Review

Evaluation of Various Nitrogen Indices in N-Fertilizers with Inhibitors in Field Crops: A Review

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Abstract: Nitrogen (N) management remains a global challenge for the sustainability of diversified farming systems. Field crops are often over-supplied with nitrogen by farmers aiming to high productivity. Although the increase of nitrogen rates leads in many instances to high yields, degree of effectiveness for nitrogen use remains low. Urease and nitrification inhibitors are technologies which have been present in the fertilizers market at least 50 years. Inhibitors exploitation ensures long-term nitrogen release and improved N-uptake by plants and N-storage in seeds and silage. Avail of inhibitors, such as the decline of nitrogen leaching in form of NO_3^- , reduction of emissions in NH_3 form, and rise of yield, are some of the desirable attributes that are derived from their integration in fertilization schedules. This review reports the evaluation of applied nitrogen, with inhibitors, and field crops based on nitrogen indices. The examined N-indicators include Nitrogen use efficiency (NUE), Nitrogen Utilization Efficiency (NUE), Nitrogen Agronomic Efficiency (NAE), Nitrogen Harvest Index (NHI), and N uptake. This review gathered all, to the best of our knowledge, available data regarding the utilization of nitrification and urease inhibitors under an exclusively agronomic perspective. Either dual or single use of nitrification and urease inhibitors has been reported to significantly increase yield components and promote nitrogen uptake. To conclude, the assessment of N-related indices is vital to promoting sustainability in diversified farming systems, while the integration of inhibitors in national N fertilizations schemes may contribute to system profitability through enhancement of N-supply to crops.

Keywords: nitrogen indices; urease inhibitors; nitrification inhibitors; NUE; NHI; NAE; NUE; field crops

1. Introduction

1.1. The Need for Slow-Release Fertilizers

While the world population has almost doubled in last 50 years, and meat consumption has been skyrocketing, an increase in agricultural production is required to match projected demand; therefore, agriculture aims to rise crop performance [1–3]. As a result, over the past decade, intensification of crops has been achieved through excessive amounts of nitrogen application [4]. For the time being, many researchers have observed that more than half of the applied N fertilizer in crops is currently lost to the environment [5–7]. In particular, Lassaletta et al. demonstrated that only 47% of globally applied nitrogen is transformed into harvest products, in contrast to 68% in the 1960s [6,8].

Inefficient N use in agriculture has created several environmental problems and concerns [9]. The over application of inorganic fertilizers to the soil, along with nitrogen leaching is responsible for the contamination of groundwater [10]. Another problem that has arisen due to the excessive use of inorganic fertilizers is eutrophication, a form of water pollution, caused mainly by nitrogen [11]. Moreover, regarding water quality issues related to agriculture, an inspection of N emission from different routes and sources in inland waters and water catchment areas are attended, in order to guarantee water quality [12,13].

Since intensive agriculture has such an important impact on climate change and the environment, more environmentally friendly practices have been adopted in the last few years. Consequently, cultivation practices must be accomplished in a more precise way to increase crop performance; hybrid breeding is considered one of these practices [14]. Furthermore, the capacity for land, natural resource management, and conflict prevention need to be improved [15]. At the same time, although the fertilizer industry has changed considerably [16], nitrogen remains by far the main element used in synthetic fertilizers [17]. However, the need for improved nitrogen use efficiency in crops is imperative to design sustainable farming systems [5]. As a result, novel fertilizers with inhibitors and new technologies were introduced in the global market to reduce nitrogen leaching and enhance nitrogen utilization [18]. Slow-release fertilizers (SRF) are regularly related to nitrogen-based fertilizers [19]. Nitrogen management must be improved to minimize the undesired and detrimental environmental degradation, while achieving sustainable nourishment of the multiplying population. The overall efficiency of applied N differs widely among climatic zones and crops [20].

1.2. Short History and Broad Classification of Slow-Release Fertilizers

The aforementioned reasons led to a new trend in the fertilizer industry: slow- or controlled-release fertilizers (SRF or CRF). There is no endorsed dissimilarity between slow-release and controlled-release fertilizers [21]. These fertilizers are also known as controlled-availability fertilizers, delayed-release fertilizers, metered-release fertilizer, or slow-acting fertilizers [20]. SRF was firstly reported during the 1920s, although their market did not show growth until the 1960s [22]. The industry of these fertilizers is evolving considerably in the 21st century with an annual growth rate of 6.5% from 2014 to 2019 [22].

Classifications and definitions of SRFs vary depending on the legislation consulted. According to the European Committee for Standardization (CEN), there are three requirements for the characterization of fertilizer as SRF. Firstly, release of up to 15% of the fertilizer nutrients must occur within 24 h of application; secondly, 75% of them should be released in 28 days; and thirdly, at least about 75% release must be conducted at the stated release time. Slow controlled-release fertilizer (SRF) is defined as a new type of fertilizer with a lower carbon content than conventional [22]. Additionally, in the 57th Official Edition, the Association of American Plant Food Control Officials (AAPFCO) defined slow-release fertilizer as a fertilizer that depletes its nutrients later, after its application [23]. Yamamoto et al. noticed that the main feature of these fertilizers is the duration of nutrient release; SRFs have a longer nutrient release time than traditional ones; hence, nutrient uptake is prolonged by plants [24].

There are many differences between slow-release and conventional fertilizers. The main difference that directly concerns farmers and producers is the cost. SRFs are significantly more expensive than traditional fertilizers. Besides, their technology (with regard to its mode of operation) and application method are more familiar to farmers. However, the nutrient efficiency supply of SRF is higher compared to traditional. Last but not least, is the negative environmental impact which is remarkably higher with the use of traditional fertilizers [22]. However, the risk is that their release is not well stabilized and is influenced by some additional factors, such as microbial activity, pH, organic matter, temperature, and moisture [25].

The gradual release of nutrients is accomplished by a variety of mechanisms. Some of these include controlled water solubility of the material by semi-permeable coatings, blockage, protein materials, or other chemical forms, by slow hydrolysis of low molecular weight water-soluble compounds, or by other unknown means [26,27].

According to the literature, there are many classifications of SRFs. Indeed, many researchers have mentioned that there is no united and standardized classification for this type of fertilizer [22,28]. In the literature, many categorizations vary over time [29]. The latest classification was reported by Fu et al. [22]. This classification of SRF is based on the principle of slow controlled release, and there are three classes: (1) physical type, including coated and matrix-based; (2) chemical type, including chemically bonded and chemically inhibited; and (3) compound type, including physical combination (coated with matrix method), physical-chemical combination, and chemical combination (chemical combination with inhibitor method).

1.3. A Brief Overview of the Study

The use of urease and nitrification inhibitors is an approach that is adopted to improve fertilizer performance in agriculture and lessen urea and nitrogen emission of pollutants. Nevertheless, in the field, slow-release technology fertilizers might not meet N crop demands and would not show an agronomic benefit over conventional N fertilizer applications [30]. The development of nitrification and urease inhibitors is a time-consuming and expensive process on account of their special traits [21]. One of these is the restriction of rainfall or irrigation conditions which deactivate the formulation for slow release for both inhibitors; nitrification and urease [31]. Additionally, a higher urea volatility was observed with late-fall and winter applications in cold and wet soils compared to spring applications in warmer soils [32].

