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Nitrogen: from discovery, plant assimilation, sustainable usage to current enhanced efficiency fertilizers technologies – A review

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ABSTRACT: From 1913 onwards, the global situation changed from a scenario of nitrogen (N) scarcity to an abundance of ammonia (NH_3) produced synthetically via the Haber-Bosch process. Several N compounds have been synthesized since then, with urea becoming the main source of N, accounting for 55 % of current N consumption. However, N efficiency in agroecosystems is low and, normally, N recovery in cultivated plants is less than 50 %. This occurs because a large amount of reactive N is lost to the environment, inducing various forms of pollution, threatening human and environmental health, in addition to causing a negative economic impact on the farmer. The main processes responsible for low N efficiency are NH_3 volatilization, leaching, and N denitrification. Considering global NH_3 volatilization losses of 14 %, it can be assumed that up to 8.6 million Mg of urea are lost every year in the form of NH_3. For each ton of NH_3 produced, 1.9 to 3.8 Mg of CO_2 is emitted into the atmosphere. Therefore, increasing N use efficiency (NUE) without compromising yield is a necessity and a challenge for crop improvement programs and current management systems, in addition to reducing greenhouse gas emissions. In this context, enhanced efficiency fertilizers (EEFs), which contain technologies that minimize the potential for nutrient losses compared to conventional sources, are an alternative to increasing the efficiency of nitrogen fertilization. Currently, EEFs are classified into three categories: stabilized, slow-release, and controlled-release. This study aims to understand the technologies used to produce EEFs and the factors that govern their availability to plants. This review covers the following topics: the discovery of N, N dynamics in the soil-atmosphere system, N assimilation in plants, strategies to increase NUE in agrosystems, NH_3 synthesis, NH_3 volatilization losses, N fertilizer technologies, the importance of characterization of EEFs, conventional nitrate or ammonium-based fertilizers to reduce gaseous losses of NH_3 and future prospects for the use of N fertilizers in agriculture.

Keywords: urea, nitrogen cycle, ammonia production, Haber-Bosch.

INTRODUCTION

With the advent of plant and animal domestication, early civilizations began to cultivate the soil, leading to the development of agriculture and allowing our ancestors to settle down in a fixed place. However, at that time, there was no knowledge about the importance of mineral elements for plant growth and development. It was common practice at that time to increase crop yields by enhancing the soil with animal manure, ash, or marl applications. Up to the end of the 18th century, chemical elements had yet to be discovered and named, including nitrogen (N), which was discovered by Daniel Rutherford (Galloway et al., 2013).

The aforementioned achievement was fundamental to understanding that N is an essential nutrient for plant development. With time, N-rich biological materials began to be applied in agriculture to increase food production and keep up with unprecedented population growth. However, these N sources consisted of finite reserves of bird and bat feces, commonly known as guano, found on Pacific islands. At the beginning of the 20th century, natural N sources were replaced by chemically produced N fertilizers obtained using the Haber–Bosch process, wherein dinitrogen gas (N_2) from the atmosphere reacts with hydrogen (H_2) under high pressure and temperature conditions, leading to the formation of ammonia (NH_3) (Galloway et al., 2017). Haber–Bosch process was a technological breakthrough in the fertilizer sector, as it enabled the production of synthetic N fertilizers using NH_3 on a large scale, such achievement was honored with the Nobel Prize in chemistry in 1918 for Fritz Haber and 1931 for Carl Bosch (Erisman et al., 2008).

Unlike the world's first civilizations, which were constrained by the limited availability of natural N sources, modern society is concerned about the large amount of chemical N used in agriculture and its undesirable effects on local ecosystems. Overall, less than 50 % of the N fertilizers applied into agroecosystems are absorbed by plants and incorporated into agricultural products (Zhang et al., 2015; Houlton et al., 2019), while the remaining portion ends up in water bodies and the atmosphere, leading to groundwater contamination, biodiversity reduction, and air pollution (Mulvaney et al., 2009; Behera et al., 2013; Cameron et al., 2013; Martínez-Dalmau et al., 2021; Otto et al., 2022). Nitrogen-fertilizers are associated with acid rain (Mohajan, 2018), greenhouse gas emissions, and global warming (Chai et al., 2019), which is highlighted as one of the greatest challenges facing society today (Yoro and Daramola, 2020). Nitrogen fertilizer use worldwide has increased N_2O (nitrous oxide) atmospheric concentrations. This is especially relevant because N_2O is a greenhouse gas with a warming potential 298 times greater than carbon dioxide (Signor and Cerri, 2013). This gas is highlighted as one of the main greenhouse gases responsible for global warming (Tian et al., 2020). Agricultural activity has been identified as the main source of N_2O emissions, accounting for 70 % of N_2O emissions between 2007 and 2016 (Martínez-Dalmau et al., 2021).

Sodium nitrate, extracted from mines on the Chilean coast, was the first inorganic N fertilizer used by humans. Later, in 1913, the Haber-Bosch process enabled the production of NH_3, and several N fertilizers were then developed using NH_3 as raw material (Table 1). Urea became the most widely used N fertilizer mainly due to its high N concentration (46 %) and low production costs (Cantarella et al., 2018). However, when applied over the soil surface, urea is subjected to hydrolysis by the urease enzyme, causing significant losses of NH_3 through volatilization. In addition to economic losses for the end-users, volatilized NH_3 can be transferred to different environments, causing undesirable effects similar to those previously reported [i.e., soil acidification (Galloway et al., 2004), biodiversity loss (Sutton et al., 2013; Wurtsbaugh et al., 2019), and air pollution (Erisman et al., 2013; Hill et al., 2019)]. Although NH_3 is not considered a greenhouse gas (GHG), it contributes indirectly to NO_2 emissions (Awale and Chatterjee, 2017; Gorh and Baruah, 2019).

Table 1. Nitrogen concentration, salt index (SI), acidity index (AI) and chemical reactions from ammonia (NH_3) and N_2 gas to obtain the main nitrogen fertilizers

Fertilizers	Chemical reactions	% N	SI[1]	AI[2]
Urea	$NH_3 + CO_2 \rightarrow CO(NH_2)_2$	46	75	-84
Ammonium sulfate	$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$	21	69	-110
Ammonium nitrate	$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O \rightarrow HNO_3 + NH_3 \rightarrow NH_4NO_3$	32	105	-58
Sodium nitrate	$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O \rightarrow 2HNO_3 + Na_2CO_3 \rightarrow 2NaNO_3 + H_2CO_3$	16	100	+29
Calcium nitrate	$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O \rightarrow 2HNO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + H_2CO_3$	14	65	+19
Potassium nitrate	$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O \rightarrow HNO_3 + KCl \rightarrow KNO_3 + HCl$	12	-	-
MAP[3]	$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4$	11	30	-65
DAP[4]	$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2HPO_4$	18	34	-70
Aquamony	$NH_3 + H_2O \rightarrow NH_4OH$	10	-	-
Anhydrous amm.[5]	$N_2 + 3H_2 \rightarrow 2NH_3$	82	47	-148
N solutions	$NH_3 + CO_2 \rightarrow CO(NH_2)_2 \rightarrow CO(NH_2)_2 + NH_4NO_3 + H_2O \rightarrow UAN$	32	74	-58

[1] Salt index: increase in the osmotic pressure of the soil solution caused by the salinity of the fertilizer, determined in relation to sodium nitrate, taking as index 100. [2] Acidity index: (sign -) mass (kg) of calcium carbonate ($CaCO_3$) necessary to neutralize the acidity caused by the use of 100 kg of fertilizer, (sign +) equivalent alkalinity. [3] MAP: monoammonium phosphate. [4] DAP: diammonium phosphate. [5] Anhydrous amm: Anhydrous ammonia.

Ammonia volatilization causes significant economic constraints not only because N loss reduces N available for plants and decreases N-use efficiency (NUE) but also because growers usually overapply urea to compensate for these losses. Agricultural production will need to increase by 60 to 100 % from 2007 to 2050 to meet the food demands of the growing population (Bodirsky et al., 2014; Zhang et al., 2015). On the other hand, the anthropogenic input of N to the biosphere has already surpassed the planetary boundary (Vries et al., 2013). Bodirsky et al. (2014) and Steffen et al. (2015) calculated that the overall input of agricultural N should not exceed 62–100 Tg yr^{-1}, as values above this threshold are predicted to produce harmful air and water pollution levels. Current N inputs to the agroecosystems from fertilizers have already exceeded 100 Tg yr^{-1} (IFA, 2019), and the growing demand for food and biofuels will likely lead to further increases in N input to the ecosystem. Faced with the challenge of reducing N losses and enhancing NUE, fertilizer industries have developed several technologies to replace conventional urea, including N sources based on nitrate and ammonium (Otto et al., 2017; Corrêa et al., 2021) and enhanced efficiency fertilizers (EEFs) (Trenkel, 2010; Pan et al., 2016; Cassim et al., 2021).

