Limus®

For improved nitrogen use efficiency

BASF
We create chemistry

Technical Brochure

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Nitrogen: the engine of plant growth

Nutrients

Using energy from the sun, a plant produces carbohydrates from CO_2 and water. To do this, 14 plant nutrients are essential as we know today.

Mineral nutrients are divided into classifications of macro-nutrients and micronutrients that reflect the quantity absorbed by the plant.

Plants generally consume nutrients from minerals and soil, decaying organic substances (roots, straw, humus), organic fertilizers and mineral fertilizers, airborne inputs and biological nitrogen fixation. Although arable soils may contain substantial nutrient reserves, they are usually not in plant-available form. Microorganism activity and/or chemical processes result in only a small portion of nutrients being released every year and converted into water-soluble, plant-available form.

When the plant needs cannot be met by available nutrients, fertilizers provide supplemental nutrition.

Importance of nitrogen

The chemical element nitrogen (N) has a special role among minerals in the soil: plants need large quantities to achieve high quality and yield. Nitrogen originates under natural conditions in the soil but in contrast to all other nutrients, it does not originate from rock but from organic compounds in the soil.

Nitrogen is the fourth most common element in living tissue, after carbon, hydrogen and oxygen. An essential element in amino acids and therefore proteins, nitrogen is also a key component of chlorophyll, DNA and RNA.

Without nitrogen there can be no life: no organ regeneration, and no plant development or fruit and seed formation — and ultimately no yield.

This is why nitrogen is commonly referred to as the engine of plant growth.

Nitrogen Cycle
Step by Step

Nitrogen cycle in the soil

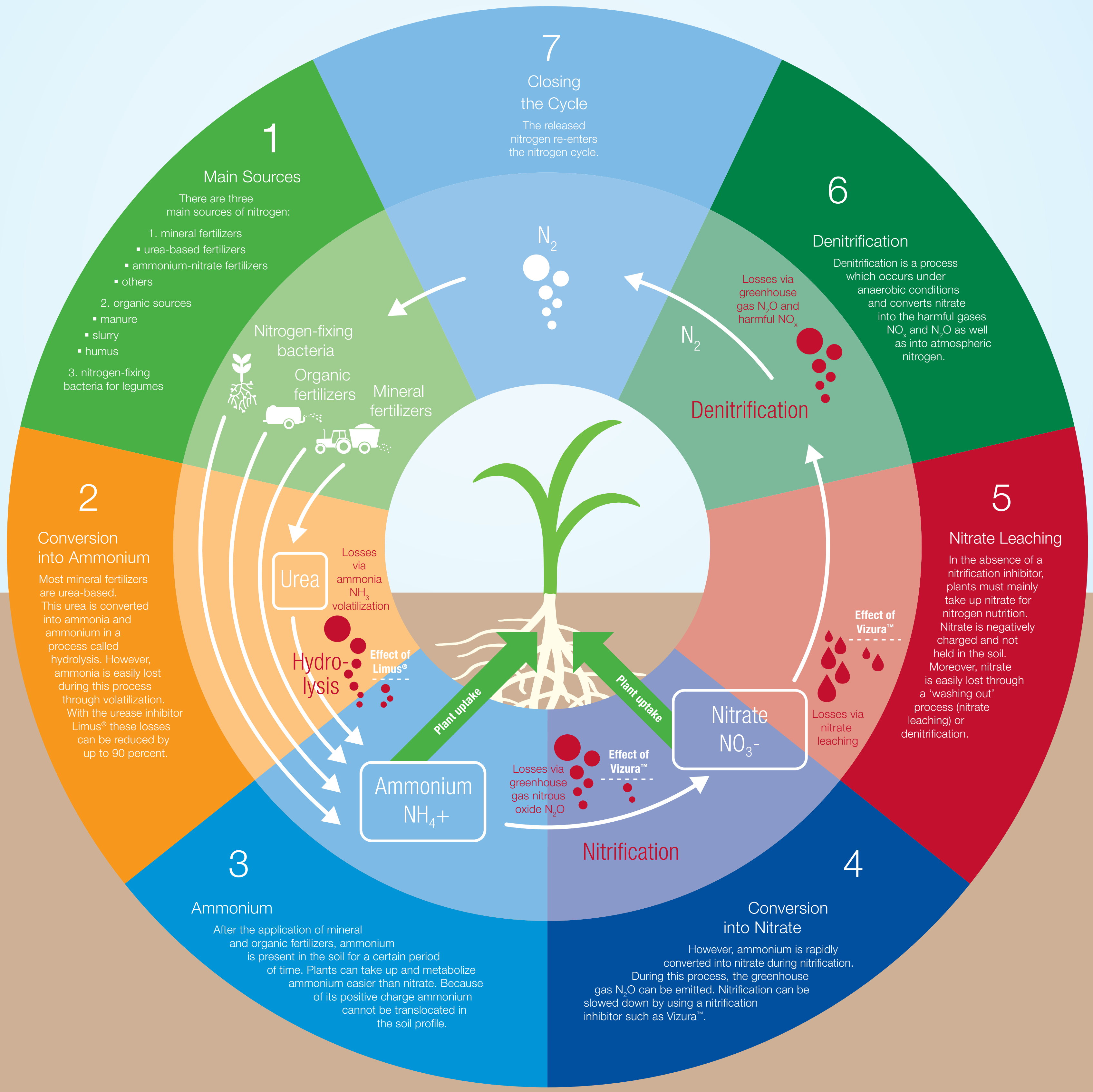
There are two large nitrogen pools in the soil: organically bound nitrogen (95 %), which is not directly plant-available, and mineral nitrogen (5 %), which is present in plant-available forms.