In order to be evaluated, fertilization types and their effectiveness, optimum fertilization rate for each crop, reduction of N losses, and nitrogen indices are used [25]. There are many indicators so as to be estimated the uptake nitrogen from plants. In older literature, indices, such as N translocation efficiency (NTE) from vegetative plant parts to grain, dry matter translocation efficiency (DMTE), contribution of pre-anthesis assimilates to yield (CPAY), and Post-anthesis N uptake (PANU), are mentioned [33,34]. However, in recent research, nitrogen use efficiency (NUE) is considered as the most calculated [35]. Another important indicator is the nitrogen harvest index (NHI), which is informed regarding distribution of nitrogen in the plant and, more specifically, in which parts of the plant the most quantities accumulate [27].

The present study aimed to review the literature in order to evaluate the nitrogen indices in N-fertilizers with inhibitors in field crops of fertilizers with inhibitors with nitrogen indices. The inflow of slow release fertilizers has become the sword of modern agricultural development. The increase of utilization of this kind of fertilizer bears testament to the fact that it is universally accepted. However, a key goal of using this type of fertilizer is also to increase the exploitation of nitrogen unit fertilizers: on the one hand, to significantly reduce nitrogen (NO_3^-) leaching into the environment; on the other hand, to increase the profitability of fertilizer use for farmers. Firstly, this review intends to cite recent literature regarding the performance of urease and nitrification inhibitors as components of fertilization programs in plenty field crops through an agronomic perspective. The use of inhibitors, either urease or nitrification or both, is evaluated in major (wheat, maize, rice, cotton) and other field crops. It is crucial that, in the fertilizer industry, horticulture and turfgrass has been common for decades as their higher price is not considered as an issue in these sectors. The methodology was either the collection of nitrogen indices values or their calculation from the given values in each study. At that point, indices values under traditional fertilizers and fertilizers inhibitors were compared. Under this context, we did not deal with environmental or soil 'issues', such as emissions. Finally, nitrogen indices are connected with each crop orientation for the main field and novel crops.

2. Fertilizers Inhibitors and Their Importance in Agriculture

2.1. Urease Inhibitors (UI)

Urea is considered as one of the most widely used nitrogen fertilizers worldwide owing to its high content of N (46%) and the relatively low cost per unit N [36]. Following urease in soil, urea undergoes hydrolysis via the urease enzyme or volatilization, increasing pH soil of surrounding area of the granules and resulting in NH_3 losses up to 16% of N applied worldwide; NH_3 losses could reach up to 40% or more under warm and humid conditions [37,38].

Urease is a nickel-dependent enzyme that catalyzes the hydrolysis of urea to two moles of ammonia (NH_3) and one molar of carbon dioxide (CO_2). The first scenario is the hydrolysis of urea which provides NH_3 which, in turn, is converted to ammonium (NH_4^+) in the soil water so that plants can receive them; the second scenario is the volatilization of N as NH_3 [37]. The action of urease inhibitors is, firstly, to slow down the conversion of urea to NH_4^+ and, secondly, to decline volatilization of NH_3 . As a result, a significant percentage of the applied urea can be diffused into soil [39,40]. There are four different ways in which urease inhibitors can inhibit urease enzymes and delay urea hydrolysis [41].

A lot of compounds, physical and chemical, have been investigated for their potential to inhibit soil urease activity [42]. However, the most successful is widely the N-(n-butyl) thiophosphorictriamide (NBPT). The NBPT market has been grown 16% per year for the last 10 years in virtue of significant low NH_3 losses compared to urea [38]. Although effectiveness is affirmed, researchers are trying to enhance the period of inhibition and the shelf life of NBPT-treated urea [38]. Utilization of NBPT decreased NH_3 loss up to 66% from urea [35].

There are three groups of synthetic compounds concerning their structure or ties mode with urease. The first one contains organic or inorganic compounds (e.g., alk(en)ylthiosulfinate, hydroquinone, p-benzoquinone) that can react with sulfhydryl (mercapto) groups of urease; the second is metal-chelating compounds (e.g., caprylohydroxamic acid, acetohydroxamic acid) that can form a complex with one of the Ni atoms at the active site of urease; and third are competitive inhibitors (e.g., hydroxyurea, phosphoramides, phenyl phosphorodiamidate (PPDA), N-(n-butyl) thiophosphorictriamide (nBTPT) that are similar to urea structure and can bind to the active site of urease but are not readily hydrolyzed by urease [39,43]. The most frequently used urease inhibitor were mentioned that is thiophosphoric-triamide (NBPT) [25,44].

2.2. Nitrification Inhibitors (NI)

Gaseous N emission in rice paddy fields were up to 10–60% of the N fertilizer applied [45]. The role of nitrification inhibitors is firstly to lessen the conversion of ammonium (NH_4^+) to nitrate (NO_3^-), which is considered as a significant pathway of nitrate leaching in agriculture [46]. Secondly, nitrous oxide (N_2O) emissions, which are considered a greenhouse gas, are reduced into atmosphere. However, N_2O emission is not a major factor for plant nutrition due to low nitrogen loss amounts [47,48]. Tens of commercial inhibitors have been patented, of which four inhibitors (Nitrapyrin, dicyandiamide (DCD), NBPT, and HQ) have application in agriculture. Nitrification inhibitors ordinarily rise NH_3 volatilization, and, if blended with urease inhibitors, reduction of NH_3 loss would partially offset [38]. The addition of nitrification inhibitors to urease decreased by 38% NH_3 losses in the wheat field [49]. In the paddy field, ammonia and nitrous oxide were declined up to 90% by using controlled release urea [50].

Moreover, nitrification inhibitors could decline soil acidification; this decline helps to reduce NH_3 loss by blocking nitrification [51]. The most used nitrification inhibitor is considered dicyandiamide (DCD) [52]. DCD has a solubility in water 23.0 g/L (at 13 °C), low relative volatility, and its mode of application is blended with urea or other solid nitrogen fertilizers [46]. 3,4-Dimethylpyrazole phosphate (DMPP) is a new nitrification inhibitor with highly advantageous properties, such as lower ecotoxic, which is blended with urea or other solid nitrogen fertilizers [53].

2.3. Combination of Nitrate and Urease Inhibitors (UI and NI)

To raise the efficacy of nitrogen use, the combination of the two above inhibitors could be applied. In other words, the two inhibition mechanisms are likely to be combined. However, the results are divided. On the one hand, results were not observed auspicious for nitrogen leaching and crop yields. This is probably due to the combination of two inhibitors and the action of one inhibitor on the other; one inhibitor can disarm the other one so nitrogen losses are not reduced [51,54].

Although the direct effect of nitrification inhibitor on the urease inhibitor was not ratified, the concentration of $\text{NH}_3/\text{NH}_4^+$ remained high for a longer period, and volatilization losses were carried on [55]. On the other hand, the interaction of the two inhibitors is influenced by soil properties [52]. Presented in Figure 1 is the activity of urease and nitrification inhibitors. Blend of urease and nitrate inhibitors still decreased NH_3 loss compared to pure urea; however, NH_3 losses are less than using only urease inhibitor [51]. Regarding only crop yield, the application of both inhibitors has led to a significant increase compared to a single inhibitor [25,56].

Figure 1. Urease inhibitors and nitrification inhibitors activity.

