain, for example, in ammonia synthesis and fertilizer manufacturing. The process of making NH_3 from atmospheric N_2 , which is energy intensive, offers opportunities by replacing technologies to lower the C emission factor from 5.1 to 2.4 t CO_2 equivalent emitting t. Similarly, the energy consumption of manufacturing urea could be reduced by 1.9 GJ t N^{-1} using more efficient technologies that are already available [121].

According to Gu *et al.* [81], technological developments play a key role in atmospheric N pollution control while effective policies mainly contribute to groundwater N pollution control. Therefore, the development and implementation of regulations is critical to orientate N fertilization practices that minimize the environmental impact [122]. Although varying N management policies have been implemented for some time in different countries, they have had variable degrees of success in achieving required food productions levels while protecting the environment. As a result, recent efforts were taken to develop tools to assess the N footprint of different activities [123] based on the fact that environmental effects of agricultural N use are ultimately a consequence of human dietary choice [124]. Figure 1 classifies the reviewed N technologies according to their degree of innovation and adoption.

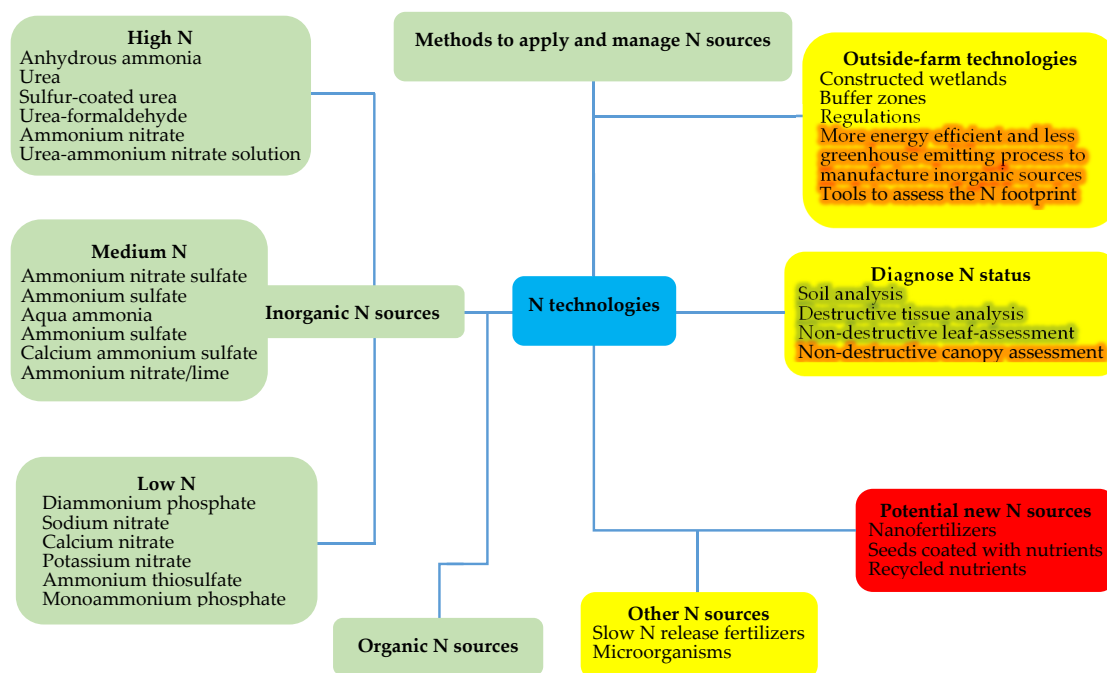


Figure 1. Mind-map of emerging and established technologies for increasing nitrogen use efficiency and reducing the environmental problems resulting from nitrogen fertilization. Red shows potential new technologies, yellow shows tested technologies with little adoption so far, and green shows established technologies.

3. Conclusions

Among potential new technologies we identified the incipient development of nanofertilizers, nutrient based formulations to coat seeds, and recycled nutrients. In a context of increasing concern regarding the environmental consequences of N, innovations outside the farm such as more energy efficient and less CO₂ emitting methods to manufacture N fertilizers, constructed wetlands and buffer zones and more effective regulations will also shape in the long-term how N fertilization will be done in the future.

A better understanding of the effects of N sources and management on the root systems of crops and how these effects relate to those on shoots is fundamental to develop better N fertilization products and management strategies that better synchronize soil N availability with crop N demand, and thus maximize NUE. Similarly, a more deliberate account of plant physiological processes, including the diversity of mineral nutrient uptake mechanisms, their translocation and metabolism has been suggested for the development of modern fertilizers [49]. Such considerations may significantly improve the physicochemical delivery of nutrients, their composition, amount and timing of application to meet crop uptake needs.

The fertilizer sources used nowadays have been approximately the same over the last 60 years. Throughout the world, additional funding for fertilizer research is needed to increase site-specific NUE across large, key agricultural regions of the world. Additional training and education is needed to develop future expertise across nations to implement NUE research findings on farms [37]. The development of fertilizers has been driven by identifying cheap sources of plant nutrients. Although such a characteristic is essential to produce affordable food, the observance of knowledge of plant physiology could significantly benefit the development of new fertilizer sources [49]. An example is producing fertilizers with formulations that include more than one nutrient. Although plants would preferentially transport more than one and inhibit the uptake of others [125,126], synergism in nutrient uptake has been demonstrated for N [127] and other nutrients [128,129] with proper formulations.

The price is the main barrier to the adoption of more efficient formulations such as controlled-release fertilizers. Incentives in the form of subsidies may be an option to increase their adoption in countries where subsidies are common instruments of the agricultural policy. Subsidies could target farmers or more efficient fertilizer sources directly. Water and air quality markets, where N savings that result from the use of more efficient fertilizer sources are traded, could complement public policies and constitute an incentivization instrument for countries that do not subsidize agriculture.

Integrated N management strategies allow for the achievement of production goals while minimizing the risk of environmental pollution [29,130,131]. Sources of N and timing of application determine the most suitable method for application. The interest in implementing new knowledge about methods of application is stimulating the development of sensors to diagnose the N status of crops in real time throughout large areas. Decision support systems are, in this context, becoming fundamental tools to integrating several variables to optimize the source, rate and method of application.

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

Abbreviations

N	nitrogen
NI	nitrification inhibitor
PGPB	plant growth-promoting bacteria
NUE	nitrogen use efficiency

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