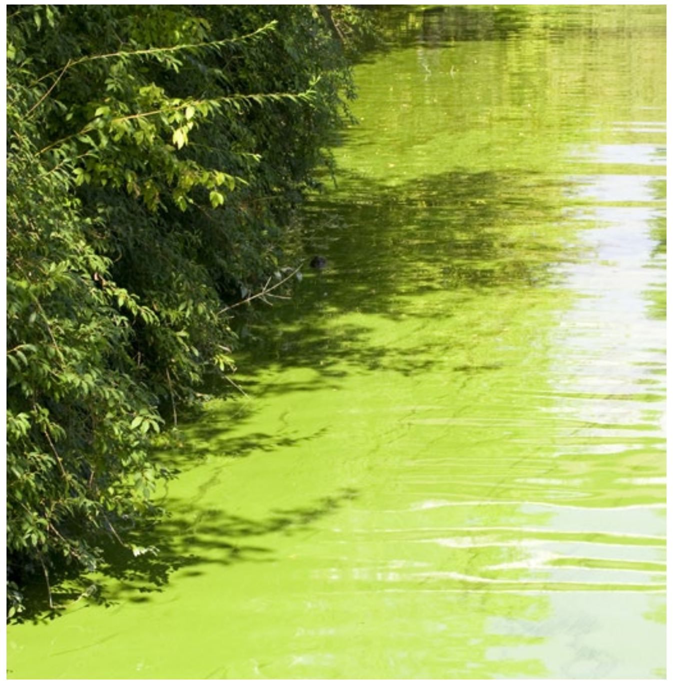
Organic fertilizers, plant residues and the nitrogen bound by legumes (e.g., soybeans, beans and peas) flow into the organic nitrogen pool.

The mineral nitrogen pool, which consists of ammonium (NH_4+) and nitrate (NO_3-), develops from nitrogen dissolved in rain and nitrogen that enters the soil through mineral fertilizers. Ammonium and nitrate are essentially the only forms of nitrogen that plants absorb.

The organic nitrogen and the mineral nitrogen pools are in a state of constant exchange. For instance, organic nitrogen is constantly being transformed into ammonium and nitrate (a process known as mineralization), while soil organisms cause the organic fixation of mineral nitrogen (immobilization).

Nitrogen depletion in the soil occurs when strong rainfall causes leaching (nitrate leaching) or when, as a result of conversion processes, nitrogen containing gases escape into the atmosphere (e.g., nitrous oxide losses).