3. Nitrogen Indices

3.1. Nitrogen Use Efficiency (NUE)

Nitrogen efficiency is reduced by seasonal conditions, crop diseases, N losses from the soil as gases, leaching of N, or immobilization of N in organic forms. The efficiency of the conversion of fertilizer into grains/seeds and shoots is considered as one of the major grower concerns. NUE index presents the yield in seed and biomass (kg) per unit of applied N fertilizer N. It is a net number [57]. The equation is as follows:

$$\text{NUE} = \frac{\text{N uptake}_{\text{fert}} - \text{N uptake}_{\text{control}}}{\text{applied N fertilizer}} \quad (1)$$

$\text{N uptake}_{\text{fert}}$ = total N (in shoots and seeds) under applied N fertilization,
 $\text{N uptake}_{\text{control}}$ = total N (in shoots and seeds) without fertilizer.

This indicator can be differentiated depending on the production direction of the crop. In case the produced product is only seeds (and not biomass), then it concerns N uptake in seed or tubers in the case of potatoes. In NUE parameter, N could come not only from fertilizer N (applied N) but also from soil mineral N (N_{min}). However, in this study, only applied N was considered.

3.2. Nitrogen Utilization Efficiency (NUE)

This ratio indicates seed yield (kg ha^{-1}) to N concentration (kg N ha^{-1}) in the above-ground part of the crop [58]. The equation is:

$$\text{NUE} = \frac{\text{Seed yield}}{\text{Above ground N}} \quad (2)$$

To use the above index, it is necessary to calculate the entire nitrogen content of the whole above-ground part of the plant, including seeds.

3.3. N Yield and Protein Yield

To evaluate crop yield in N, the concentration in N (%) was multiplied by the crop dry weight (kg ha^{-1}).

$$\text{N yield} = \text{N concentration (\%)} * \text{Yield biomass (kg ha}^{-1}\text{)} \quad (3)$$

The protein yield was multiplied by yield N (kg ha^{-1}) on Jones' factor which is a nitrogen: protein conversion factor [59].

$$\text{Protein yield} = \text{N yield} * \text{Jones's factor} \quad (4)$$

3.4. Aboveground N Uptake

N uptake by the upper plant tissues and the reproductive organs is described by Equation (5) and can be used in multiple crops.

$$\text{N uptake} = \text{N yield upper parts (kg N ha}^{-1}\text{)} + \text{N seed yield (kg N ha}^{-1}\text{)} \quad (5)$$

The upper part of the plant includes stems and leaves.

3.5. Nitrogen Harvest Index (NHI)

NHI was introduced by Ye et al. [60], and the formula is:

$$\text{NHI} = \frac{\text{N seed}}{\text{N uptake}} \quad (6)$$

N seed = nitrogen content in seeds,

N uptake = nitrogen content in whole plant.

3.6. Nitrogen Agronomic Efficiency (NAE)

NAE index was given by Craswell and Godwin with the below equation [61]:

$$\text{NAE} = \frac{\text{Grain yield}_{\text{fertilized}} (\text{kg}) - \text{Grain yield}_{\text{unfertilized}}}{\text{Applied N (kg)}} \frac{\text{kg seed}}{\text{kg N fertilizer}} \quad (7)$$

4. Factors Affecting Nitrogen Indices

A widely used indicator is the nitrogen use efficiency (NUE) which illustrates how to enhance nitrogen exploitation, namely how much nitrogen is applied to the crop and how much is used by plants [61]. The most efficient way to lessen N losses and cost is the enhancement of NUE [62]. The degree of effectiveness of N fertilizers declined with the increase of N fertilizer inputs; this increased application has harmful effects [63]. Moreover, many factors affect NUE, such as flooding, soil compaction, low SOM content, and, especially, drought reduced NUE [64]. Furthermore, breeding is aimed to enhance crop yields through NUE [65]. Legumes have a high NUE due to their ability to fix atmospheric N in the aboveground part of plants (their shoots and grains compared to grasses) [66]. In maize crops, higher NUE was observed in the cold-dry season compared to the hot-wet season [67]. Furthermore, nitrogen uptake and NUE were increased with the reduction of irrigation level up to 25% in maize, for both hot and cold seasons [67]. However, the effect depends on the irrigation rate and the weather. In soya crop, NUE could be enhanced with the genetic upgrade, and higher yield and higher quality products will be accomplished [68]. Attia et al. (2015) mention that intercropping of soya-corn positively affected NUE [69]. According to Kakabouki et al., NUE index was increased, while the fertilizer nitrogen rate was decreased; in soybean, cultivation NUE was 0.26 under

80 kg N ha⁻¹, and 0.17 under 120 kg N ha⁻¹ [52]. In wheat crop, NUE has risen in conventional tillage compared no-tillage [70]. NUE varied from 19.2 to 22.7 (kg of grain produced per kg of N supply) in comparison with conventional tillage [71].

Regarding NUE, there is a turning point of fertilized nitrogen above which NUE is begun to decrease or yield response slows down. In maize, it was noted that this amount of nitrogen is 150 kg N ha⁻¹, and, for winter wheat, it is approximately 50 kg N ha⁻¹ [72]. It is considered as general rule for many crops, especially in the case of wheat (*Triticum aestivum* L.), that NUE was higher with low N rate (42.7 kg DM kg⁻¹ N) than at high N rate (32.9 kg DM kg⁻¹ N) [73]. NUE, in many crops, has risen in recent decades, which reduce N loss from agricultural production.

In the case of a growth period with low internal nutrient concentration, NUtE could provide information about the relationship between plant carbon and nutrient economies [74]. In wheat crops, N utilization efficiency was raised with a decreased fertilizer rate of 210 kg hm⁻² and a 50% ratio of N as topdressing [63]. The application of no-tillage instead of conventional tillage led to an increase in NUtE only in sequel wheat-faba bean, and wheat-berseem and not wheat-wheat [71]. NutE was higher at low rate nitrogen (55.6 kg DM kg⁻¹ N) than at high rate nitrogen (41.9 kg DM kg⁻¹ N) in bread wheat (*Triticum aestivum* L.) [73]. A comparison between perennial and annual grassland revealed higher NUtE in perennials owing to the rise of nitrogen concentration in perennial plant parts [74].

N uptake or N yield was observed highly dependent on nitrogen rate in soya, even though soya belongs in legume family [52]. Similar results are noticed for flaxseed crops; while nitrogen rate was increased, N total in plants was significantly risen [56]. Plant N uptake was improved with a reduced fertilizer rate in wheat crops [63]. Szumigalski and Van Acker (2006) observed that N yield was significantly affected by crop [75]. Another factor that in effect here is the presence of crop herbicide; N yield was noticed higher after application of crop herbicide [75]. Additionally, N uptake was higher under conventional tillage compared to no-tillage. In bread, wheat grain protein content was found to be significantly influenced by N application rate timing of N application, and the highest rate gave the highest concentration of protein [76].

Another significant index is the nitrogen harvest index (NHI), which is a ratio between N accumulated in grain to N accumulated in whole plant. In soybean cultivation, NHI did not statistically differ for three nitrogen rates (80, 100, and 120 kg N ha⁻¹) and tillage; the more fertilized nitrogen, the lower NHI in soybean crop; namely, the lowest NHI value was under 120 kg N ha⁻¹. However, NHI was noticed around 0.8 for all operations due to the orientation of production were the seeds [52]. In flaxseed crop, NHI was ranged from 37.9 (without fertilizer) to 58.3 (60 kg N ha⁻¹) [56]. NHI ranged from 71 to 78% [70]. Lower NHI was observed after a wheat crop sequence for years than crop rotation [70].

In soybean crop, NAE was affected by fertilization nitrogen rate. It was increased under an elevated nitrogen rate [52]. NAE was raised by rotation in wheat crops [70].