While most of the food production increase over the last decades was supported by synthetic N fertilizers application, a huge concern is also raised due to the undesirable consequences of N losses from the agrosystems to biosphere (Erisman et al., 2008; Tyagi et al., 2022). Moreover, higher food demand predicted for the upcoming years (Searchinger et al., 2019) can even intensify synthetic N fertilizer usage, which may aggravate existing problems associated with either N fertilizers production or their unsustainable applications (Gao and Serrenho, 2023).

This study addresses crucial issues associated with N discovery, its dynamic in the soil-atmosphere system, and paths of N assimilation by plants. Since urea stands out among the main N sources used for plants worldwide, this review framed the benefits and drawbacks inherent to urea usage. Over the past years, advancements have been made to decrease most disadvantages associated with urea use, such technologies were also lighted up herein. Through encompassing wide aspects associated with N uses, this review may guide stakeholders on better N management to support sustainable food production within the near future.

This review aims to present the history of N discovery, fertilizer production, and the N dynamics into the soil-plant-atmosphere continuum. This study also covers the environmental, economic, and human health problems associated with NH_3 volatilization and the conventional and novel fertilizer technologies to improve NUE and reduce N losses to produce food, fiber, and energy for the growing population.

Nitrogen discovery

Nitrogen was discovered in 1772 by Scottish scientist Daniel Rutherford (Weeks, 1934). Other scientists, such as Carl Scheele, Henry Cavendish, and Joseph Priestley, also studied the element, which they called "burnt air" in reference to the absence of oxygen. However, Rutherford received official credit for its discovery, as he was the first to publish his results (Galloway et al., 2013). Because the N_2 accounts for 78 % of the air's volume and is inert, chemist Antoine-Laurent Lavoisier called it *azote*, meaning lifeless in Greek (Galloway et al., 2013), a term still used in some countries, such as France.

The term "nitrogen" was coined in 1790 by the French chemist Jean-Antoine-Claude Chaptal in reference to saltpeter (potassium nitrate), then known as *nitro*, combined with the French suffix *gène* (producer) (Bebout et al., 2013). Nitrogen was added as the 7th element of the periodic table in 1790, and by the second half of the 19th century, N became known as a common element in plant and animal tissues, which was, therefore, indispensable for all organisms (Galloway et al., 2004).

Before the emergence of N fertilizers obtained by chemical synthesis, farmers used to apply natural sources of N to fertilize plants, including cattle manure, guano, and nitrate mineral salts, as well as growing leguminous plants for biological N fixation (Galloway et al., 2013). In 1898, William Crookes, president of the British Science Association, communicated at a meeting in the United Kingdom that the world's N supply was running out and challenged chemists to develop an industrial process to convert atmospheric N_2 into compounds that could be used for agricultural production (Galloway et al., 2017). It was not until 1908 that such a process was developed, when German chemist Fritz Haber succeeded in synthesizing NH_3 by reacting atmospheric N_2 with H_2 (Equation 1). It would then be up to chemist and engineer Carl Bosch to adapt Haber's laboratory system to an industrial scale, which was successfully completed five years later.

$$N_2 + 3H_2 \xrightarrow{\text{300 atm, 400 °C}} 2NH_3$$
$$\text{Eq. 1}$$
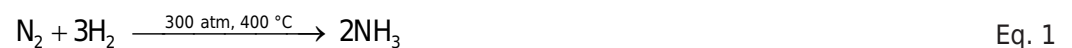
The reaction became known worldwide as the Haber–Bosch process. The nationalism of World War I also drove Haber–Bosch process development in Germany as a strategy to create a continuous supply of ammonia for use in the manufacture of ammonium nitrate, nitroglycerin, and trinitrotoluene. Nevertheless, the discovery leveraged food production to an unprecedented level. It is estimated without Haber–Bosch process, the amount of food produced worldwide would be sufficient to feed only 4 billion people per year (Erisman et al., 2008).
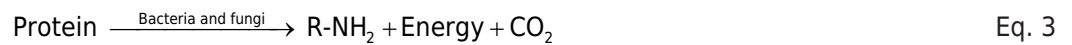
Nitrogen dynamics in the soil–atmosphere system

Nitrogen is the nutrient that most interacts with the environment, participating in numerous reactions in the soil. From greatest to least, the N reservoirs occur in Earth's mantle > atmosphere > continental crust > oceanic crust > oceans > biomass (Mysen, 2019). The higher N abundance in the mantle reflects the N cycling mechanisms through subduction zones over time. N-rich sediments descend into the mantle (Goldblatt et al., 2009; Palya et al., 2011), while the remaining part is released as N_2, which returns to the oceans and atmosphere (Mallik et al., 2018).

Atmosphere is the main N source into the soil, formed by 78 % of N_2 gas, unlike other elements that come from rocks. Several mechanisms are involved in the transfer of atmospheric N to the soil. For example, atmospheric electrical discharges release large

amounts of energy that break the triple bond of N_2 ($N\equiv N$), forming oxides that subsequently react with water to produce nitric acid (HNO_3), which is carried to the soil by rain (Park et al., 2006). The major route of N entrance into the soil from the atmosphere is biological N fixation, whereby microorganisms convert N_2 to NH_3 (Equation 2) and then to other organic forms essential to biological systems (Cantarella, 2007). N-fixing microorganisms express the enzyme nitrogenase and include free-living species, such as *Azotobacter* and cyanobacteria, as well as symbiotic forms, such as bacteria from the genus *Rhizobium*, commonly found on legume roots (Batista et al., 2018).

$$N_2 + 8e^- + 8H^+ + 16ATP \xrightarrow{\text{Nitrogenase}} 2NH_3 + H_2 + 16ADP + 16Pi \qquad \text{Eq. 2}$$
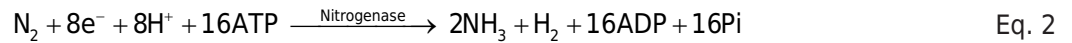
Only about 5 % of the N is found in mineral form in soil, and organic compounds account for most of the soil N pool (95 %). Organic N, however, is not available to plants. For absorption, plants depend on N mineralization, which transforms organic N forms into inorganic N (NH_4^+) by heterotrophic soil microorganisms. Mineralization process involves two steps: (i) aminization of organic N into an amino compound (R-NH_2) (Equation 3) and (ii) ammonification of R-NH_2 into ammonium ion (NH_4^+) (Equations 4 and 5), as described by Havlin et al. (2017).

$$\text{Protein} \xrightarrow{\text{Bacteria and fungi}} \text{R-}NH_2 + \text{Energy} + CO_2 \qquad \text{Eq. 3}$$

$$\text{R-}NH_2 + H_2O \longleftrightarrow NH_3 + \text{R-OH} + \text{Energy} \qquad \text{Eq. 4}$$

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^- \qquad \text{Eq. 5}$$

After the formation of NH_4^+ in soil, the cation may follow different pathways. It can be immobilized by soil microorganisms, fixed onto 2:1-type clay minerals, adsorbed on the soil exchange complex, lost via NH_3 volatilization, absorbed by plants, or further processed through nitrification reactions. Immobilization is the opposite of mineralization, which is represented by the left arrows in equations 4 and 5. It occurs when decomposing microorganisms require more N than they can obtain from waste materials and, therefore, need to consume mineral N forms from the soil solution to synthesize protein cellular components (Weil and Brady, 2018). Mineralization and immobilization occur simultaneously and depend on the C/N ratio of decomposing organic residues. As for NH_4^+ fixation, a similar process takes place in 2:1-type clay minerals such as illite, vermiculite, and montmorillonite. These minerals have adsorption sites (ditrigonal spaces) for positive ions with a similar size to the ionic radius of K^+ and NH_4^+, which makes it possible to fix these species (Nieder et al., 2011; Scherer et al., 2014). Depending on environmental conditions, mineral-fixed NH_4^+ may return to the soil solution and become available to plants (Batista et al., 2018).

