

## Urea (NBPT) an alternative in the nitrogen fertilization of annual crops

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### Abstract

Nitrogen fertilizers are necessary, because thanks to them, crop production is improved. After water and temperature, it is considered as the third most important factor in the production of plant-based foods. Urea as a fertilizer, has the advantage of providing a high nitrogen content (46%), which is essential in the metabolism of the plant. The biggest disadvantage is the loss of nitrogen (N) in the form of ammonia gas (NH<sub>3</sub>), coming from its decomposition when applied to the soil. Slow-release urea is used to reduce volatilization losses after the hydrolysis phase and by leaching after ammonium nitrification. To reduce volatilization losses and maintain an adequate availability of N in the soil, different agronomic management strategies have been evaluated. The triamide N-(n-butyl) thiophosphoric (NBPT), urease inhibitor, temporarily prevents the enzymatic degradation of urease and minimizes the loss by volatilization of NH<sub>3</sub>, thereby increasing the absorption of N from fertilizer by the crop. The study was carried out during 2018. The paper elaborated addresses the role of N in cultivated plants, some ecological implications, the use of urea and especially a compilation of the characteristics of NBPT urea and of the most relevant research on the use of this fertilizer and its impact on increasing yield in annual crops.

**Keywords:** coated fertilizers, urea hydrolysis, urease.

Reception date: September 2019

Acceptance date: October 2019

In order to maintain agricultural production levels, world demand for nitrogen fertilizers increased from 108.2 million tons (t) in 2011 to 109.9 million t in 2012, at a growth rate of 1.6%. In 2018, 116 million t were produced, with a growth of 1.3% (Cantarella *et al.*, 2018). Of the total increase in demand, of 7 million t of nitrogen between 2012 and 2018, 50% would be from Asia, 16% from the United States of America, 13% from Europe, 7% from Africa and 1% from Oceania. In America, most of the increase is expected to be from Latin America (13%), mainly from Brazil, Argentina, Colombia and Mexico (Felix, 2013). In this sense, Cantarella *et al.* (2018) indicate that of the total nitrogen-based fertilizer produced in 2019, 55% will be urea.

Nitrogen (N) is the chemical element that directly influences agricultural production quantitatively and qualitatively. Increase leaf area, leaf expansion, leaf thickness and photosynthesis rate. The supply of N improves the photosynthetic process and, consequently, increases the duration of the leaf area, net assimilation rate, biomass production and yield (Khanzada *et al.*, 2016). The deficiencies of this element reduce the production of dry matter because it decreases the radiation intercepted by the plant canopy and the efficiency of converting this energy into biomass.

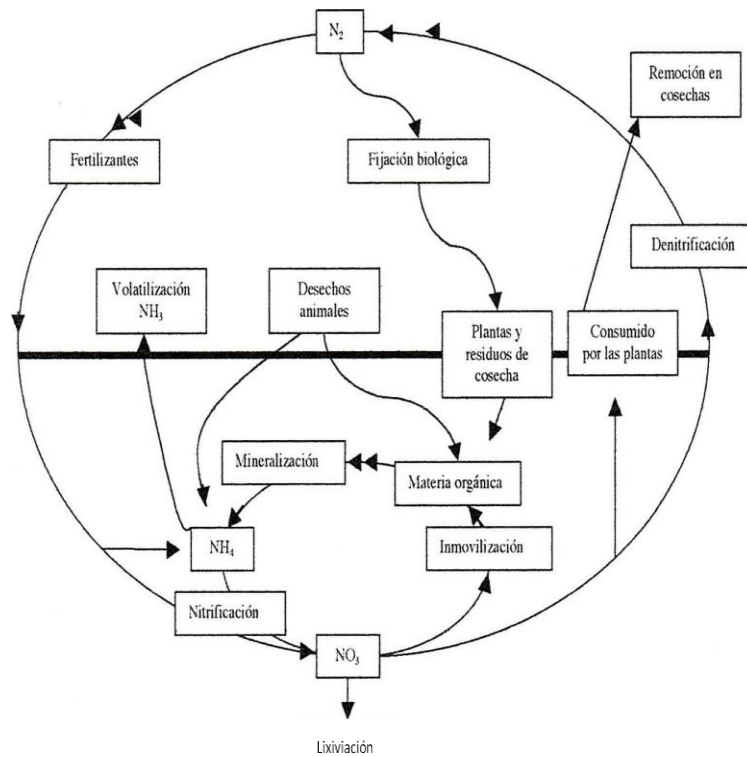
N is absorbed by plants mainly in the form of nitrate ( $\text{NO}_3^-$ ) or ammonium ( $\text{NH}_4^+$ ) ions. Plants use these two forms in their growth processes. Almost all of the N they absorb is in the form of nitrate. There are two reasons: the first, nitrate is mobile in the soil and moves in the water to the roots of the plants, where it is absorbed. In addition, ammonium is bound to the surface of soil particles and cannot move towards the roots. The second, under appropriate conditions of temperature, aeration, humidity and soil pH, microorganisms transform all forms of soil nitrogen into nitrate (Galloway *et al.*, 2004).