5. Impact of N Inhibitors on Fertilizer N Indices of Field Crops

The addition of inhibitors has been reported to regulate the allocation of nitrogen in individual plant parts and lead to an increase of stored nitrogen in fruits, such as tomato cultivation [77]. Moreover, N losses to the environment due to leaching and emissions, in this way increasing the nitrogen use efficiency, are moderated with the use of inhibitors [78–81]. However, this attribute should be combined with proper nitrogen rates in order to be ensured efficient yield and reduced emissions simultaneously [82]. Utilization of (N-(n-butyl) thiophosphorictriamide (NPBT) result in increased yield from 0.8 to 10.2% in various crop species [38]. Concerning the operating costs of the enhanced efficiency nitrogen fertilizers, application rates are crucial for sufficient yield and exploitation of environmental benefits [83,84].

A lot of inhibitors have been incorporated worldwide in many fertilization plans in many crops. Except from synthetic inhibitors, lower-cost materials, such as calcium chloride, sodium thiosulphate, and other natural NI, have been suggested for further evaluation in field-scale [85,86]. Nitrification and urease inhibitors performance is significantly affected by timing (relevant crop growth stage), type (single or split), and rate of application [42,87–90]. Soil pH is also a key factor that guides the effectiveness of various inhibitors; while soil pH rises, slow release fertilizers activity is benefited and action of the inhibitors is not repressed [91]. It is imperative to be paid attention in increased rates of applied nitrogen since risk for N losses to the environment simultaneously raises [92,93]. However, some researcher observed that nitrogen use efficiency after the introduction of inhibitors is not always improved in complex cropping systems in terms of yield [81,94]. Therefore, it is imperative that use of inhibitors should be defined in today's agriculture [18,95].

5.1. Wheat

The utilization of nitrification and urease inhibitors could be causally linked to the reduction of required N input in various crops. One of the first experiments reveals that application of pure nitrate yielded in lower accumulation of N in contrast to mix of ammonium and nitrate with DCD supplies; pure ammonium could have a toxic effect on plants, and nitrate nutrition may be relatively more energy-consuming [96]. Many strategies are aimed at reducing yield-scaled N oxides and enhancing bread quality in rainy Mediterranean areas [83]. The dual-use of inhibitors has been reported to significantly increase wheat yield and promote N uptake at harvest [97]. Yield components and NUE were increased and profitability remains high [97]. In cases of drought conditions, split-application of urea with both nitrification and urease inhibitors is proposed to provide sufficient yield, high-quality characteristics, and balanced nitrogen management [98]. The addition of a nitrification inhibitor (3,4 dimethylpyrazole succinic acid—DMPSA) and urease inhibitor (N-(n-butyl) thiophosphorictriamide—NBPT) serves a binary purpose; the reduction of NH_3 and N_2O emissions [99]. Agronomic and quality attributes of wheat exhibited significant positive results by using the urease inhibitor N-(2-Nitrophenyl) phosphoric triamide (2-NPT) in split-applied urea at 180 kg N ha^{-1} [100]. The nitrification inhibitor DMPP in ammonium sulfate was able to aid late growing wheat genotypes by delaying the nitrification process for more than 6 weeks (Table 1) [101]. Nitrogen use efficiency could be further enhanced in cases of seed inoculation with microbes. This is a technique that proved quite efficient in wheat crop when it is combined with coated urea and urease inhibitor NBPT (Table 2) [102]. The same authors suggested that 140 kg N ha^{-1} in urea form, along with seed inoculation, leads to higher wheat grain yield and satisfying nitrogen use efficiency (Table 2) [103]. However, nitrification inhibitors are limited in calcareous soils ($\text{pH} > 7$) [97]. Higher NUE and wheat yield have not been previously reported (Table 3) [97]. DMPP applied in urea did not improve yield components and nitrogen use efficiency of durum wheat in Italy [104]. Moreover, the increase in NUE in wheat at a range of 9% after the introduction of nitrification and urease inhibitors is not necessarily linked with an increase in grain yield (Table 3) [105]. In an analysis of various nitrogen management practices, the split application of urease inhibitors as topdressing at shooting stage of wheat managed to increase NUE value (>0.6), boost wheat grain yield, reduce N losses, and moderate net returns to farmers [88]. If wheat market price is relatively high, use of nitrification and urease inhibitors will increase net returns, providing US $\$107 \text{ ha}^{-1}$ at wheat price $\$220 \text{ Mg}^{-1}$ when enhanced urea is applied at 70 kg N ha^{-1} at planting [106]. On the same wheat price, net profit cut to half when nitrogen fertilization was split-applied. Profitability rate in spring wheat under fertilization with the nitrification inhibitor nitrapyrin fluctuated between 25–33% across years, whereas the urease inhibitor NBPT in urea led to a rate of 50–52%, separately (Table 3) [97].

5.2. Maize

In general, nitrification inhibitors could become an important component of crop rotation systems in order to increase yields and enhance agronomic efficiency [107]. Fertilizers with nitrification inhibitor increased NUE in the following year after application compared to a conventional fertilizer [108]. However, the mixture of inhibitors does not always ensure high yields [109] and occasionally performs even worse than conventional fertilizer in maize plants (Tables 1 and 2) [110]. The more complicated, the less effective were noticed for inoculated fertilizers [81]. Slow-release N fertilizer, with the method of organic coating, did not improve N uptake, NUE, or maize yield compared to conventional urea, 46% N (Table 3) [111]. On the contrary, a comparison of urea and polyolefin coated urea revealed that although total N_2O emission value of the coated technology was almost one out of three of pure urea, similar patterns were observed on a cornfield [112]. Another study in maize was mentioned that urease inhibitor was used in urea at a rate of 96 kg N ha^{-1} (Table 2) [113]. Coating with NBPT in urea led to a significant increase in maize yield and NUE compared to conventional N application rate at 120 kg N ha^{-1} . Researchers highlighted that application of NBPT coated urea increased efficiently the total N uptake and reduced the required N application with a view to higher yield. At the tassel fully emerged stage of maize, 21% higher NUE were approximately noticed under urea with NBPT than non-treated urea in a pot experiment [114]. Furthermore, significant reduced ammonia losses were observed [114]. In pre-plant applications of urea with NBPT urease inhibitor at 150 kg N ha^{-1} , applied either broadcast or broadcast and incorporated, showed 1.87-fold greater corn grain yield than control and 1.96-fold higher corn grain N uptake relative to control (Table 2) [115]. Urea with NBPT at a rate of 180 kg N ha^{-1} showed greater agronomic efficiency than conventional urea, whereas, at the rate of 120 kg N ha^{-1} , there was no significant difference [116]. In similar cases as wheat, seed inoculation with microbes led to an increase in NUE and yield [103]. Nevertheless, serious economical limitations arise from the exploitation of synthetic inhibitors and more intensive nitrogen sources. According to Galindo et al. (2019), the highest profitability in maize cultivation (approximately per 60 kg sack US \$360) occurred under fertilization with urea at 100 kg N ha^{-1} and with the addition of *Azospirillum brasilense* (Table 2) [103]. The profit decreased under the use of NBPT in urea (approximately US \$160 at 100 kg N ha^{-1}) and almost eliminated in the absence of the bacterium (approximately US \$6 at 100 kg N ha^{-1}). Although, use of double inhibitors (nitrification and urease) may increase costs, revenue from corn yield will balance the profit. Broadcast applied urea with dual inhibitors led to US \$619 ha^{-1} return in maize cultivation, derived from a three-year study, an amount 5.6% greater than the application with polymer-coated urea and 10.7% lower than anhydrous ammonia (Table 3) [117]. A meta-analysis in maize revealed that the nitrification inhibitor DCD provided approximately $\$110 \text{ ha}^{-1}$, a value significantly higher than using the NI DMPP [118].