Atmospheric N emissions occur naturally in soil via NH_3 volatilization, mainly under alkaline pH conditions (Equation 6). According to Cantarella (2007), at pH 5.2, only 0.01 % of soil N is present in NH_3 form, increasing to 1 % at pH 7.2 and 50 % at pH 9.2. However, agricultural soils rarely contain such high pH values, which naturally limits NH_3 volatilization. Losses are intensified by applying N fertilizers, particularly urea, resulting in economic losses and negative environmental and health impacts. In the atmosphere, NH_3 can be oxidized by the hydroxyl (OH) radical, forming the short-lived amino radical (NH_2), which undergoes further oxidation with nitrogen oxide (NO), nitrogen dioxide (NO_2), ozone (O_3), or the hydroperoxyl radical (HO_2) to ultimately form molecular nitrogen (N_2), N_2O or NO (Pai et al., 2023). Production of NO, N_2O and N_2 is dependent on the oxygen concentration in the atmosphere. Nitrogen dioxide and NO are produced through the NH_3 oxidation pathways and increase as O_2 concentrations decrease (Zhu et al., 2013). For this reason, current N_2 concentrations in the atmosphere are dependent on O_2 from photosynthesis, contributing to the complete oxidation of NH_3. This process is important, because incomplete NH_3 oxidation is responsible for around 8 % (and up to 16 %) of the global anthropogenic N_2O source (Pai et al., 2023).

$$NH_4^+ \longleftrightarrow NH \uparrow + H^+ \ (pKa = 9.3) \qquad \text{Eq. 6}$$
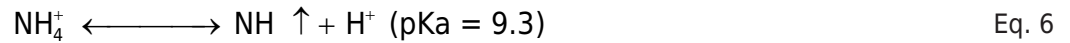
Part of the NH_4^+ in soil is converted to nitrate (NO_3^-) through the nitrification reaction, which divided into two steps, as follow: (i) nitritation, whereby NH_4^+ is oxidized to nitrite (NO_2^-) by the action of bacteria from the group *Nitrosomonas* spp. (Equation 7), releasing H^+, which acidifies the medium, and (ii) nitration, whereby NO_2^- is oxidized to NO_3^- by *Nitrobacter* spp. (Equation 8), as described by Havlin et al. (2017).

$$2NH_4^+ + 3O_2 \xrightarrow{\text{\textit{Nitrosomonas}}} 2NO_2^- + 2H_2O + 4H^+ \qquad \text{Eq. 7}$$

$$2NO_2^- + O_2 \xrightarrow{\text{\textit{Nitrobacter}}} 2NO_3^- \qquad \text{Eq. 8}$$

Therefore, nitrification is a reaction performed by soil microorganisms. Its intensity depends on the supply of NH_4^+, nitrifying populations, soil pH, aeration, moisture, and temperature. After N is nitrified, it can be absorbed by plants, immobilized by soil microorganisms, denitrified, or lost by leaching. Leaching losses are the relevant route for these species, given that NO_3^- ions are not adsorbed onto negatively charged soil colloids, and soils with positive charges have low adsorption energy for negative ions ($H_2PO_4^{2-} > MoO_4^{2-} > SO_4^{2-} > NO_3^- = Cl^-$) (Vieira, 1988).

Usually, leaching losses of NO_3^- are not as expressive as NH_3 volatilization losses in terms of the amount of N. In a meta-analysis performed by Wang et al. (2019), the authors found overall NO_3^- losses through the leaching process were on average 9 % of the N applied. In contrast, according to the meta-analysis of Silva et al. (2017), NH_3 volatilization losses usually were, on average, 31 % of applied N. Nevertheless, NO_3^- leaching losses deserve attention due to their potential to damage the environment and human health through surface water and groundwater contamination, which has been associated with the development of methemoglobinemia and stomach cancer (Ward et al., 2018).

Denitrification occurs in soils in the absence of O_2. Under these conditions, facultative anaerobic bacteria use NO_3^- ions rather than O_2 as final electron receptors during respiration (Cameron et al., 2013). Nitrate undergoes a four-step reaction and is ultimately reduced to N_2, which is rapidly lost to the atmosphere (Equation 9). However, in order for NO_3 to be reduced by microorganisms, the soil must contain available (oxidizable) C, which is used in the process as a source of electrons. Although denitrification is higher under anaerobic conditions, it can also occur in aerobic soils at sites found within soil aggregates where the O_2 diffusion rate into pore water is 10,000 times lower than in air (Cantarella, 2007).

$$NO_3^- \xrightarrow{2e^-} NO_2^- \xrightarrow{e^-} NO \xrightarrow{e^-} N_2O \uparrow \xrightarrow{e^-} N_2 \uparrow \qquad \text{Eq. 9}$$
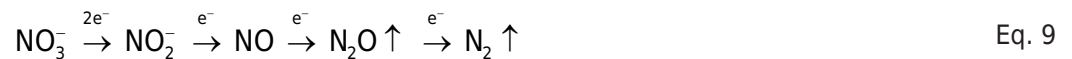
From an environmental point of view, denitrification is a crucial part of the global N cycle. It is the main biological process through which N returns to the atmosphere in the N_2 form, contributing to the removal of excess NO_3^- from agricultural systems and thereby minimizing the eutrophication of downstream waters (Seitzinger et al., 2006). In some systems, however, such as flooded rice paddies, denitrification losses are much more relevant, accounting for up to 34 % of the applied N (Shi et al., 2020). The ratio of N_2O to N_2 formed during denitrification is determined by the availability of oxidizable C and NO_3^- in soil (Cantarella, 2007). For example, high NO_3^- concentrations almost completely inhibit the reduction of N_2O to N_2, whereas high concentrations of oxidizable C increase the availability of electrons, favoring the reduction of NO_3^- to N_2. Usually, the amount of N fertilizer transformed into N_2O species is small, and accounts for less than 1 % of the N fertilizer applied (Carvalho et al., 2021).
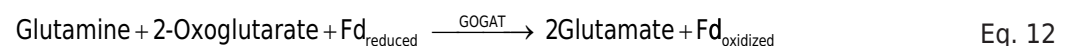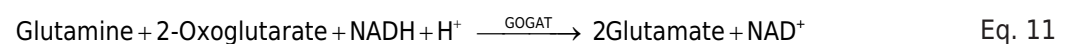
Nitrogen in plants

Nitrogen is essential for plants growth and development, it is required in large quantities by plants due to its participation in nucleotides and amino acids, nucleic acids, proteins, and photosynthesis macromolecules such as chlorophyll (Taiz et al., 2014). Symptoms of N deficiency in plants are: general chlorosis in older leaves and stunted growth (Figure 1). Transfer of N from the soil to plant roots occurs preferably by mass flow, which involves the passage through a mobile aqueous phase (soil solution) from a wetter region to a drier one close to the root surface (Malavolta et al., 1997). Plants can absorb both inorganic (NH_4^+ and NO_3^-), amidic (urea) and organic (amino acids and peptides) forms of N through high-affinity transporters (HATS) and low-affinity transporters (LATS) (Näsholm et al., 2009; Nacry et al., 2013). However, plants absorb mainly inorganic forms because organic N, when made available in the soil solution through organic matter mineralization, is rapidly metabolized by heterotrophic microorganisms and converted to inorganic N, as described in equations 3 to 5.

Ammonium and NO_3^- availability in the soil vary according to the aeration condition. While the predominant N form in aerated soil is NO_3^-, NH_4^+ is the dominant form under anaerobic and acid conditions (Zhu et al., 2011). While plant roots have uptake systems for nitrate and ammonium with different affinities (Xu et al., 2012), the roots of plants most prefer NH_4^+ uptake over NO_3^- (Hachiya and Sakakibara, 2017). Nitrate can only be used by plants after being reduced to NH_4^+ via a two-step reaction catalyzed by enzymes. The first step occurs in the cytoplasm through the action of nitrate reductase, which converts NO_3^- to NO_2^-. The reduced ion is then transported to chloroplasts (leaves) or proplastids (roots), where it is converted to NH_4^+ by the action of nitrite reductase (Li et al., 2013). Most of the NO_3^- absorbed by plants is transported to the leaves for metabolization, as this plant component has sufficient energy reserves obtained through photosynthesis. Then, NH_4^+ absorbed from the soil solution or produced by metabolization of NO_3^- is assimilated into amino acids via a series of sequential reactions catalyzed by two enzymes, namely glutamine synthetase (GS) and glutamate synthetase (GOGAT), which is commonly referred to as the GS–GOGAT pathway. The GS is responsible for reacting NH_4^+ with glutamate to form glutamine (Equation 10), an amino acid used by plants for intracellular N transport (Taiz et al., 2014).