Maddonni *et al.* (2004) mention that the response of a crop to the application of nitrogen through fertilization, involves both absorption and its use for the production of dry matter. The lack of response of a crop to nitrogen nutrition may be related to problems in nutrient absorption due to the time, form of application, type of fertilizer, available amount of initial nitrogen in the soil and its moisture content. The loss of N due to ammonia volatilization is the main cause of low urea efficiency and environmental pollution. In recent years, urease hydrolysis inhibitor molecules have been introduced, which decrease the losses of N by volatilization.

The efficacy of these inhibitors is still evaluated (Trenkel, 2010; Cantarella *et al.*, 2018). The objective of this trial was to gather information to know the role of N in agriculture, its ecological implications, the use of urea, and urea NBPT as a slow-release fertilizer and its incidence in the increase in yield in annual crops.

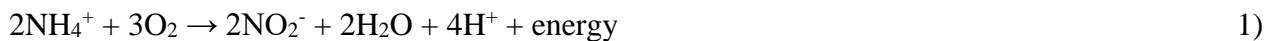
### **Nitrogen cycle in the soil**

Most of N in the soil is part of the organic matter, so it is not usable for it. Only about 2% of this nitrogen is made available to plants per year. Figure 1 shows the nitrogen cycle, the N of organic matter is mineralized by means of two microbial processes. In the first, proteins and related compounds are broken down into amino acids by the reaction called aminization. Soil organisms obtain energy from this process and use part of the N of the amino compounds in their own cellular structure.



**Figure 1. Nitrogen cycle. Adapted from Beegle (2004) and taken from Elizondo (2006).**

In the second process, called ammonification, the amino compounds are transformed into ammonia (NH<sub>3</sub>) and ammonia (NH<sub>4</sub><sup>+</sup>). The two processes, aminization and ammonification, are known as mineralization (Cantarella *et al.*, 2018). Ammonium is converted into nitrate primarily by two groups of bacteria. Those of the genus *Nitrosomonas* convert ammonium to nitrite.



Then, nitrobacter converts nitrite to nitrate.



This two-stage process is called nitrification. The nitrification rate in soils is strongly dependent on temperature, water content and soil pH. The optimum temperature for nitrification varies depending on the geographic location and the depth of the soil. This variation is apparently caused by the adaptation of bacteria to the environment. Consequently, soils in cold areas have a lower optimum temperature for nitrification than soils in warmer areas. Similarly, soils with deep horizons, which are usually exposed to low temperatures, have lower optimum temperatures for nitrification than surface horizons.