5.3. Rice

The nitrification inhibitor nitrapyrin (2-chloro-6-(trichloromethyl)-pyridine, CP) significantly increased yield and NUE of rice in paddy soil under a 5-year study in China [119]. Moreover, another study on rice revealed that the urease inhibitor NBPT slightly increased yield compared to the typical urea application at 270 kg N ha^{-1} . However, total N uptake was approximately 10% higher than the fertilized control [120]. High soil temperature might act as a limiting factor for the performance of 2-chloro-6-(trichloromethyl)-pyridine in rice cultivation (Table 1) [121]. Application of nitrification inhibitors should be site-specific, depending on several soil properties due to the strong linkage of the inhibitors with the bacteria communities [122]. More complicated mixes, such as a nitrification inhibitor (DCD), along with urease inhibitor (hydroquinone) at 300 kg N ha^{-1} and biochar, might improve rice yield, NUE, and profitability (Table 3) [123]. Though the comparison of mode of action (i.e., urease inhibitors, nitrification inhibitors, or slow-release) did not differentiate the enhanced efficiency nitrogen fertilizers, yet the individual analysis of each

product still revealed that NBPT [N-(n-butyl) phosphoric triamide] and neem coated were proved effective in the rise of rice yield, in contrast to PPDA and DCD, which were not effective [88]. In rice, the technology of coatings is also considered as an effectual way to improve NUE, yield, and decrease N loss through denitrification, ammonia volatilization (AV), leaching, and surface runoff [124,125].

5.4. Cotton

In cotton crop, N yield was significantly increased by applying fertilizers with inhibitors; N yield was noticed $286.75 \text{ kg N ha}^{-1}$ under urea with DCD + NBPT compared to $198.5 \text{ kg N ha}^{-1}$ which mentioned under urea (Table 3) [126]. There was an increase of 44.4% in N uptake or N yield with the use of urease and nitrification inhibitors. Furthermore, NUtE was significantly higher under urea with both inhibitors; NUtE was commemorated in 23.06 and 20.52 under pure urea. Nevertheless, the dual use of nitrification and urease inhibitors did not result in significant increases in cottonseed and lint yield with NAE remaining low across years [127]. With the application of urease inhibitors, fertilizers (in a split way) were observed to have a 4–12% yield rise for two cultivation years, whereas NUE was noticed similar to that between conventional and urease inhibitors [128]. Furthermore, conventional and urease inhibitors were identically yielded at rates of 140 kg ha^{-1} and 210 kg ha^{-1} , respectively [128]. On the other hand, utilization of NBPT, DCD with urea, and polymer-coated urea did not affect yield, fiber quality, and N use under a drip-fertigated system in the arid region (Table 3) [82,129].

5.5. Other Field Crops

Nitrogen management proved to be enhanced in split-applied ammonium sulfate nitrate plus a nitrification inhibitor (3,4-dimethylpyrazole phosphate—DMPP) at $\frac{3}{4}$ of the typically recommended rate (urea at 160 kg N ha^{-1}) in potato cultivation in Brazil (Table 1) [90]. Furthermore, an application rate of 112 N kg ha^{-1} of polyolefin coated urea was yielded equal with 269 N kg ha^{-1} of traditional fertilizers. However, large size tubers were significantly lower with polyolefin coated urea compared to traditional fertilizer [112]. In potato crop, NUE ranged from 201 to 7.102, was calculated with tuber yield, and was declined with the increase of applied fertilizer; the more applied nitrogen, the higher values of NUtE due to a nonlinear relationship between nitrogen fertilizer and tuber potato yield [130]. This nonlinear relationship is presented at every crop. Regarding the total N uptake, values ranged from 97 kg N ha^{-1} (control, without fertilizer) to 191 kg N ha^{-1} (Urea + DCD + NBPT) in sweet potato crop. Additionally, NUE was significantly affected by inhibitors and was noticed high under urease and nitrification inhibitors. The highest NUE value was 0.492 in urea with double inhibitors treatment and the lowest was 0.016 in urea treatment. As regards NHI, in urea + DCD + NBPT treatment was observed the highest value (0.86). The lowest was noticed in control (0.62). With respect to NAE, the values ranged from 17.23 (Urea) to 47.047 (Urea + DCD + NBPT) (Tables 2 and 3) [25]. The nitrification inhibitor DCD did not enhance the stalk yield of sugarcane resulting in similar values when applied at 120 kg N ha^{-1} [131]. Separately, the nitrification inhibitor CP in reduced rates of nitrogen (180 kg N ha^{-1} for tomato) applied as urea led to an increase in total yield and NUE, as it emerges from the study of Min et al. [77]. The addition of NI at reduced N application rates increased the total average yield approximately by 16% in comparison with the reduced N application rates. There was also a remarkable enhancement of NUE, since the addition of NI increased approximately by 84% the nitrogen use efficiency compared to reduced N applied rates.

Grassland yield 11% more, NUE was observed 33% higher, and 47% decrease in aggregated N loss (sum of NO_3^- , NH_3 , and N_2O , totaling 84 kg N ha^{-1}) with new types of fertilizers called enhanced-efficiency fertilizers [81]. Grassland productivity is proved to be enhanced with the utilization of urea fertilizers with the urease inhibitor NBPT [132]. The use of NI DCD and UI NBPT increased significantly camelina production in terms of grain yield, marking approximately 36% higher production than conventional urea [133]. The NI DMPP and the UI NBPT at a rate of 40 kg N ha^{-1} were not able to increase biomass productivity and nitrogen agronomic efficiency of ryegrass (*Lolium perenne*) [134]. On the contrary, reduced rates of DMPP in urea resulted in higher yields and fewer N losses to the environment in pasture [135]. This pattern was not observed in grain sorghum (*Sorghum bicolor*), where DMPP fertilization rates should be increased to observe a significant enhancement in yield and nitrogen agronomic efficiency [136]. N_2O emissions from urea were greatly reduced up to 81 and 35% using DCD and polyolefin-coated urea, respectively, in the barley field.

N fertilizer losses from polyolefin coated urea was noticed at only 1.9%, in contrast to DCD (10%). As a result, slow-release fertilizer with coated was indicated more profitable in irrigated barley crops [112]. Dry matter production and NUE were revealed lower under urea [$\text{CO}(\text{NH}_2)_2$] than ammonium nitrate (NH_4NO_3), urea ammonium nitrate (UAN), and ammonium thiosulfate [$(\text{NH}_4)_2\text{SO}_4$] in bermudagrass just the first growing season, and not the second [137]. The use of the nitrification inhibitor DMPP (3,4-dimethylpyrazole phosphate) increased the marketable yield of cabbage by the first year [138], whereas slow-release N products (urea with sulfur or methylene urea) did not increase cabbage yield [31].

Table 1. Nitrification inhibitors use in different crops/regions/rates and their association with Nitrogen efficiency indices.