$$\text{Glutamate} + NH_4^+ + ATP \xrightarrow{GS} \text{Glutamine} + ADP + P_i \qquad \text{Eq. 10}$$
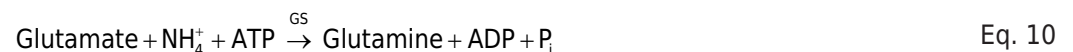
High levels of glutamine in chloroplasts stimulate GOGAT activity, promoting the transfer of the amide group of glutamine to 2-oxoglutarate, producing two glutamate molecules (Equations 10 and 11). Glutamate, like glutamine, can be used as N supply to synthesize other amino acids through transamination reactions. It can also return to the NH_4^+ assimilation cycle described in equation 10. Because plants have two different sites for N assimilation (roots and leaves), they express two types of GOGAT: nicotinamide adenine dinucleotide-dependent GOGAT (NADH-GOGAT) in proplastids of non-photosynthetic tissues, such as roots (Equation 11), and ferredoxin-dependent GOGAT (Fd-GOGAT) in photosynthetic tissues, such as chloroplasts (Equation 12) (Taiz et al., 2014).

$$\text{Glutamine} + \text{2-Oxoglutarate} + NADH + H^+ \xrightarrow{GOGAT} \text{2Glutamate} + NAD^+ \qquad \text{Eq. 11}$$

$$\text{Glutamine} + \text{2-Oxoglutarate} + Fd_{reduced} \xrightarrow{GOGAT} \text{2Glutamate} + Fd_{oxidized} \qquad \text{Eq. 12}$$

In case of excess N fertilization, especially with sources that release high levels of NH_4^+ in soil, plants switch from the GS–GOGAT pathway to an alternative route known as the glutamate dehydrogenase (GDH) pathway (Ashraf et al., 2018). Given that plants prefer

absorbing NH_4^+, which can be readily assimilated into amino acids, high NH_4^+ levels can quickly saturate the GS–GOGAT pathway. Thus, to continue absorbing ammoniacal N, plants activate the GDH pathway (Equation 13), which, because of its lower affinity for NH_4^+, can be used for sustained absorption and assimilation of these ions.

$$2\text{-Oxoglutarate} + NH_4^+ + NADPH \xrightarrow{\text{GDH}} \text{Glutamate} + NAD(P)^+ \qquad \text{Eq. 13}$$
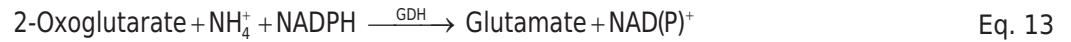
In addition to causing metabolic changes in plants, excess NH_4^+ can trigger competition and reduces the absorption of cations with lower affinity for membrane transporters, such as Ca^{2+}, Mg^{2+}, and K^+ (Weil et al., 2020). Affinity of cationic species decreases in the following order: $NH_4^+ > K^+ > Mg^{2+} > Ca^{2+}$ (Malavolta et al., 1997). Intensive absorption of NH_4^+ can also increase soil acidity (Zhao et al., 2007). In this sense, when plants absorb NH_4^+, they excrete a proton (H^+) through the roots, formed by the dissociation

Figure 1. Nitrogen (N) deficiency in corn plants in the field (a), corn ears at R2 phenological stage (Blister - kernels resemble "blisters" with clear liquid) (b), corn ears at R6 phenological stage (Physiological maturity – kernels at maximum dry matter accumulation (c), error in adjusting the machine for applying ammonium sulfate to corn crops, greener bands with more fertilizer and less green bands with less fertilizer (d). Soybean in nutrient solution with N (e), soybean in nutrient solution without N (f), sugar cane in nutrient solution with N (g), and sugar cane in nutrient solution without N (h). Photos a, b and d were provided by Evandro Antonio Minato. Photo c was provided by Bruno Maia Abdo Rahmen Cassim. Photos e, f, g and h were provided by Tadeu Takeyoshi Inoue and Marcelo Augusto Batista.

of H_2CO_3 through respiration in an attempt to maintain the electrochemical balance within plant cells (Hinsinger et al., 2003). As the soil pH decreases, plants' absorption of micronutrients such as Cu, Zn, Fe, and Mn increases. In the case of NO_3^-, the opposite effect is observed (i.e., NO_3^- absorption decreases soil acidity by promoting the excretion of OH^-, formed by reducing NO_3^-).

Strategies to enhance NUE: from plant to agrosystems management

Extensive efforts have been devoted to increase NUE by the cultivated plants, and when plant breeding is framed to reach this proposal, several components are reported to be involved to NUE, as a consequence, there exist various paths to gene expression and thereafter enhancing the parameter aforementioned (Xu et al., 2012; Do Vale et al., 2014). Through a wide literature review, Lammerts van Bueren and Struik (2017) pointed out other challenging aspects associated with plant breeding aiming at improving NUE, to state the main limitations: i) knowledge gained improving a given plant cannot be adopted to another; ii) short- and long-season crops respond differently to N management, similar pattern is also observed for vegetative and grain producing crops. Moreover, plants subjected to improvement and under the existence of large interaction between the environment by genotype (E X G) on the expression of target traits, such interaction may not sustain the traits obtained in other environments (Han et al., 2015; The et al., 2021).

Regarding the target plants' traits sought by the plant breeders, they are quite diverse and specific according to the crop. Overall, several attempts have been made to improve the root system architecture to reach depth soil layers and potentially enhances N uptake (Garnett et al., 2009; Li et al., 2015; Kiba and Krapp, 2016), however, this strategy may be limited due to low mobility of some nutrients present within the upper soil layers, such as phosphorus (Ho et al., 2005). Besides enhancing N uptake, efforts have been devoted to increase N assimilation and remobilization by crops (Masclaux-Daubresse et al., 2010). Moreover, since the N is firstly assimilated into the plants through amino acids path [Masclaux-Daubresse et al. (2010); Equation 10], strategies to enhance photosynthesis and then amino acids biosynthesis are pointed as an indirect via to increase NUE (Hawkesford, 2014). In this sense, increasing Sorghum's photosynthetic capacity through extending leaf greenness favoured higher N uptake (34 kg ha^{-1}) during the grain filling as compared with the same parameter recorded for a regular hybrid (Borrell and Hammer, 2000).

Despite the extensive efforts dedicated to enhance NUE by the main crops, e.g., corn, wheat and oilseed, and the significant correlations observed between N levels with either below or above ground plants' traits, most correlations seem physiologically unclear (Lammerts van Bueren and Struik, 2017). To integrate various approaches inherent to the plant and environment (i.e., root exudate, rhizobium availability and nitrate transport system and physiological parameters) are suggested to unravel the complexity associated with NUE improving into the plants (Lammerts van Bueren and Struik, 2017; Reich et al., 2014).

Regardless of the crop been grown, across the different agroecosystems strategic managements can be adopted to favour rational N management, decreasing N input or recycling the nutrient already applied into the agroecosystem, which in turn enhances NUE. In this sense, precision agriculture technologies allow analyse and managing the fields according to their spatial and temporal variability, thus, using precision agriculture the N can be applied either where is most scarce in a given field or within the plant stage where the N is most required (Bongiovanni and Lwenberg-DeBoer, 2004; Hedley, 2015). Under both conditions NUE is improved, resources wastage is mitigated, while crop production sustainability is enhanced (Karunathilake et al., 2023). Another promising alternative to increase NUE is through crop rotation, cultivating a legume in rotation with a cash crop, which increases N fixation (Otto et al., 2020; Bohórquez-Sánchez et al., 2023) and potentially reduces the N inputs into the systems. Besides improving NUE,

increasing crop diversity into the agroecosystems favoured corn yield (~28 %) and this management was able to mitigate grain yield losses especially under drought conditions, where grain yield losses preventing varied between 14 and 89 % (Bowles et al., 2020).

When conventional tillage and no-tillage systems are compared as practices to enhance NUE, within the short term, soil tillage in the former system increases soil organic matter (SOM) mineralization and thereafter the N rates mineralized, which can be either uptake by the plant or to be extensively lost via runoff (Zhang et al., 2020). As a result of SOM degradation, poor soil quality and low N availability are associated with conventional tillage (Govindasamy et al., 2023). On the other hand, Conservation Agriculture through no-tillage adoption is highlighted a promise strategy to increase SOM quality and increases the mineral N content over time (Canisares et al., 2021; Zhang et al., 2020). Thus, no-tillage adoption stands out as an alternative to improve NUE.