Nitrifiers need water and oxygen to carry out the oxidation of ammonium and nitrate. Optimum conditions for oxidation have been found when the soil is at field capacity. The pH of the soil has a strong effect on the nitrification rate. In general, nitrification stops once the pH values

fall below 4.5 or increase above 9. The inhibition observed at low pH values can be caused by high toxic levels of aluminum or high concentrations of nitrous acid. In contrast, the inhibition observed with high pH values is generally caused by high levels of ammonia in the soil solution (Cabrera, 2007).

### **Nitrogen losses and their environmental effect**

The greatest losses of nitrogen from the soil are due to harvest removal, volatilization and leaching. In case of excess moisture, mineral nitrogen ( $\text{NO}_3^-$ ) can be leached beyond the reach of edible root crops. Leaching is defined as the downward movement of  $\text{NO}_3^-$ ; through the soil by infiltration and water flow. Additionally, under certain conditions, some inorganic forms of nitrogen can be converted to gases and lost into the atmosphere. The main routes are denitrification and volatilization (Galloway *et al.*, 2004).

#### **Denitrification**

Denitrification is the opposite process to biological fixation in which nitrogen oxides ( $\text{NO}_3^-$  and  $\text{NO}_2$ ) are reduced step by step by the enzyme reductase to nitric oxide (NO) and nitrous oxide ( $\text{N}_2\text{O}$ ), which is finally transformed in gaseous nitrogen ( $\text{N}_2$ ), which implies loss of N from the soil to the atmosphere and environmental pollution. (Trenkel, 2010). When an abundant supply of nitrogen is provided, denitrification results in a significant loss of nitrogen, which could have been used by crops (Loomis and Connor, 2002; Galloway *et al.*, 2004).

The most active organisms in the denitrification, are the bacteria of the groups of the *Alcaligenes*, *Bacillus* and *Pesudomonas* abundant in the soil. The main characteristic of their metabolism is that under anaerobic conditions they use more nitrate than oxygen as an electron acceptor for respiratory activity. This process can occur in fine textured soils with poor drainage or in well drained soils during brief periods of saturation. The N applied to crops as fertilizer is not fully recovered by them. One of the gases emitted is  $\text{N}_2\text{O}$ , a compound that increases the greenhouse effect in concentrations of  $0.6\text{-}0.9 \mu\text{L m}^{-3} \text{ year}^{-1}$  and contributes to the thinning of the ozone layer (Maddonna *et al.*, 2004; Mora *et al.*, 2007; Grisell *et al.*, 2007).

#### **Volatilization**

$\text{NH}_3$  is a volatile gas and is dispersed into the atmosphere from aqueous solutions. In water:



This balance depends on the pH of the soil solution, above a pH of 5 the gas losses increase. That is why volatilization causes significant losses in dry, acid and calcareous soils (Loomis and Connor, 2002; Maddonna *et al.*, 2004). The loss of N by volatilization of  $\text{NH}_3$  may be the main cause of the low efficiency of some ammonia fertilizers. Ammonia gasification is an important route of dispersion of N in nitrogen fertilizers that have urea in their formulation and are applied to the soil surface.

The magnitude of the losses in ‘direct sowing’ is affected by environmental factors (humidity, temperature and wind), soil (pH, buffer capacity, cation exchange capacity, organic matter) and cultivation (quantity and type of crop residues), source and dose of N. In turn, rapid hydrolysis of urea results in greater losses of  $\text{NH}_3$ , because its velocity depends on urease activity (Barbieri *et al.*, 2010).

## Leaching

Nitrate leaching ( $\text{NO}_3^-$ ) is inevitable despite the implementation of best agricultural practices, such as water resource management and adequate nitrogen fertilization. Nitrate is the most oxidized form of nitrogen found in nature, nowadays it is recognized as a contaminant of water for human consumption (Baeta, 2016). Nitrate losses vary according to the phenological phases of the plants, being greater in the germination, growth and development stages, decreasing in the harvest stage; it is also independent of the source of fertilizer (Reyes *et al.*, 2012).