Inhibitor	N Application Rate	Crop(s)	Yield (Approximate Upward and Downward Trends Provoked by the Utilization of Inhibitors)		NUE	NUtE	NHI	NAE (kg Seed/Tuber Increased kg N ⁻¹ Applied)	Country References
Nitrification inhibitors (NI)			Compared to unfertilized control	Compared to fertilized control without inhibitors	Compared to fertilized control without inhibitors			Compared to unfertilized control	
CP	Urea: 180 kg N ha ⁻¹	tomato	↑ 120%	↑ 21%	↑ 55%	-	-	-	China [77]
DMPP	Ammonium sulphate nitrate: 160 kg N ha ⁻¹ (split-applied)	potato	↑ 104%	↑ 13.9% (urea at 160 kg N ha ⁻¹)	↑ 50%	48–51 (at maturation)	-	-	Brazil [90]
DMPP	Urea: 180 kg N ha ⁻¹ (single application)	maize	↑ 34.4%	↑ 1.7% (urea at 225 kg N ha ⁻¹)	↑ 4.8% (grain NUE)	-	0.79	14.6	China [110]
DMPP	Urea: 300 kg N ha ⁻¹ (split-applied 50:50)	maize	↑ 70.4%	↑ 7% (urea at 300 kg N ha ⁻¹ split-applied)	↑ 4.3% (three-year average)	-	-	12.7	China [139]
Nitrapyrin	Urea: 225 kg N ha ⁻¹ (split-applied)	cotton	↑ 35% (lint yield)	↑ 4% (lint yield; urea at 225 kg N ha ⁻¹ split-applied)	↑ 5.7%	7	-	-	China [140]
DCD	Urea: 160 kg N ha ⁻¹ (split-applied)	cotton	↑ 3.2-fold (lint yield) ↑ 3-fold (seed cotton yield)	↑ 13% (lint yield) ↑ 8.2% (seed cotton yield; urea at 160 kg N ha ⁻¹)	-	12–21	0.72	20.6 (seed cotton)	Greece [126]
CP	Urea: 180 kg N ha ⁻¹ (single application)	rice (early and late)	↑ 129% (five-year average; early rice) ↑ 56.7% (five-year average; late rice)	↑ 9.7% (five-year average; early rice; split-applied urea at 180 kg N ha ⁻¹) ↑ 9.6% (five-year average; late rice; split-applied urea at 180 kg N ha ⁻¹)	↑ 10.3% (early rice) ↑ 8.8% (late rice)	-	-	20.8 (early rice) 17.9 (late rice)	China [121]

Table 1. Cont.

Inhibitor	N Application Rate	Crop(s)	Yield (Approximate Upward and Downward Trends Provoked by the Utilization of Inhibitors)		NUE	NUtE	NHI	NAE (kg Seed/Tuber Increased kg N ⁻¹ Applied)	Country References
DMPP	Urea: 50 kg N ha ⁻¹ (at sowing)	wheat	↑ 30.2% and ↑ 26.5% (in two different locations)	↑ 7% and ↓ 6.1% (single applied at sowing in two different locations; urea at 50 kg N ha ⁻¹) ↑ 0.3% and ↑ 15.9% (single applied at the end of tillering in two different locations; urea at 50 kg N ha ⁻¹)	↑ 12% and ↓ 4% (single applied at sowing in two different locations; urea at 50 kg N ha ⁻¹) ↑ 13% and ↑ 49% (single applied at the end of tillering in two different locations; urea at 50 kg N ha ⁻¹)	39.3 and 7 (in two different locations)	0.73 and 0.69 (in two different locations)	18.2 and 8.9 (in two different locations)	Australia [141]
DCD + biochar	Urea: 300 kg N ha ⁻¹ (split-applied)	rice	↑ 62.5% (in 1st year) ↑ 47.7% (in 2nd year)	↑ 4.1% (in 1st year; split-applied urea at 300 kg N ha ⁻¹) ↑ 10% (in 2nd year; split-applied urea at 300 kg N ha ⁻¹)	↑ 4.6% and ↑ 7.2% (in 1st and 2nd year)	46.3 and 44.9 (in 1st and 2nd year)	-	11 and 10.3 (in 1st and 2nd year)	China [123]
DMPP	Urea: 120 kg N ha ⁻¹ (split-applied; Palm stearin coated urea DMPP 100% 0.464 g/100 g urea)	rice	-	↑ 12.9% (split-applied urea at 120 kg N ha ⁻¹)	-	-	-	-	Malaysia [142]
Nitrapyrin	Urea: 120 kg N ha ⁻¹ (single application at tillering)	wheat	↑ 39.9%	↑ 3.2% (applied at tillering; urea at 120 kg N ha ⁻¹) ↑ 4.6% (split-applied; urea at 120 kg N ha ⁻¹)	↓ 5% (applied at tillering; urea at 120 kg N ha ⁻¹) ↑ 5.7% (split-applied; urea at 120 kg N ha ⁻¹)	-	-	7.3	Spain [83]

Table 1. Cont.

Inhibitor	N Application Rate	Crop(s)	Yield (Approximate Upward and Downward Trends Provoked by the Utilization of Inhibitors)		NUE	NUtE	NHI	NAE (kg Seed/Tuber Increased kg N ⁻¹ Applied)	Country References
DMPSA	Urea: 120 kg N ha ⁻¹ (single application at tillering)	wheat	↑ 34.6%	↓ 0.7% (applied at tillering; urea at 120 kg N ha ⁻¹) ↑ 0.6% (split-applied; urea at 120 kg N ha ⁻¹)	↑ 1.6% (applied at tillering; urea at 120 kg N ha ⁻¹) ↑ 12.3% (split-applied; urea at 120 kg N ha ⁻¹)	-	-	6.3	Spain [83]
DMPP	Urea: 300 kg N ha ⁻¹ (split-applied 50:50)	wheat	↑ 88.6%	↑ 6.4% (urea at 300 kg N ha ⁻¹ split-applied)	↑ 2.4% (three-year average)	-	-	10.3	China [139]
DMPP	Ammonium sulphate: 120 kg N ha ⁻¹	wheat	↑ 14.4%	↑ 6.3% (ammonium sulphate at 120 kg N ha ⁻¹)	↑ 3.6%	-	-	3.2	Iran [101]

Percentages are presented as average values with one decimal of the increase or decrease in yield and several indexes. Data is derived from tables, figures and graphs from literature and indicate approximate values as mean of sites/years/replications. Increases or decreases are not always statistically significant at different significance level, depending on study level. Nitrogen efficiency values were either calculated or estimated as differences of percentages.

Table 2. Urease inhibitors use in different crops/regions/rates and their association with Nitrogen efficiency indices.

Inhibitor	N Application Rate	Crop(s)	Yield (Approximate Upward and Downward Trends Provoked by the Utilization of Inhibitors)		NUE	NUtE	NHI	NAE (kg Seed/Tuber Increased kg N ⁻¹ Applied)	Country References
Urease inhibitors (UI)			Compared to unfertilized control	Compared to fertilized control without inhibitors	Compared to fertilized control without inhibitors			Compared to unfertilized control	
NBPT	Urea: 96 kg N ha ⁻¹	maize	↑ 203% or 3.03-fold	↑ 49% (urea at 120 kg N ha ⁻¹)	↑ 45%	-	-	-	Malaysia [113]
NBPT	Urea: 178.4 kg N ha ⁻¹	maize	↑ 85% (urea: 28.4 kg N ha ⁻¹)	↑ 5.6% (urea at 178.4 kg N ha ⁻¹)	-	-	-	29.4	Canada [115]

Table 2. Cont.