Effects of nitrogen losses

Nitrogen losses occur as a result of organic and/or mineral fertilization and tillage. These are mainly ammonia losses and losses resulting from either nitrate leaching or the release of nitrous oxide into the atmosphere. While nitrogen losses generally result in an economic cost for the grower, they also have a negative impact on the environment.

Ammonia losses

Ammonia losses occur mainly in livestock production, specifically during organic fertilizer storage and application. Significant ammonia losses also occurs after the application of urea-containing fertilizers.

In addition ammonia is a key component of smog; it binds with other pollutants and particles, maintaining them in air layers at or around ground level.

As a nitrogen-containing gas, ammonia can be carried over great distances by the wind. Rain precipitation then often injects ammonia into natural ecosystems where it acts as a nitrogen fertilizer and might have undesired effects. Some plant species have a stronger reaction to nitrogen fertilization and grow better (gras), while suppressing the development of other species (rare flowering plants), other plants are impaired in their development. In short, ammonia has a substantially negative impact on bio diversity.

Once ammonia enters the soil, it is nitrified relatively quickly, depending on temperature. This goes hand in hand with soil acidification, which under extreme conditions can lead to the release of toxic metals that damage plants and contaminate groundwater. Ammonia can also indirectly contribute to groundwater nitrate contamination and the formation of nitrous oxide as a result of secondary reactions.

Nitrate leaching

Nitrate is water-soluble. Because negatively charged soil particles predominate in soil, the negatively charged nitrate ion — unlike the positively charged ammonium ion — will not bind to soil particles. Nitrate is therefore highly mobile in the soil and can be effectively translocated in the soil profile through diffusion and surface water movements. After heavy rainfall or low plant uptake, nitrate can leach out of the soil profile and accumulate in groundwater. From a toxicological perspective, threshold values have been set worldwide for groundwater levels (to avoid a transformation into severe toxic nitrite).

Nitrate is the predominant form of nitrogen for plants, which is why nitrate in surface water bodies stimulates water plant and algae growth. As algae and/or water plants decay, the resulting oxygen depletion may, under extreme conditions, lead to mortality in fish populations.

Release of nitrous oxide into the atmosphere

Nitrous oxide (N_2O) occurs during nitrification (conversion of ammonium into nitrite and nitrate through soil bacteria) as well as when nitrate exists in the soil under oxygen-poor conditions (denitrification). Next to carbon dioxide and methane, nitrous oxide is one of the most dangerous greenhouse gases. Its global warming potential is 300 times that of CO_2. Even small nitrous oxide losses may represent a cost factor to growers as well as negative environmental impact.

Regulations, conventions and laws for containing nitrogen losses

Ammonia

In 1999, the multi factor Gothenburg Protocol to reduce acidification, eutrophication and ground-level ozone emissions also set ceilings for ammonia emissions. Part of the Convention on Long-Range Transboundary Air Pollution, the Gothenburg Protocol has been ratified by many countries in the northern hemisphere. The protocol was revised in 2012 to include national emission reduction commitments for 2020 and beyond. It also offers new parties especially from South-East Europe, Caucasus and Asia to access.

This convention was implemented in Europe in the context of the NEC Directive (National Emission Ceiling), along with emission ceilings per EU member states till the year 2010. Two digit reductions in ammonia emissions for many European countries till 2030 compared to 1990 are already proposed. An additional and much more significant reduction of these emission quantities is currently under discussion.

Nitrate

Many countries around the world have defined groundwater nitrate limits for toxicological reasons. In Europe, various laws and regulations govern this area. For instance, the Nitrates and Groundwater Directives set the maximum groundwater nitrate concentration at 50 mg/l if the water is used as drinking water. The Water Framework Directive provides guidance on nitrate levels in surface water bodies. Many countries have also set targets for the reduction of nitrogen inputs in the form of nitrate in order to protect neighboring seawater bodies. In some countries e.g. Germany the situation regarding nitrate content in groundwater bodies did not improve in the last decades – in some regions the situation even deteriorated. As a consequence the national implementation of the nitrate directive will be sharpened with huge impact on fertilization.