In synthesis, denitrification, volatilization and leaching, decrease the efficiency of the use of the nitrogen that is added, it is estimated that only half of N in the form of fertilizer applied to the crops is incorporated into their biomass, while the other half is lost in a gaseous way to the atmosphere or leached from the ground into bodies of water (Galloway *et al.*, 2003; Vivian *et al.*, 2018). N by passing through other terrestrial ecosystems, reduces biodiversity, pollutes the air, water and aggravates global warming (Schlesinger, 2009; Baeta *et al.*, 2016).

## Urea

Urea is the main source of nitrogen fertilization in the world, especially in developing countries; the advantages of this fertilizer in relation to others are: higher N content, it can be incorporated into the soil prior to planting and as it is an acid reaction fertilizer, it can be used in neutral or slightly alkaline soils, in addition to its low cost of transport per unit of N and safer handling (Trenkel, 2010; Cantarella *et al.*, 2018). To produce it, ammonia and carbon dioxide are reacted in the presence of a catalyst, in a special vessel at temperatures between 170 and 210 °C and pressures ranging from 170 to 400 atmospheres. The reactions are as follows (Galloway *et al.*, 2004).



The concentrated liquid from these reactions contains about 80% urea. This product can be diluted for use in the form of solutions or it can be further concentrated and pearled or granulated to obtain solid urea (Galloway *et al.*, 2004). Due to its high solubility, it can be dissolved and applied in the irrigation water. In foliar applications, it can be quickly absorbed by the leaves. Once urea comes into contact with soil or plants, urease quickly converts it to  $\text{NH}_3$ . During this process, the N contained in the urea is susceptible to gaseous losses by volatilization such as  $\text{NH}_3$  (Witte *et al.*, 2011).

Barbieri *et al.* (2010) confirm the above, since they found that volatilization losses of N as ammonia are important when applied nitrogen fertilizers contain urea in their formulation. The importance of the moment and form of application, in addition to the dose of fertilizer used, can induce an improvement in absorption efficiency.

Volatilization losses of  $\text{NH}_3$  from urea, up to  $30 \text{ kg N ha}^{-1}$ , when applied to volley, equivalent to a 25% loss of the fertilizer added. In evaluations carried out in a coffee plantation in the central area of Colombia in vegetative growth, they found that after 20 days of nitrogen fertilization on the soil surface, the accumulated nitrogen volatilization in granulated urea was 20%. Regarding the time of application, if the fertilizer is supplied during the maximum nitrogen demand of the plant, the immobilization and losses of the soil-plant system can be reduced and therefore, the efficiency in the use of nitrogen can be increased.

In this sense, small grain cereals absorb up to 90% of nitrogen before the flag leaf stage. Ballesteros *et al.* (2015) indicated that when all of the nitrogen is applied in the triticale stage of tillering for forage, subsequent fertilizer fractionation is not justified. Regarding the fractional supply of urea, several investigations have been carried out, including.

Pino and Añez (1997) who found that urea fractionation had no effect on yield or head conformation on lettuce; however, Pichardo *et al.* (2007) in an investigation in bean cultivation 'cochinera', they reported that with the fractional application of  $132 \text{ kg N}$  (50% at the time of sowing and 50% at 40 days after sowing), greater efficiency in use was achieved of radiation for biomass ( $1.05 \text{ g MJ}^{-1}$ ), efficiency in the use of water for biomass and yield ( $3.49$  and  $1.24 \text{ g m}^{-2} \text{ mm}^{-1}$ , respectively) and consequently, greater biomass and yield with  $1046.9$  and  $371.3 \text{ g m}^{-2}$ , respectively.

Escalante *et al.* (2015), in an experiment conducted on 'peanut' beans in Montecillo, Mexico, concluded that the supply of  $50 \text{ kg N}$  at the time of sowing and  $50 \text{ kg N}$  at 40 days after sowing, biomass was increased (12.5% ) and the grain yield (36.9%), with respect to the control treatment ( $0 \text{ kg N}$ ). As for the type of ideal nitrogen fertilizer, today, it is considered that the input must have at least three fundamental characteristics (Shavit *et al.*, 2013): 1) that only needs a single application throughout the period of growth of the plant, with the proportion of nitrogen required for its optimal development; 2) present a maximum of agronomic productivity; and 3) have minimal detrimental effects on the earth, water and environment.