Inhibitor	N Application Rate	Crop(s)	Yield (Approximate Upward and Downward Trends Provoked by the Utilization of Inhibitors)		NUE	NUtE	NHI	NAE (kg Seed/Tuber Increased kg N ⁻¹ Applied)	Country References
NBPT	Urea: 180 kg N ha ⁻¹ (single application)	maize	↑ 36%	↑ 3% (urea at 225 kg N ha ⁻¹)	↑ 7.1% (grain NUE)	-	0.79	15.3	China [110]
NBPT	Urea: 300 kg N ha ⁻¹ (split-applied 50:50)	maize	↑ 64.8%	↑ 3.5% (urea at 300 kg N ha ⁻¹ split-applied)	↑ 2.5% (three-year average)	-	-	11.7	China [139]
NBPT	Urea: 270 kg N ha ⁻¹	rice	↑ 55%	↑ 2%	↑ 4%	-	-	10.7	China [120]
2-NPT	Urea: 180 kg N ha ⁻¹ (split-applied)	wheat	↑ 59%	↑ 2.1% (urea at 180 kg N ha ⁻¹)	↑ 2.3%	-	-	-	Germany [100]
NBPT	Urea: 160 kg N ha ⁻¹ (split-applied)	cotton	↑ 3.3-fold (lint yield) ↑ 3.2-fold (seed cotton yield)	↑ 18.7% (lint yield) ↑ 14.5% (seed cotton yield; urea at 160 kg N ha ⁻¹)	-	13–21.5	0.72	22.4 (seed cotton)	Greece [126]
NBPT	Urea: 120 kg N ha ⁻¹ (single application at planting)	sweet potato	↑ 34%	↑ 6.9% (urea at 120 kg N ha ⁻¹)	↑ 1.7-fold	-	0.84	36.3	Greece [52]
NBPT	Urea: 150 kg N ha ⁻¹ (split-applied)	wheat (inoculated with <i>Azospirillum-brasilense</i>)	-	↑ 18%	↑ 24%	-	-	-	Brazil [102]
NBPT	Urea: experimentation on 0–200 kg N ha ⁻¹ rates	wheat	-	↑ 0.76%	↑ 24.5% (1st year) ↓ 35.4% (2nd year)	-	0.62–0.69	8–12	Brazil [103]
NBPT	Urea: 300 kg N ha ⁻¹ (split-applied 50:50)	wheat	↑ 85.7%	↑ 4.8% (urea at 300 kg N ha ⁻¹ split-applied)	↑ 2.3% (three-year average)	-	-	10	China [139]

Table 2. Cont.

Inhibitor	N Application Rate	Crop(s)	Yield (Approximate Upward and Downward Trends Provoked by the Utilization of Inhibitors)		NUE	NUtE	NHI	NAE (kg Seed/Tuber Increased kg N ⁻¹ Applied)	Country References
NBPT	Urea: 400 kg N ha ⁻¹ (either single or split-applied)	bermudagrass	-	↑ 27% (total herbage accumulation)	↑ 14%	-	-	23	Brazil [140]
NBPT	Urea: 50 kg N ha ⁻¹ (at the end of tillering)	wheat	↑ 29% and ↑ 12% (in two different locations)	↑ 6% and ↓ 16.9% (single applied at sowing in two different locations; urea at 50 kg N ha ⁻¹) ↓ 0.6% and ↑ 2.6% (single applied at the end of tillering in two different locations; urea at 50 kg N ha ⁻¹)	↓ 3% and ↓ 43% (single applied at sowing in two different locations; urea at 50 kg N ha ⁻¹) ↓ 2% and ↑ 10% (single applied at the end of tillering in two different locations; urea at 50 kg N ha ⁻¹)	41.5 and 42.2 (in two different locations)	0.74 and 0.83 (in two different locations)	17.5 and 4 (in two different locations)	Australia [143]
Hydroquinone + biochar	Urea: 300 kg N ha ⁻¹ (split-applied)	rice	↑ 69.3% (in 1st year) ↑ 49.2% (in 2nd year)	↑ 8.4% (in 1st year; split-applied urea at 300 kg N ha ⁻¹) ↑ 11.1% (in 2nd year; split-applied urea at 300 kg N ha ⁻¹)	↑ 10% and ↑ 12.6% (in 1st and 2nd year)	44.4 and 42.1 (in 1st and 2nd year)	-	12.3 and 10.6 (in 1st and 2nd year)	China [123]
NBPT	Urea: 120 kg N ha ⁻¹ (single application at tillering)	wheat	↑ 37.6%	↑ 1.5% (applied at tillering; urea at 120 kg N ha ⁻¹) ↑ 2.9% (split-applied; urea at 120 kg N ha ⁻¹)	↑ 4.4% (applied at tillering; urea at 120 kg N ha ⁻¹) ↑ 15.1% (split-applied; urea at 120 kg N ha ⁻¹)	-	-	6.9	Spain [83]
NBPT	Urea: 60 kg N ha ⁻¹ (single application)	flax	↑ 17.2%	↑ 8.1% (single application; urea at 60 kg N ha ⁻¹)	↑ 3-fold	-	0.85	1.7	Greece [56]

Percentages are presented as average values with one decimal of the increase or decrease in yield and several indexes. Data is derived from tables, figures and graphs from literature and indicate approximate values as mean of sites/years/replications. Increases or decreases are not always statistically significant at different significance level, depending on study level. Nitrogen efficiency values were either calculated or estimated as differences of percentages.

Table 3. Nitrification and urease inhibitors use in different crops/regions/rates and their association with Nitrogen efficiency indices.

Inhibitor	N Application Rate	Crop(s)	Yield (Approximate Upward and Downward Trends Provoked by the Utilization of Inhibitors)		NUE	NUtE	NHI	NAE (kg Seed/Tuber Increased kg N ⁻¹ Applied)	Country References
Nitrification (NI) + Urease inhibitors (UI)			Compared to unfertilized control	Compared to fertilized control without inhibitors	Compared to fertilized control without inhibitors			Compared to unfertilized control	
Nitrapyrin + NBPT	Urea: 240 kg N ha ⁻¹	wheat	↑ 78%	↑ 7.2% (urea at 300 kg N ha ⁻¹)	↑ 30%	-	-	10.8	China [97]
DCD + Hydroquinone	Urea: 125 kg N ha ⁻¹ (split-applied)	wheat	↑ 3.7-fold	↑ 8.6% (split-applied urea at 125 kg N ha ⁻¹)	↑ 9.3%	47.5	-	28.6	China [105]
DMPSA + NBPT	Urea: 120 kg N ha ⁻¹ (single application at tillering)	wheat	↑ 25.8%	↓ 7.2% (applied at tillering; urea at 120 kg N ha ⁻¹) ↓ 5.9% (split-applied; urea at 120 kg N ha ⁻¹)	↑ 16.2% (applied at tillering; urea at 120 kg N ha ⁻¹) ↑ 26.9% (split-applied; urea at 120 kg N ha ⁻¹)	-	-	4.7	Spain [111]
DCD + NBPT	Urea: 31.5 kg N ha ⁻¹ at planting Urea: 70 kg N ha ⁻¹ at planting Urea: 63 kg N ha ⁻¹ split-applied	wheat	↑ 0.6% ↑ 33.7% ↑ 17.2%	↓ 5% (urea at 31.5 kg N ha ⁻¹ at planting) ↑ 25.6% (urea at 70 kg N ha ⁻¹ at planting) ↑ 8.2% (urea at 63 kg N ha ⁻¹ split-applied)	↓ 94% (urea at 31.5 kg N ha ⁻¹ at planting) ↑ 3.5-fold (urea at 70 kg N ha ⁻¹ at planting) ↑ 2-fold (urea at 63 kg N ha ⁻¹ split-applied)	-	-	0.32 8.1 4.6	USA [106]
DCD + NBPT	Urea: 240 kg N ha ⁻¹ (side-banded at planting)	cotton	↑ 75% (lint yield)	↑ 11% (lint yield; urea at 240 kg N ha ⁻¹)	7.5 kg per kg N compared to 4.5 kg in fertilized control	-	-	-	China [82]
DCD + NBPT	Urea: 160 kg N ha ⁻¹ (split-applied)	cotton	↑ 3.4-fold (lint yield) ↑ 3.2-fold (seed cotton yield)	↑ 20.5% (lint yield) ↑ 14.5% (seed cotton yield; urea at 160 kg N ha ⁻¹)	-	14–23	0.72	22.4	Greece [126]