Nitrous oxide

The reduction of nitrous oxide emissions was first addressed by the Kyoto Protocol, which calls for a voluntary reduction of climate gas emissions. In the context of its EU 2020 initiative, the European Union has set a 20 % emissions reduction target for 2020 (compared to 1990) in the non-industrial sector (which includes agriculture).

In December 2015 the "United nation Framework convention on climate change" in Paris was finalized successfully with an agreement to limit the global temperature increase by max. 2 °C. As a consequence the European Commission started an initiative to reduce GHG emissions (including N_2O) also from European agriculture. Ambitious reduction targets are already discussed.

Urea: agriculture's daily bread

Urea as a fertilizer

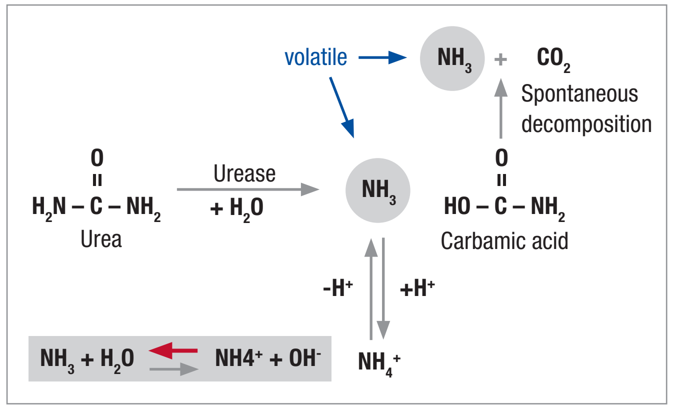
On a global scale, urea is the most important nitrogen fertilizer. It is comparatively easy to produce and has a very high nitrogen content. As a result, transportation and storage costs per unit of nitrogen are very low.

Urea itself is hardly absorbed by the plant. It must first be converted into ammonium or nitrate before it can serve as a source of nitrogen.

Urea conversion

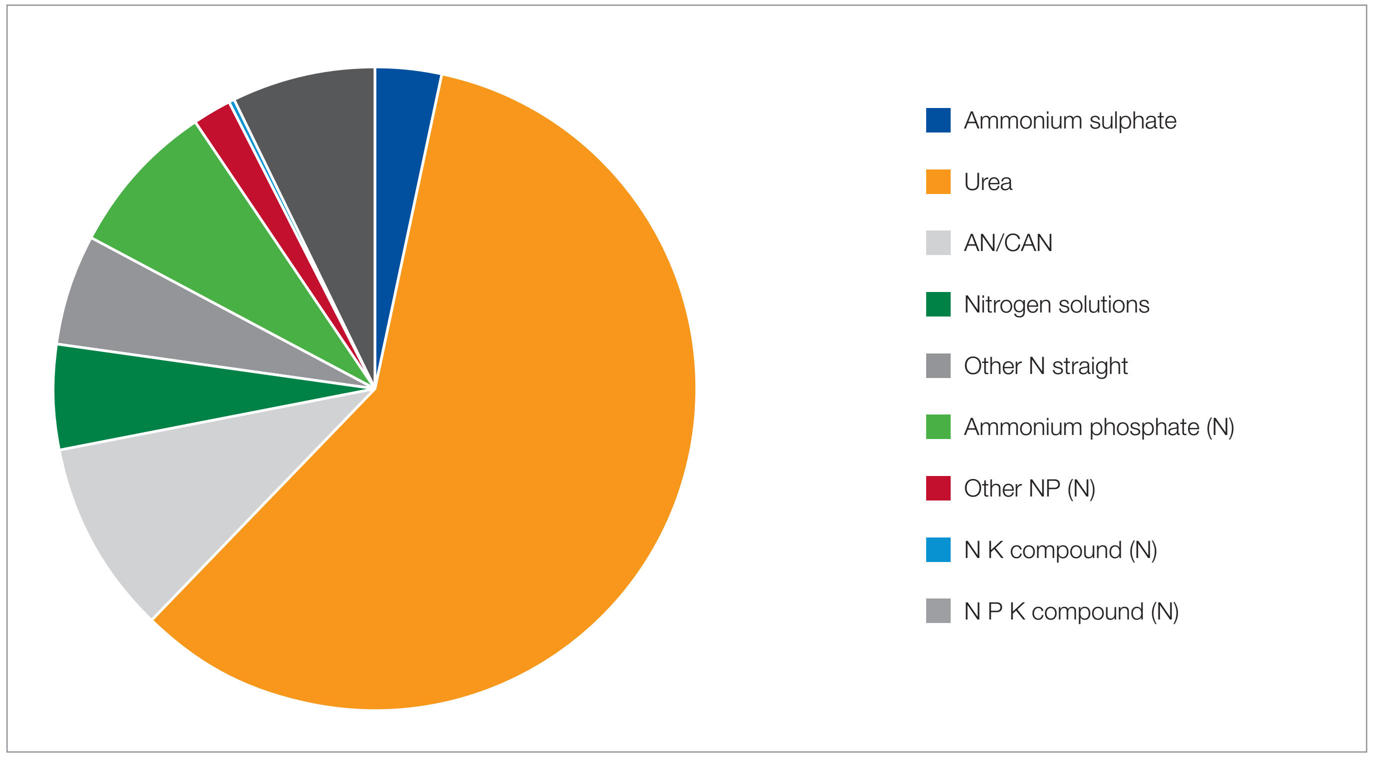
Urease, an enzyme that is ubiquitous in soil, is responsible for the first step in the urea conversion process. In the presence of water, urea is not stable, and conversion occurs immediately following application.