In this context, it was observed that in no-till, the improvement of subsoil acidity due to gypsum application increased corn root growth, N uptake, grain yield, and NUE (Caires et al., 2016). According to the authors, the increased in 19-38 % in corn grain yield, depending on the N application rate, is due to the greater absorption of NO_3^- in the subsoil as a result of the increase in corn root length due to the use of gypsum. All strategies in no-till that allow the development of the root system can enhance NUE, improve grain yield, and reduce environmental risks due to NO_3^- leaching.

Nitrogen origin and energy source for ammonia synthesis

The N_2 needed for the Haber–Bosch's reaction (Equation 1) can be easily obtained from the air, and most of the energy costs of NH_3 production are due to H_2 production from fossil fuels and its subsequent combination with N_2. According to Liu et al. (2020), about 72 % of the global production of NH_3 is derived from natural gas, 22 % from coal, and 5 % from fuel oil and naphtha. The greater use of natural gas is explained by its greater abundance and lower value compared with other energy matrices.
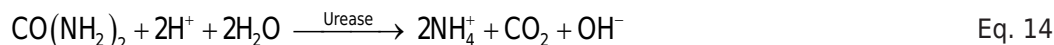
It should be noted that the Haber–Bosch process is not sustainable in the long term, as fossil fuels are a finite energy source and contribute to GHG emissions. For each ton of NH_3 produced, 1.9 to 3.8 Mg of CO_2 is emitted into the atmosphere, depending on the fossil fuel used (Demirhan et al., 2018). Such emissions account for, on average, 1 % of global anthropogenic CO_2 emissions annually (Smith et al., 2020). Two methods have been proposed to reduce the environmental impacts caused by NH_3 production: (i) increase the NUE of N fertilizers and (ii) obtain H_2 from renewable processes, such as the gasification of modern biomasses (e.g., ethanol, biodiesel, wood methanol) and water electrolysis using electricity and sunlight (a process known as green ammonia production) (Chehade and Dincer, 2021). Currently, of the 180 million Mg of NH_3 produced per year, 80 % is used for N fertilizer production (Cardoso et al., 2021). The major N fertilizers are listed in table 1. Urea is the most widely used N source for meeting crop requirements.

Ammonia volatilization with urea use

Global demand for N fertilizers amounted to 110 million Mg in 2019 (IFA, 2019), 56 % of which was produced in the form of urea, which is the most common fertilizer worldwide (Table 2). Urea is widely used for crop nutrition due to its high N concentration (46 %), wide market availability, and low production costs (Chien et al., 2009; Cantarella et al., 2018). However, when applied to the soil surface, urea is lost mainly through NH_3 volatilization, representing a loss of more than 60 % of the N applied (Pan et al., 2016), depending on the soil and air temperatures (Tasca et al., 2011), soil moisture (Cassim et al., 2021), soil pH (Sunderlage and Cook, 2018), soil buffering capacity (Zheng et al., 2018), straw mulching on the soil surface (Dick, 1984) and fertilizer rate (Corrêa et al., 2021).

Urea is hydrolyzed by the action of the enzyme urease, as demonstrated in equation 14. Because urea hydrolysis consumes H^+, there is an increase in pH near fertilizer granules,

changing the balance between soil ammonia and ammonium (Equation 15), favoring the transformation of NH_4^+ to NH_3, which is rapidly lost to the atmosphere in the gaseous form (Rochette et al., 2009).

$$CO(NH_2)_2 + 2H^+ + 2H_2O \xrightarrow{\text{Urease}} 2NH_4^+ + CO_2 + OH^- \qquad \text{Eq. 14}$$

$$NH_4^+ \longleftrightarrow NH_3 \uparrow \qquad \text{Eq. 15}$$

When volatilized, the NH_3 can be deposited nearby or become airborne, traveling long distances and reacting with acids to form ammonium aerosols such as ammonium sulfate [$(NH_4)_2SO_4$] and ammonium bisulfate [$(NH_4)HSO_4$] (Galloway et al., 2004). These processes exert undesirable effects on the environment. Thus, the deposition of N in terrestrial and aquatic ecosystems may lead to soil acidification and water eutrophication, which ultimately result in the death of certain plant communities and aquatic animals, such as fish and crustaceans (Sutton et al., 2013; Wurtsbaugh et al., 2019). The economic costs of freshwater eutrophication in the United States are estimated at USD 2.4 billion per year, including loss of lakefront property values (49 %), costs of purchasing bottled water due to poor water taste and odor (25 %), recreational losses (24 %), and costs of protecting endangered species (2 %) (Dodds et al., 2009; Wurtsbaugh et al., 2019).

In addition to the formation of ammonium aerosols, volatilized NH_3 may react with atmospheric HNO_3 to form ammonium nitrate, which is one of the main particulate matters (fine airborne particles measuring less than 2.5 μm in diameter) that are harmful to human health (Paulot and Jacob, 2014). These fine particles have the potential to generate lung diseases and cancer (Wyer et al., 2022). Losses due to NH_3 volatilization and subsequent deposition on the soil also contribute to indirect emissions of N_2O, with the ability to accelerate global warming and destroy the O_3 layer (Houlton et al., 2019). Such effects negatively impact climate change and increase exposure to free O_3, which may cause cough, asthma, chronic respiratory diseases, and cancer in humans (Townsend et al., 2003; Erisman et al., 2013).

Finally, NH_3 losses also result in economic losses to farmers. For example, the current demand for urea is 61.38 million Mg yr^{-1} (Table 2). Considering the global mean of NH_3 loss due to volatilization (14 %) estimated by Bouwman et al. (2002), it can be presumed that up to 8.6 million Mg of urea is lost every year in the form of gas (NH_3), representing an economic loss of USD 74.2 billion.

Table 2. List of the most used nitrogen fertilizers with global consumption value

Fertilizers	Chemical formula	Consumption global	Consumption
		Tg ano^{-1}	%
Urea	$CO(NH_2)_2$	61.38	56
Amonium sulfate	$(NH_4)_2SO_4$	3.63	3
Ammonium nitrate	NH_4NO_3	5.39	5
Calcium/magnesium amm. nit.[1]	Mix of NH_4NO_3, $CaCO_3$, $MgCO_3$, $CaSO_4$	3.41	3
anhydrous ammonia	NH_3	3.96	4
N solutions (UAN)	Mix of NH_4NO_3, $CO(NH_2)_2$, H_2O	5.39	5
MAP[2] e DAP[3]	$NH_4H_2PO_4$, $(NH_4)_2HPO_4$	9.68	9
Nitrogen-phosphorus-potassium	$N-P_2O_5-K_2O$	9.13	8
Other sources N	NH_4Cl, NH_4HCO_3	8.03	7
Total[4]		110	100

[1] Calcium/magnesium amm. nit.: Calcium/magnesium ammonium nitrate. [2] MAP: monoammonium phosphate. [3] DAP: diammonium phosphate. [4] Demand for nitrogen fertilizers in 2019. Source: adapted from Behera et al. (2013).

Technologies for replacing conventional urea

Nitrogen losses from the agroecosystem are mitigated by using enhanced efficiency fertilizers (EEFs) (Lam et al., 2022). Urea has become the main source for the development EEFs development, given its wide use and the need to minimize NH_3 volatilization losses (Guelfi, 2017). Currently, EEFs are classified into three categories according to the technologies used for their production, namely, stabilized, slow-release, and controlled-release (Trenkel, 2010). Stabilized fertilizers can be further subdivided into those containing additives for urease inhibition and for nitrification inhibition.

Urease inhibitors aim to temporarily block urease activity in the soil and decrease the rate of urea hydrolysis, thereby allowing more time for N fertilizers to be incorporated into the soil by rainfall. Inhibitory additives generally consist of organic molecules or metals with affinity for the active sites of urease. Before the organic molecules advent, Shaw (1954) investigated the metals action and identified the following sequence of urease inhibition power: $Ag^+ = Hg^{2+} > Cu^{2+} > Cd^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+} = Sn^{2+} = Mn^{2+} = Pb^{2+}$. It should be noted, however, that application of heavy metals (Ag^+, Hg^{2+}, Cd^{2+}, and Pb^{2+}) to the soil can cause environmental problems.

Urea treatment with boric acid (H_3BO_3) may also lead to urease inhibition, given that the molecule acts as a competitive inhibitor. Boric acid has a similar conformation to that of urea, thereby competing for the same enzymatic sites (Benini et al., 2004).