Table 3. Cont.

Inhibitor	N Application Rate	Crop(s)	Yield (Approximate Upward and Downward Trends Provoked by the Utilization of Inhibitors)		NUE	NUtE	NHI	NAE (kg Seed/Tuber Increased kg N ⁻¹ Applied)	Country References
DCD + NBPT	Urea: 120 kg N ha ⁻¹ (single application at planting)	sweet potato	↑ 37.8%	↑ 9.9% (urea at 120 kg N ha ⁻¹)	↑ 18-fold	-	0.85	43	Greece [25]
DCD + Hydroquinone + biochar	Urea: 300 kg N ha ⁻¹ (split-applied)	rice	↑ 81.9% (in 1st year) ↑ 45.8% (in 2nd year)	↑ 16.5% (in 1st year; split-applied urea at 300 kg N ha ⁻¹) ↑ 8.6% (in 2nd year; split-applied urea at 300 kg N ha ⁻¹)	↑ 12% and ↑ 11.7% (in 1st and 2nd year)	46.3 and 41.6 (in 1st and 2nd year)	-	14.5 and 9.9 (in 1st and 2nd year)	China [123]
DCD + NBPT	Urea: 60 kg N ha ⁻¹ (single application)	flax	↑ 22.7%	↑ 13.2% (single application; urea at 60 kg N ha ⁻¹)	↑ 4.2-fold	-	0.85	4.4	Greece [56]
DCD + NBPT	Urea: 202 kg N ha ⁻¹ (single broadcast application)	maize	↑ 69.4%	↑ 0.27% (single application; urea at 202 kg N ha ⁻¹)	-	-	-	29.4	USA [117]
DMPP + NBPT	Urea: 300 kg N ha ⁻¹ (split-applied 50:50)	maize	↑ 74.6%	↑ 9.6% (urea at 300 kg N ha ⁻¹ split-applied)	↑ 6.8% (three-year average)	-	-	13.4	China [139]
DMPP + NBPT	Urea: 300 kg N ha ⁻¹ (split-applied 50:50)	wheat	↑ 83.7%	↑ 3.7% (urea at 300 kg N ha ⁻¹ split-applied)	↑ 2.7% (three-year average)	-	-	9.8	China [139]

Abbreviations: NI, nitrification inhibitor; UI, urease inhibitor; CP/nitrapyrin, 2-chloro-6-(trichloromethyl)-pyridine; DMPSA, 3,4-dimethylpyrazole succinic; DCD, dicyandiamide; DMPP, 3,4-dimethylpyrazole phosphate; NBPT, N-(n-Butyl) ThiophosphoricTriamide; 2-NPT. Percentages are presented as average values with one decimal of the increase or decrease in yield and several indexes. Data is derived from tables, figures and graphs from literature and indicate approximate values as mean of sites/years/replications. Increases or decreases are not always statistically significant at different significance level, depending on study level. Nitrogen use efficiency (NUE) values were either calculated or estimated as differences of percentages.

6. Conclusions

The potentiality of urease and nitrification inhibitors to increase nitrogen use efficiency from the mass application of agricultural fertilizers has long been identified. Fertilizer inhibitors are considered an integral part of the fertilizer market. However, the undefined and non-optimal growth stage of crops that demand nitrogen supply, the irregular or misplaced fertilization, and the use of non-appropriate fertilizer products raise operation costs and reduce the net profit to farmers. Therefore, decision-making on the field level should be based upon ratios and indexes. A key to increasing yields may be towards later nitrogen uptake in the growing cycle and also rise of nitrogen storage in aboveground parts of plants. Soil nitrogen losses by leaching, along with competition for photosynthesis within the plant during seed growth, require increased nitrogen storage and transport from plant tissues to seeds in large quantities. Nitrogen indicators are an indispensable tool for assessing the percentage or amount of nitrogen stored in plants or not. N management indexes could describe better the large scene, indicating the positive or negative effects of inhibitors in various agronomic situations. Nitrogen Use Efficiency (NUE) is widely used to show the nitrogen recovery efficiency of *all crops* depending on many factors, either environmental or agricultural. Nitrogen Utilization Efficiency (NUE) is a rather less common index; however, it could be quite useful in *cotton* and *cereals* to show the amount of seed/lint or produced dry matter concerning total N plant uptake. NUE revealed if applied nitrogen is stoked to the product of each crop (seed, lint, etc.) or remains at the above-ground part of the plant. Nitrogen Agronomic Efficiency (NAE) is particularly important to optimize the nitrogen fertilization rates and predict the increase of seed yield per kilo of N fertilizer, with yield gains for unit of N fertilizer applied. This index is ideal for the estimation of required fertilizer. This index is useful for *all grain-producing plant* (cereals, legumes, pseudocereals, and industrial hemp). Additionally, NAE could be used in many novel crops such as sweet potato. Finally, Nitrogen Harvest Index (NHI) is quite important for *wheat* and other crops, where protein content and yield need to be calculated. NHI and N yield is needed in crops in which nitrogen absorption, and therefore protein, is essential throughout the whole plant, such as silage crops. However, the farmer determines the final use of these indexes since different trade end-use of the final product requires diverse nitrogen allocation. For this purpose, seed/grain/tubers yield is better expressed through NUE, NUE, and NAE indexes. NUE also expresses the allocated nitrogen in various plant tissues and is useful when the crop is cultivated for silage. On the contrary, NHI describes better the quality characteristics of the final products. This review inclines to the conclusion that N-related indices have a fundamental role in N fertilization management for sustainable agricultural production systems. However, their prudent use requires an accurate assessment of these indices by eliminating knowledge management practices based on the production direction (target) of each crop along with the accurate interpretation of the respective indicators.

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Abbreviations

N, nitrogen; NI, nitrification inhibitor; UI, urease inhibitor; CP/nitrapyrin, 2-chloro-6-(trichloromethyl)-pyridine; DMPA, 3,4-dimethylpyrazole succinic; DCD, dicyandiamide; DMPP, 3,4-dimethylpyrazole phosphate; NBPT, N-(n-Butyl) Thiophosphoric Triamide; 2-NPT; NUE, Nitrogen Use Efficiency; NUtE, Nitrogen Utilization Efficiency; NAE, Nitrogen Agronomic Efficiency; NHI, Nitrogen Harvest Index.

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