Figure 1: Formation of NH_3 with increase in pH at the site of formation



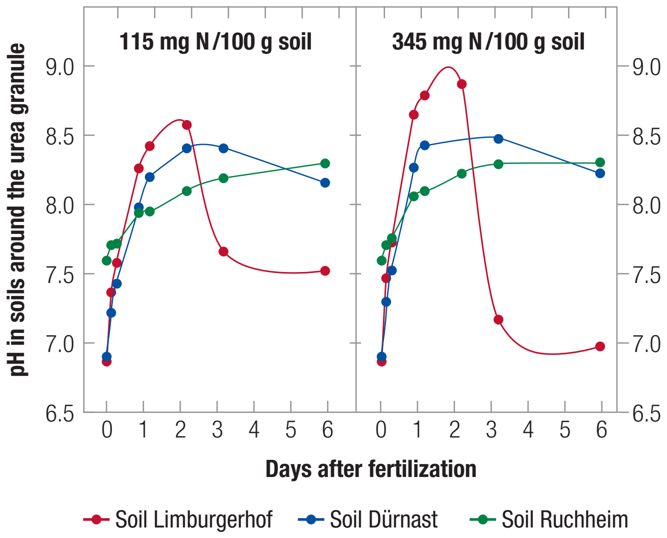
Urea is not directly transformed into one ammonia in the soil; it is first converted into ammonium and carbamic acid, which then spontaneously decomposes into another ammonia and carbon dioxide.

Figure 2: Consumption of N fertilizer (% of total N), IFA 2013



Because ammonia is alkaline, an alkaline zone forms around the urea granule or prill and a pronounced localized pH spike occurs. Due to that pH increase the equilibrium reaction between NH_3 and NH_4 is shift to the side of NH_3 (red arrow in figure 1, page 9) and emissions appear.

Figure 3: pH increase in three soils after urea application



pH tends to determine whether or not water and ammonia will form ammonium. Since urea conversion via the urease enzyme leads to a local pH increase, what usually remains is gaseous ammonia that gets released into the atmosphere. This means the full quantity of nitrogen is not available to the plant.

The conversion rate and resulting ammonia losses, depend on a number of factors. Chief among them is temperature. Other influencing factors include urease activity, cation exchange capacity and soil pH. This results in high ammonia losses in light soils and no-till zones. Losses of ammonia between 7 % and 80 % have been recorded in model tests under laboratory conditions (see figure 8, page 15).

Ammonia losses reduce yield potential

Diminished plant nutrition reduces yield potential. Optimal nitrogen availability for the plant results in more consistant yield, improved plant quality and thus economic benefits for the farmers.