In the first studies of organic compounds, the best results were obtained with N-(n-butyl) thiophosphoric triamide (NBPT). This compound became the main additive for urease inhibition and was marketed worldwide. However, NBPT is not the direct urease inhibitor; it must be first oxidized to its analog, N-(n-butyl) phosphoric triamide (NBPTO). Factors influencing this conversion are unclear, but the reaction in aerobic soils is fast (occurring in minutes or hours). By contrast, it can take days under anaerobic conditions (Watson, 2000; Cantarella et al., 2018). Following the conversion of NBPT to NBPTO, the O and NH_2 groups of NBPTO form chemical bonds with urease, trapping the active site of the enzyme at three points – two at the Ni atom and one at the oxygen atom (Manunza et al., 1999). This prevents urea hydrolysis, consequently minimizing NH_3 loss by volatilization.

Nitrification inhibitors are used to decrease N_2O losses and NO_3^- leaching. The additives delay the biological oxidation of NH_4^+ to NO_3^- in soil by inhibiting *Nitrosomonas* spp. These bacteria are responsible for the conversion of NH_4^+ to NO_3^- (Qiao et al., 2015), as demonstrated in equation 6, representing the nitration step. On the other hand, permanence of N in the form of NH_4^+ for longer periods may lead to NH_3 volatilization. In a meta-analysis published by Wu et al. (2021), urea treated with nitrification inhibitors had a 36 % increase in NH_3 volatilization loss. For example, in personal data from a field experiment conducted in southern Brazil, urea treated with nitrification inhibitor increased N losses by NH_3 volatilization by 10 % (45 kg ha^{-1} NH_3) and 23 % (85 kg ha^{-1} NH_3) in relation to urea (41 and 69 kg ha^{-1} NH_3) for clayey and sandy soils, respectively (Figure 2). These results raise important implications regarding the use of nitrification inhibitors as a tool to improve NUE and reduce environmental impacts because they contribute to the main route of N loss (i.e., volatilization). Globally, the most studied and marketed nitrification inhibitors are dicyanamide, 2-chloro-6-(trichloromethyl)pyridine (Nitrapyrin), and 3,4-dimethylpyrazole phosphate (Taggert et al., 2021).

Slow-release fertilizers are products that have reduced dissolution rates in soil. Such properties can be obtained by reducing the solubility of N fractions that compose the products (Trenkel, 2010). For this, urea is condensed with aldehydes in a reactor under controlled conditions of pH, temperature, molar ratio, and reaction time to form polymer chains with C molecules of crotonaldehyde, isobutyraldehyde, or formaldehyde (Yamamoto et al., 2016; Guelfi, 2017). Some of the best-known slow-release N fertilizers include urea formaldehyde, urea crotonaldehyde, and urea isobutyraldehyde.
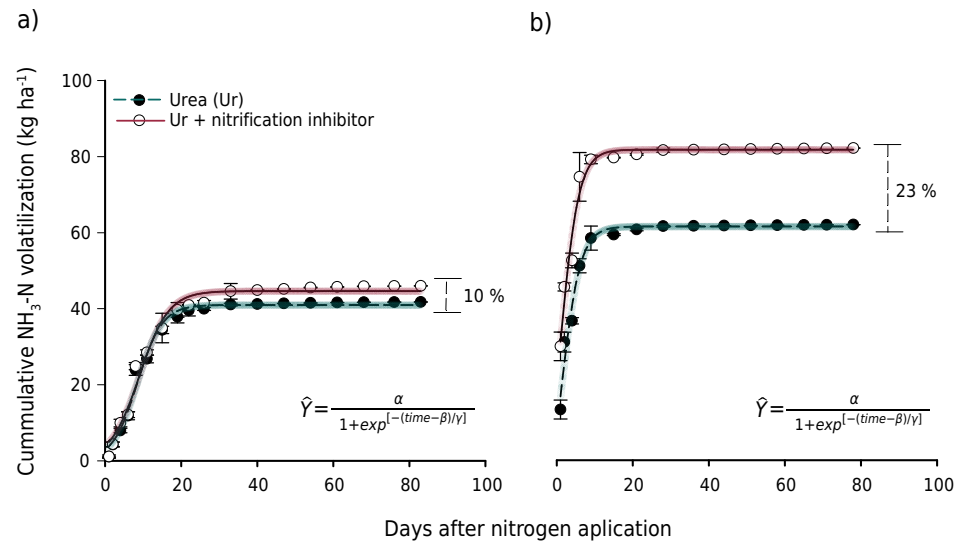
a)   b)

Figure 2. Cumulative volatilization of NH$_3$-N after broadcasting applications of the urea (Ur) and Ur + nitrification inhibitor in corn for: Clayey soil at a rate of 200 kg ha^{-1} of N (a) and sand soil at a rate of 150 kg ha^{-1} of N (b). Results were submitted to no-linear regression analysis using the logistic model $Y=\alpha/1+exp[-(time-\beta)/\gamma]$. Data with overlapping vertical bars with 95 % confidence interval in the curve.

For urea formaldehyde, differences in the degree of polymerization (insolubility) and molecular weight (chain length) influence N release rates. Nitrogen release rate from urea isobutyraldehyde and urea crotonaldehyde depends on differences in particle size, given these products have a defined chemical composition. However, the nitrogen rate of release from these fertilizers, even if slow, may vary according to the decomposition and hydrolysis of the urea–aldehyde product in the presence of CO_2 and NH_4^+, soil microbial activity, and soil temperature, pH, and moisture (Jahns et al., 2003).

Controlled-release fertilizers have coated granules that function as a barrier to prevent direct contact of N with its surroundings. This allows N release to be controlled and synchronized according to crop demands, resulting in reduced losses by volatilization and leaching (Cahill et al., 2010; Azeem et al., 2014). This class of fertilizer can be divided into three categories according to the coating material: (i) fertilizers coated with elemental sulfur (S^0), (ii) fertilizers coated with elemental sulfur and polymers, and (iii) fertilizers coated with polymers only (Guelfi, 2017). Figure 3 shows the scanning electron micrographs of an uncoated urea granule and the three types of controlled-release fertilizers.

Elemental sulfur was one of the first materials used for coating, given it is relatively inexpensive and acts as a plant nutrient (Timilsena et al., 2014). Nitrogen release from S^0-coated granules depends on the activity of microorganisms that oxidize S^0, which, in turn, depends on pH, moisture, and temperature. For these reasons, some researchers do not consider S^0-coated urea a controlled-release fertilizer; rather, they consider it a slow-release product (Trenkel, 2010). Furthermore, S^0 coating is not uniform, and cracks are commonly observed. To circumvent these problems and improve the controlled release of N, it is common to add a layer of polymers to create a product known and patented as hybrid fertilizer (S^0 + polymers) (Detrick, 1997). Despite the improvements afforded by additional polymer layers, problems associated with coating uniformity still persist. Thus, the most advanced technology of controlled-release fertilizers involves the use of one or several layers of polymers to coat granules without S^0.

The release mechanism of polymer-coated nutrients, which is sensitive to temperature and moisture conditions, can be described in three stages: (i) latency period, (ii) constant release, and (iii) decay period (Shaviv et al., 2003). In the first stage, water present in
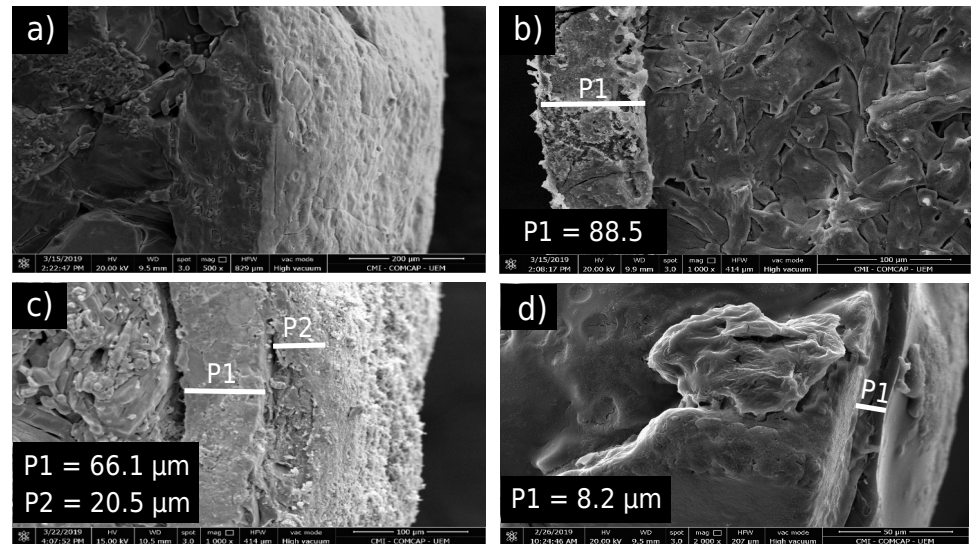
Figure 3. Electron micrographs and coating material thickness of the controlled-release fertilizer categories. Conventional uncoated urea (a), urea coated only with S^0 (b), S^0 and polymer coated urea (P1 S^0 coating and P2 polymer coating) (c) and urea coated with polymer only (d).