A strategy to add urea to cultivated plants and increase their yield is to use slow-release fertilizers (NBPT). The fertilizer industry has developed a special type of urea that prevents, or at least reduces, losses and minimizes environmental pollution (Trenkel, 2010).

### **Urea NBPT**

Nitrogen fertilization should consider agronomic and environmental visions as crop yield and less pollution to contribute to the sustainability of agricultural systems; Slow-release fertilizers integrate these two visions (Zaman *et al.*, 2013). The main process of obtaining controlled release fertilizers is to protect a conventional fertilizer by coating or microencapsulation, making it a

semipermeable material, controlling the penetration of water and releasing the most soluble nutrients present in conventional fertilizer, these being used by plants according to their needs (Watson *et al.*, 2008; Shavit *et al.*, 2013).

A variety of coatings have been applied to fertilizer particles to regulate their solubility in the soil. These additives are chemical compounds that delay and stabilize the release of nitrogen from fertilizers. Controlling the nutrient release rate can offer multiple performance, economic and environmental benefits. Coatings are most often applied to granulated or pearled nitrogen fertilizers. Since urea has the highest N content in common soluble fertilizers, it is the base material for most coated fertilizers (Prasad and Shivay, 2015).

To delay hydrolysis, it has been proposed to apply urea in association with urease inhibitors, thus the molecule favors root assimilation over a long term, which acts essentially as a slow-release nitrogen fertilizer (Prasad and Shivay, 2015; Vivian *et al.*, 2018). Polymer-coated urea slowly releases nitrogen to the soil-plant system and is only applied in planting. The use of NBPT urea can reduce ammonia loss by 50% to 60% compared to untreated urea (Lema *et al.*, 2017). Urease inhibitors provide farmers with an additional tool to keep the N applied in the radical zone, causing greater agronomic use of the element and environmental benefits.

Urease inhibitors decrease the volatilization rate of ammonia and increase nutrient availability for the plant (Cantarella *et al.*, 2018). Regarding leaching, the addition of NBPT urea reduces the accumulation of nitrates in the water tables (Zaman *et al.*, 2013). There is evidence in annual crops that show the benefits of using this type of fertilizer. The use of NBPT urea in rice reduced losses due to the volatilization of ammonia compared to conventional urea; the magnitude of the effectiveness of adding NBPT to urea is associated with soil conditions and climate (Baeta *et al.*, 2016).

Li *et al.* (2015) report in winter wheat, that high amounts of volatilized  $\text{NH}_3$  ranged from 11% to 25% of simple urea applied in soils in the north and northwest of China; however, when they used urea modified with NBPT the losses of  $\text{NH}_3$  decreased 83% compared to conventional urea. Vivian *et al.* (2018) when investigating the effectiveness of NBPT urea in reducing the volatilization of  $\text{NH}_3$  in summer corn planted in different soils and environmental conditions, found that weather factors such as precipitation, air temperature and wind speed significantly affected the volatilization of  $\text{NH}_3$  in conventional urea.

These results suggest that the use of NBPT urea has the potential to mitigate  $\text{NH}_3$  losses from alkaline soils on the Loess Plateau, China. In this sense, Maqsood *et al.* (2016) in calcareous soils in Pakistan, they found that the use of the thiameric N- (n-butyl) thiophosphoric urease (NBPT) inhibitor has shown a significant reduction in the volatilization of N. Ousman and Alemayehu (2015) conclude that the use of urease inhibitors, significantly improve the absorption of nitrogen, reduce vaporization, nitrification and leaching.