Figure 4: Nitrogen deficiency in corn

How to reduce ammonia losses?

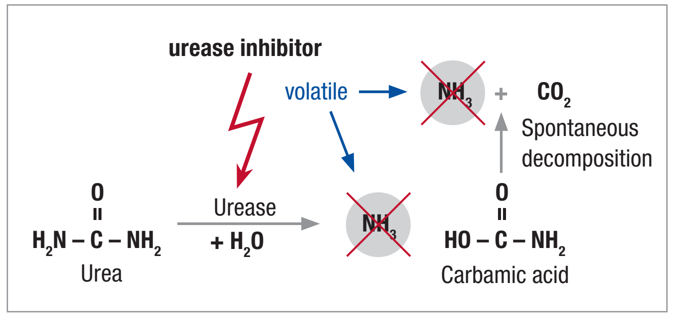
These gaseous losses can be avoided by using

- **Rain or irrigation (> 10 mm), where urea is washed in**
  Global perspective irrigation for arable crops is limited. Therefore many farmers depend on rain-fed production, where rainfall is hardly predictable.
- **Incorporation (tilling > 10 cm) into the soil**
  However, due to crop farming practices incorporation might not be possible. Taking winter cereals, for example, where sowing and fertilizing are conducted in different seasons, tilling is not practicable.
- **Urease inhibitors**

What is a urease inhibitor?

One way to reduce ammonia losses is to treat urea-containing fertilizers with a urease inhibitor (UI). A UI effectively prevents the conversion of urea into ammonia and carbamic acid by blocking the enzyme that drives the conversion, i.e., urease. Under laboratory conditions, supplementing with UI has been shown to prevent ammonia losses at least 70 % — and in some cases nearly 100 %.

Figure 5: Effect of UI — A UI inhibits the activity of the enzyme urease for a certain period of time



Gets the full potential for farmers: Limus®

Introducing Limus®

Limus®, a urease inhibitor developed and patented by BASF, has been developed using the latest research and technology. It is one of the most effective urease inhibitors worldwide both in terms of its active ingredient efficacy and formulation stability.

Mode of action of a standard urease inhibitor

Urease is an extracellular enzyme produced by plants and microbes. It enters the soil through secretion or when plants and microbes die and decompose. Urease has an active site that can bind urea and hydrolyze it to ammonia and carbon dioxide. When ammonia and carbon dioxide leave the active site, it is available to hydrolyze another urea molecule continuously.

The AI (e.g. NBPT[1]) blocks the urease enzyme, slows down urea hydrolysis and hence ammonia volatilization.

Different urease enzymes in soil

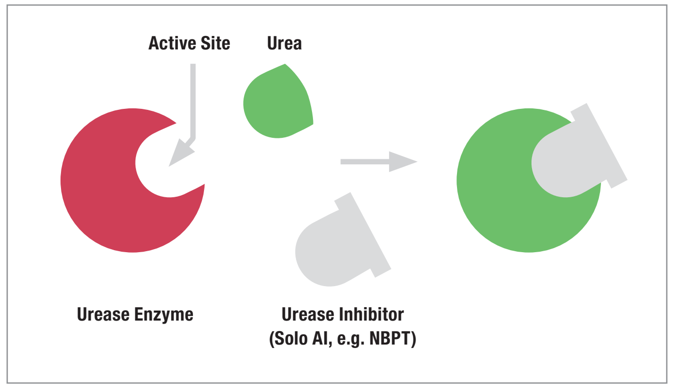
Soils differ in their urease enzyme composition and urease activity. A broad range of organisms in soil (bacteria, fungi and plants) produce slightly different urease enzymes. Different urease enzymes require different urease inhibitors.

The unique Limus® mode of action

What sets Limus® apart is the combination of two active ingredients (NBPT & NPPT[2]). Limus® is about 40% more effective than single AI (NBPT) by blocking the activity of a broader variety of urease enzymes. A patented new formulation enables efficient application and offers more flexibility with regard to storage, mixing with urea-based fertilizers and fertilizer application.