the soil, mainly in the form of vapor, penetrates the coating up to the granule core, swelling the granule, and a small fraction of the fertilizer in the form of urea is dissolved. Subsequently, in the second stage, as water continues to penetrate, more solid fertilizer is dissolved, and the internal pressure increases, allowing the nutrient to be slowly released through membrane diffusion. However, if the internal pressure exceeds the limit value, the coat is ruptured, providing immediate release of the nutrient. If this does not occur, N release reaches the third stage, when most of the fertilizer has already been dissolved and released, reducing diffusion (Lawrencia et al., 2021).

Polymer coatings, such as polyurethane (Ni et al., 2011), polyethylene (Wei et al., 2017), polystyrene (Yang et al., 2012), polyolefin (Xu et al., 2013), polyvinyl chloride (Hanafi et al., 2000), polyacetate (Niu and Li, 2012), and polyacrylamide (Liang et al., 2009), may be of synthetic origin. Coatings, such as starch (Jin et al., 2012), pulp (Pang et al., 2019), lignin (Chen et al., 2020), chitosan (Chiaregato et al., 2022), alginate (Llive et al., 2020), wheat gluten (Enríquez et al., 2012), and natural rubber (Riyajan et al., 2012), may also be of natural origin. Although synthetic polymers have lower costs and offer more controlled release than organic polymers (Timilsena et al., 2014), their residual accumulation in soil can lead to a new form of pollution, as they are microplastic sources. For these reasons, research on controlled-release fertilizers has aimed to improve the control mechanisms and costs of organic polymers, given that they are biodegradable.

Importance of EEF characterization

With the introduction of EEFs to the N fertilizer market, the characterization of N-fertilizer sources became an important tool for understanding the mechanism of enhanced efficiency technologies. However, there are few scientific papers on this topic. New organic molecules for urease or nitrification inhibition are constantly launched in the market to increase NUE. For instance, a new stabilization agent consisting of two active ingredients, Duromide + NBPT, reduced NH_3 losses by 33 % compared with NBPT alone (Cassim et al., 2021). 1,2,3-Triazole seems to have better performance than the conventional nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) in retaining NH_4^+-N (Taggert et al., 2021).

Research on slow-release fertilizers such as urea formaldehyde resulted in the identification of methyleneureas (methyleneurea, methylenediurea, and polymethylene), which are correlated with the polymerization degree (insolubility) and molecular weight (chain length) of the fertilizer (Alexander and Helm, 1990; Guelfi, 2017). These properties influence N-release duration and, consequently, crop yields. X-ray diffraction of urea formaldehyde (Figure 4) revealed the presence of methylenediurea, explaining the intermediate molecular weight and degree of polymerization of the fertilizer, which results in slower release than conventional urea. Notably, this slow-release fertilizer contains urea unreacted with formaldehyde (Figure 4) so that part of the N can become readily available to plants. Despite this fact, no yield gains were obtained with the application of urea formaldehyde containing 70 % of slow-release compounds, while products containing 55–60 % led to significant yield gains (Cassim et al., 2020).

Nitrogen release from controlled-release fertilizers is influenced by coating composition and thickness. Azeem et al. (2016) observed that the duration of N release from polymer-coated urea increased with increasing coating thickness, and Gao et al. (2015) found that the type of coating used, whether polymer or elemental sulfur, influenced the behavior of the N-release curve. This is because the performance of S^0 coating depends on coating uniformity (lack of cracks) and the activity of microorganisms responsible for S^0 oxidation. Polymers, on the other hand, allow controlled N diffusion through their permeable membranes; thus, the release of N is influenced by the amount and thickness of the coating, resulting in better synchronization of N release with plant requirements.

Nitrogen fertilizers characterization is important not only for agronomic performance but also for the monitoring and creation of regulations for product specification, especially with regard to EEFs. Many commercial EEFs do not disclose information on the composition or thickness of the coating material. Minato et al. (2020) identified using scanning electron microscopy that some controlled-release products lack granule coating, leading to the release of 98 % of applied N within 24 h. As a result, the rate of NH_3 volatilization of such products is similar to that of conventional urea. Characterization of N sources available on the market is both a challenge and a necessity.
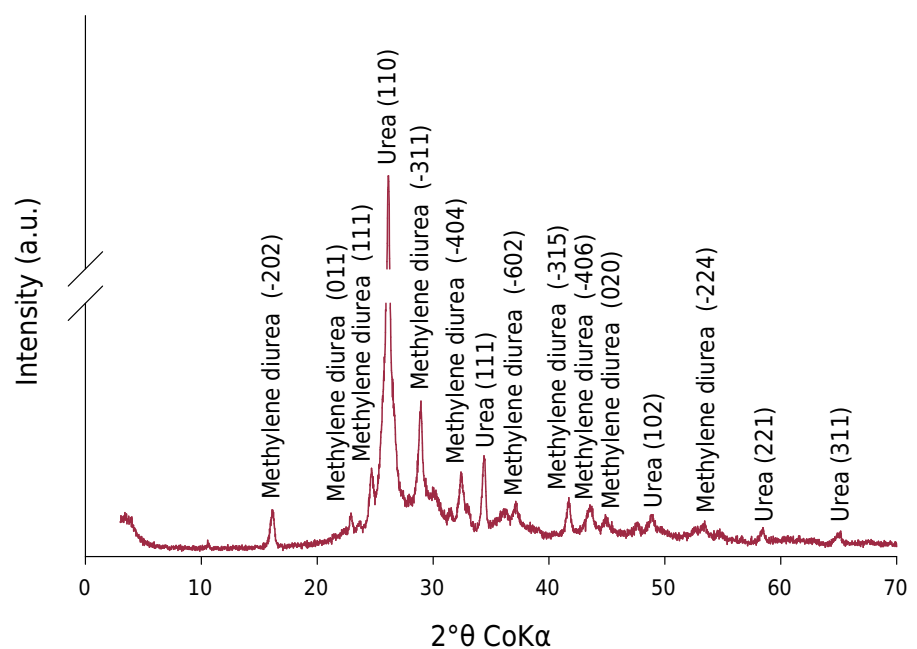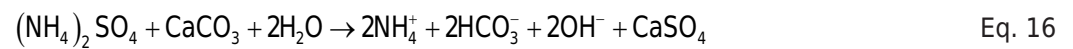

Figure 4. X-ray diffraction of the urea formaldehyde (UF) for enhanced efficiency nitrogen fertilizer characterization.

Ammoniacal/nitric fertilizers: conventional sources to decrease ammonia volatilization losses

As demonstrated by meta-analyses conducted by Silva et al. (2017) and Zhang et al. (2019), EEFs developed by the N fertilizer industry reduce NH_3 volatilization losses by 39 to 52 % compared with conventional urea. On the other hand, little to no loss occurs when ammoniacal/nitric fertilizers, such as ammonium sulfate and ammonium nitrate (Table 3), are applied to the soil surface. Non-amide N sources dissociate into stable ionic forms, unlike urea, which is enzymatically hydrolyzed to ammoniacal N, a process that results in an increase in pH around granules and later in NH_3 volatilization.