### **NBPT urea supply and corn yield**

Barbieri *et al.* (2010) in an experiment on corn planted in Balcarce, Argentina, determined that  $\text{NH}_3$  volatilization was higher in urea compared to NBPT urea. However, the yield, grain content of N, and the efficiency in the use of nitrogen were not significantly increased. A

similar response was described by Zamudio *et al.* (2018) in trials conducted in Ixtlahuaca, Villa Victoria and Temascalcingo, Mexico, where they tested six corn hybrids and two types of urea (conventional and stabilized), found no significant differences in grain yield in response to the type of fertilizer.

Gagnon *et al.* (2012) in several experiments on corn conducted in eastern Canada, evaluated the supply of urea and coated urea, concluded that the magnitude of the response varied over the years. In wet years (2008 and 2009) with the addition of NBPT urea (150 kg N ha<sup>-1</sup>), an increase in grain yield of 0.8 t ha<sup>-1</sup> was achieved in 2008 and 1.6 t ha<sup>-1</sup> in 2009, with respect to common urea. Vivian *et al.* (2018) in corn experiments conducted in Tennessee, they concluded that by applying 150 kg ha<sup>-1</sup> of polymer-coated urea, the grain yield was increased on average by 2 t ha<sup>-1</sup> with respect to urea.

### **NBPT urea supply in wheat**

Espindula *et al.* (2016) when investigating wheat in Brazil, reported that with the application of slow-release urea, grain yield was increased over common urea. With 60 Kg N ha<sup>-1</sup> of urea NBPT, 37.5% more grain yield and 38% more N absorbed in relation to the supply of 60 Kg N ha<sup>-1</sup> of normal urea were obtained. Giannoulis *et al.* (2016), testing various doses of NBPT urea in durum wheat, found that with 120 kg ha<sup>-1</sup>, the cereal reached a yield of 4 900 kg ha<sup>-1</sup>, exceeding 180 kg treatments (4 880 kg ha<sup>-1</sup>) and 160 kg (4 290 kg ha<sup>-1</sup>) in grain production.

Dawar *et al.* (2011) conducted a field experiment to investigate the impact of the NBPT urease inhibitor on grain yield and protein content in wheat, compared to conventional urea, in both treatments 200 kg ha<sup>-1</sup> of N. were added. With NBPT urea, the production of grain and protein (6 229 and 1 084 kg ha<sup>-1</sup>) was increased in relation to urea (5 112 and 683 kg ha<sup>-1</sup>); that is, there was an increase of 18% and 37% in yield of grain and total protein, respectively.

In a research conducted in Cantenbury, New Zealand, the effect of different doses of urea with and without NBPT urease inhibitor on wheat yield and quality was evaluated, Zaman *et al.* (2010) concluded that with 300 kg N ha<sup>-1</sup> of NBPT urea, 11% more grain yield and 15.7% more protein were produced compared to conventional urea.

### **NBPT urea supply in other crops**

In Dera, Pakistan during the years 2010 and 2011, experiments were established in field conditions with the objective of evaluating the efficacy of urea applied with inhibitor, to minimize abiotic stress in potato cultivation. Urea treated at a rate of 300 kg N ha<sup>-1</sup> increased tuber yield by 51%. Potato production was 18.8 and 36.8 t ha<sup>-1</sup> for urea and urea NBPT, respectively (Khan *et al.*, 2014).

Piña *et al.* (2014) conducted an investigation where they associated sunflower and pea (*Pisum sativum* L.) based on different levels of slow-release urea (NBPT) finding that with 80 kg ha<sup>-1</sup> the production of achene was maximized (285.8 g m<sup>-2</sup>) and green pod (274.8 g m<sup>-2</sup>) with respect to the control without fertilizer (112.5 and 169.8 g m<sup>-2</sup>, respectively).