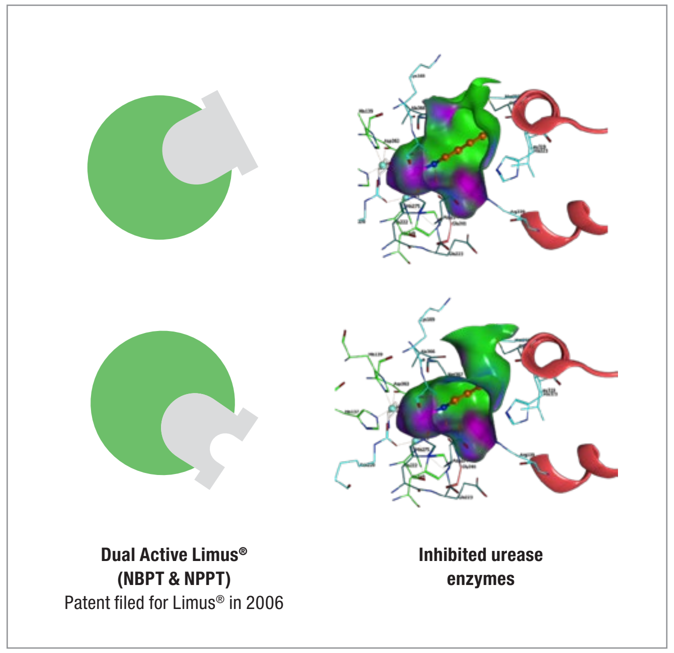
[1] N-Butyl-thiophosphoric triamide | [2] N-Propyl-thiophosphoric triamide

Figure 6: Mode of action of standard urease inhibitor



Standard urease inhibitors in general bind to urease, thus preventing conversion to ammonia.

Figure 7: How Limus® works (Dual AI)



Docking experiments with NBPT and NPPT suggest differences in binding to the active center of different ureases.

The dependable result from our decades of experience

Reduced ammonia losses with Limus®

Reducing ammonia losses (see figure 9) allows the applied urea nitrogen to work more efficiently and enhance nitrogen nutrition. This often leads to higher yields (see figure 10) or nitrogen fertilizer savings, as well as a reduced environmental pollutant load related to fertilization.

As shown in the figure below, Limus® significantly reduces the ammonia losses from urea (reduction of NH_3-N losses between 71 and 98 %).

Under lab conditions the standard recommodation of single AI leads to reduction of ammonia losses by 73 %. With Limus® you could reach the same reduction target while saving more than 40 % AI concentration.

Figure 8: Gaseous NH_3-N losses from fertilized urea and urea + Limus®
resp. after 14 d under lab conditions depending on 15 different European soils (D, F, I, E)

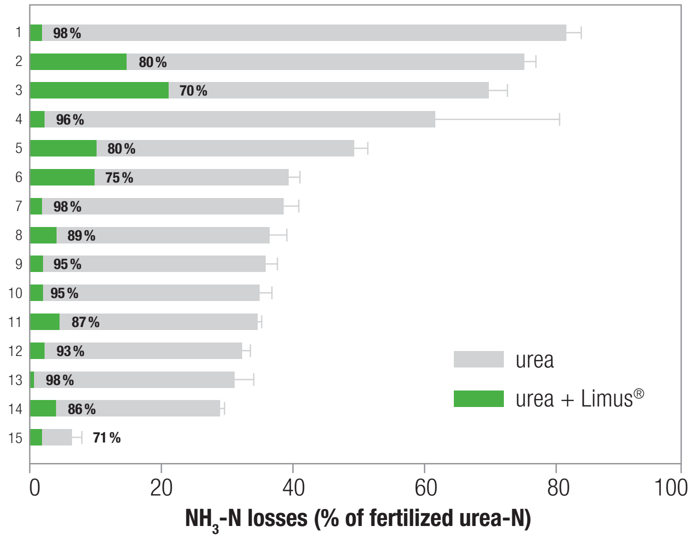


Figure 9: Limus® vs. NBPT 2012 – 2015 NH_3 emissions
Results from lab experiments: % reduction NH_3-N losses of UI (urea = 0 %, average 2 – 35 DAT)