However, in alkaline and calcareous soils with pH >7 or soils that have just received high lime rates, any N fertilizer containing N as ammonia is subject to NH_3 volatilization losses (Table 3). The influence of calcium carbonate and soil pH (Equations 16, 17 and 18) on N sources containing ammonia is described by Havlin et al. (2017).

$$(NH_4)_2\,SO_4 + CaCO_3 + 2H_2O \rightarrow 2NH_4^+ + 2HCO_3^- + 2OH^- + CaSO_4 \qquad \text{Eq. 16}$$

$$NH_4^+ + HCO_3^- \rightarrow NH_3 \uparrow + CO_2 + H_2O \qquad \text{Eq. 17}$$

$$NH_4 + OH^- \rightarrow NH_3 \uparrow + H_2O \qquad \text{Eq. 18}$$

Although soil pH influences the efficiency of ammonia sources, the occurrence of alkaline soils in large food-producing countries such as Brazil is unusual, given that, because of its tropical climate, more than 70 % of the national territory is formed by acidic soils

Table 3. Volatilization losses of NH_3 (%) to ammonium sulfate and ammonium nitrate in function of the soil pH

Source N	Rates of N	Soil pH	Volatilization losses of NH_3	Authors
	kg ha^{-1}		%	
Ammonium sulfate (AS)	200	4.5	4	Cassim et al. (2022)
AS	60	5.4[1]	3	Minato et al. (2020)
AS	90, 180, 270	5.4[2]	2; 3; 7	Corrêa et al. (2021)
AS	150	4.8[2]	2	Fontoura and Bayer (2010)
AS	280	5.3[2]	2	Fenilli et al. (2007)
AS	150	5.9[1]	3	Santos et al. (2020)
AS	168	6.7[1]	10	Del Moro et al. (2017)
AS	100	8.9[1]	34	Schwenke et al. (2014)
AS	120	10.6[1]	54	Rao and Batra (1983)
Ammonium nitrate (AN)	200	4.5	5	Cassim et al. (2022)
AN	100	5.5[2]	1	Otto et al. (2017)
AN	100	5.1[2]	0.2	Cantarella et al. (2008)
AN	100	5.7[2]	0.1	Faria et al. (2013)
AN	90, 180, 270	5.4[2]	2; 3, 4	Corrêa et al. (2021)
AN	150	4.8[2]	1	Fontoura and Bayer (2010)
AN	150	5.7[2]	0.4	Viero et al. (2014)
AN	100	6.2[1]	8	Lara Cabezas et al. (1997)
AN	550	7.6[1]	18	Fenn and Kissel (1973)
AN	120	10.6[1]	54	Rao and Batra (1983)

[1] pH determined in water; and [2] pH determined in saline solution.

(Crusciol et al., 2017). A global meta-analysis of 824 observations between 1971 and 2016 conducted by Pan et al. (2016) showed that ammonium nitrate and ammonium sulfate were the two most effective fertilizers in reducing NH_3 volatilization losses by up to 88 and 79 % compared with urea, respectively. Adoption of ammoniacal/nitric sources as opposed to EEFs by farmers is perhaps hindered by the low N concentration of ammonium sulfate (21 % N) and restrictions on the purchase of ammonium nitrate by the national armed forces, as the material can be used to produce explosives and may detonate during storage.

Ammonium nitrate is not considered flammable or combustible. However, factors such as high temperatures under confinement (260 to 300 °C) and contamination by organic or inorganic materials such as chlorides or powdered metals can lead to explosive detonation through the production of N_2O, which rapidly decomposes into N and oxygen (O_2) (Chaturvedi and Dave, 2013; Laboureur et al., 2016). For this reason, some N fertilizer companies have used calcium and magnesium carbonates to react with ammonium nitrate as demonstrated by equations 19 and 20, which can reduce heat release in an emergency situation (Klimova et al., 2011; Poplawski et al., 2016). Ammonia, one of the products of these reactions, can inhibit the undesirable exothermic process of ammonium nitrate, thereby improving safety (Poplawski et al., 2016). In figure 5, the X-ray diffractogram shows the presence of dolomite, calcium carbonate, and magnesium in a commercial fertilizer based on ammonium nitrate and calcium sulfate.

$$2NH_4NO_3 + CaCO_3 \xrightarrow{\ ^{"}H>0\ } Ca(NO_3)_2 + 2NH_3 + H_2O + CO_2 \qquad\text{Eq. 19}$$

$$2NH_4NO_3 + MgCO_3 \xrightarrow{\ ^{"}H>0\ } Mg(NO_3)_2 + 2NH_3 + H_2O + CO_2 \qquad\text{Eq. 20}$$
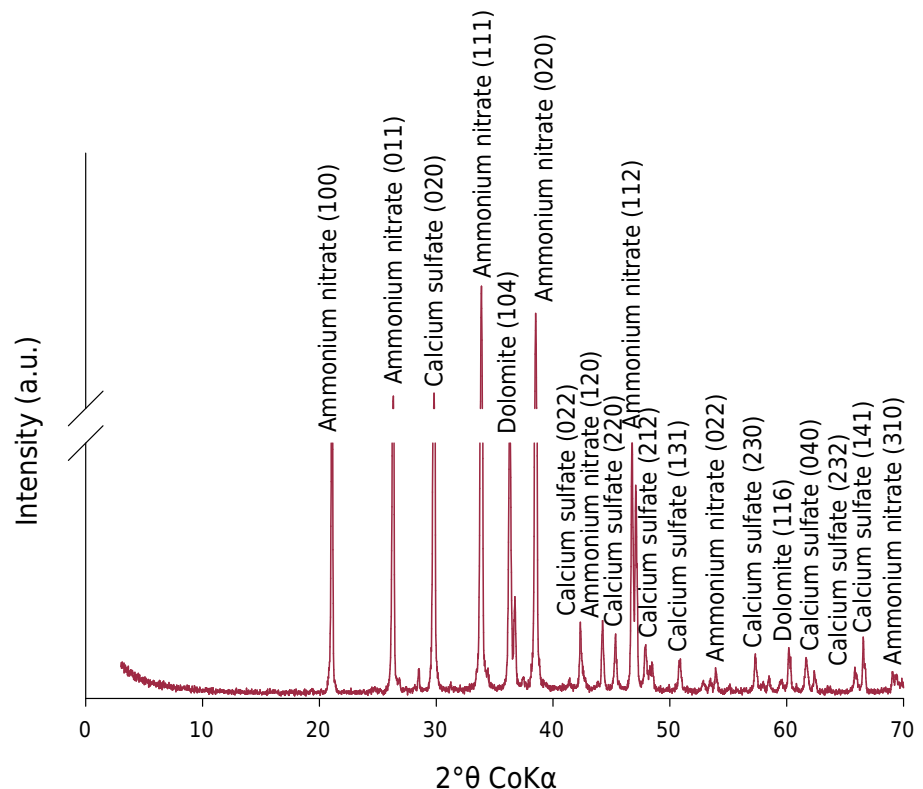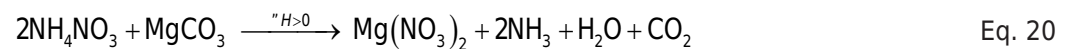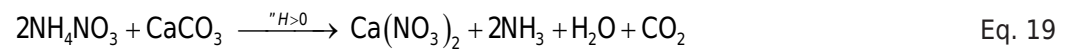
Figure 5. X-ray diffraction of the ammonium nitrate + calcium sulfate for conventional nitrogen fertilizers characterization.

FINAL CONSIDERATIONS AND FUTURE PROSPECTS

The growing demand for food, fuel, and energy driven by world population expansion will further increase the entry of N into agricultural soil and by consequence into the ecosystems, leading to more global N pollution. Besides adopting adequate management practices to reduce N losses and improve the uptake of N-fertilizers by plants, other strategies might be required to reduce the potential pollution caused by accelerated N consumption. This can be the case, for example, in the creation of environmental regulations forcing the industry to couple technologies in N fertilizers to reduce losses. These environmental regulations can be demonstrated in the large-scale adoption of urease inhibitors to mitigate gaseous NH_3 losses and their detrimental effects on water and air. In this sense, on February 1st, 2020, the German government mandated that all urea fertilizers used in the country should be incorporated into the soil or treated with urease inhibitors.

Because urea incorporation requires irrigation or mechanical practices that disrupt the no-till, surface application of urea has become the predominant practice in agricultural production systems. Soon, industries and researchers in the urea-based N fertilizer sector will be challenged to develop new molecules or mixtures of stabilizing agents, cheaper biodegradable coatings, and better controlled-release mechanisms, aiming at reducing environmental contamination by microplastic as well as modifying urea formaldehyde formulations to granules.

For companies that commercialize ammonium sulfate and ammonium nitrate, the great challenge will be to convince farmers to use less concentrated sources of N, increase the current supply of nitrate and ammonium sulfate through the implementation of new factories, and, finally, seek public policies that facilitate the purchase, storage, and transport of ammonium nitrate, given it can be used for the manufacture of explosives and the inherent explosion risk associated with this N source when stored.

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