In a growth chamber, the effect of NBPT urea on the physiology and growth of cotton (*Gossypium hirsutum* L.) under normal and high temperature conditions was evaluated. The addition of NBPT to the fertilizer had positive effects on leaf chlorophyll, leaf area, dry matter, nitrogen absorption (N) and the efficiency of N use. The absence of a significant interaction effect indicated that the N fertilization was not influenced by temperature (Kawakami *et al.*, 2013).

Zaman *et al.* (2013) at three sites in New Zealand, investigated the effect of urease inhibitor alone and in combination with the nitrification inhibitor dicyandiamide (DCD) in grasslands. The results of the tests showed that the treatment of granular urea with a urease inhibitor (NBPT) increased pasture production and efficiency in nitrogen use. The increase in biomass production is attributed to reduced losses of N through NH<sub>3</sub>, an increase in urea dispersion and a lower nitrification rate.

## Discussion

Various studies indicate that an excess of nitrogen fertilization has an impact on the environment. The emission of greenhouse gases (GHG) is closely related to the excessive use of ammoniacal fertilizers such as urea, since these increase the emission of ammonia (NH<sub>3</sub>), molecular nitrogen (N<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O). Nitrous oxide is produced by soil microorganisms by denitrification. The magnitude of this process increases in soils with high nitrate availability and high-water content. Nitrous oxide is a GHG that has approximately 300 times more atmospheric heating effect, compared to carbon dioxide (Mora *et al.*, 2007; Grisell *et al.*, 2007).

To extend its efficiency the application of urea, in addition to considering the pH, soil moisture content and nitrogen available among others, adequate agronomic management should be given, which includes the type of application, avoiding the spread of the 'volley' fertilizer (Nelson *et al.*, 2014). The optimal moment of application and dose of fertilizer are relevant, since the quantity must be adjusted and the supply of the element synchronized with the needs of crop absorption. The divided or fractional application of urea is closely related to the previous point, as highlighted by the research of Pichardo *et al.* (2007) in faba bean and de Escalante *et al.* (2015) in bean cv. peanut.

The type of urea used is relevant to increase the efficiency of this input. The advantages of urea NBPT over urea is wide. By inhibiting the action of urease, it allows hydrolysis to occur under optimal conditions, minimizing ammonia volatilization by approximately 60%. Likewise, by encouraging hydrolysis to occur in a controlled manner, NBPT urea minimizes nitrate leaching thanks to the lower presence of ammoniacal nitrogen, which can be nitrified, as a consequence of this the contamination of aquifers is less (Vivian *et al.*, 2018).

From the agronomic point of view, the benefits of using slow-release urea are wide, since it limits nitrogen losses and consequently there is a better use of the chemical element. In addition, a single application is made and the nutrient remains available throughout the growing season of the crop. It can be added superficially and increases fertilizer efficiency (Trenkel, 2010; Prasad and Shivay, 2015; Vivian *et al.*, 2018).

The NBPT urea supply has been successfully evaluated in basic crops such as corn, wheat, potatoes, sunflowers, cotton, peas and grasslands, where several researchers report increases in yield per unit area and greater efficiency in the use of nitrogen (Dawar *et al.*, 2011; Gagnon *et al.*, 2012; Kawakami *et al.*, 2013; Zaman *et al.*, 2013; Khan *et al.*, 2014; Piña *et al.*, 2014; Espindula *et al.*, 2016; Giannoulis *et al.*, 2016; Vivian *et al.*, 2018).

## Conclusions

Slow-release urea (NBPT) is an alternative that producers have to properly nourish their crops, by enhancing the assimilation and distribution of nitrogen throughout the growing season. Compared to conventional urea, field studies show a substantial increase in production, which indicates that it is a viable option to increase crop yields per unit area. By gradually releasing the fertilizer to the soil, volatilization losses of toxic nitrogen gases and nitrate leaching decrease, promoting Sustainable Agriculture and environmental conservation.

## Acknowledgments

The authors thank CONACYT for the scholarship they currently provide to the PhD student in Agricultural Sciences and Natural Resources Edgar Javier Morales Morales.

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