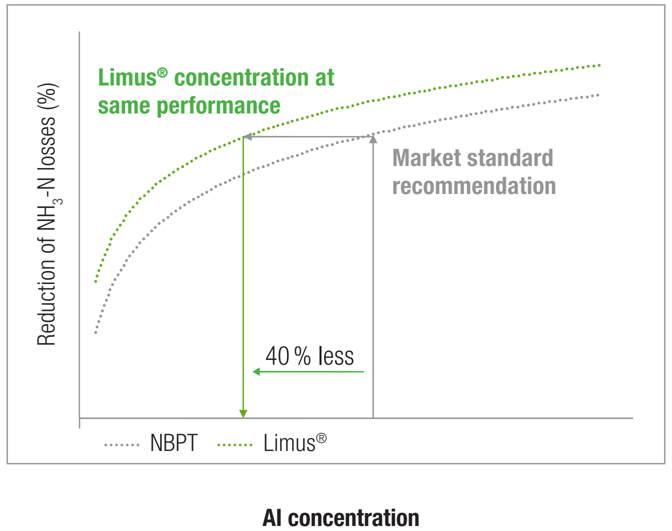
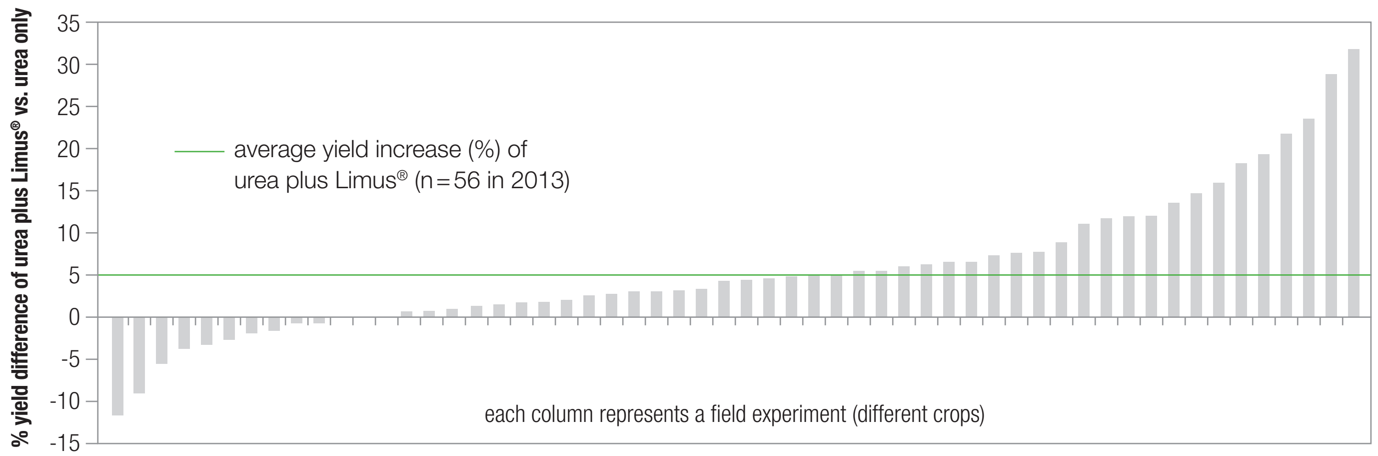


Figure 10: Yield difference of urea plus Limus® vs. urea only



Better nitrogen availability and use efficiency for more consistent and improved yield potential

Works in theory and in practice

Enhanced productivity with Limus®

The conventional approach to ensuring a homogenous nitrogen supply and compensating for ammonia losses is to increase the number and/or rate of urea applications. Fertilizers protected with Limus®, on the other hand, effectively prevent these ammonia losses while slowing the conversion of urea into ammonium. This not only simplifies fertilization programs considerably, it also allows for greater flexibility: Process steps can be eliminated and/or fertilizing times can be moved up with any crop.

The productivity gains made possible by Limus® positively impact farm operations no matter their scale or size of the fields.

Storage

Limus® brings solutions to those in the fertilizer market who face operational challenges in the transportation, application, storage and handling of urea-based fertilizers.

The formulation's stability and excellent protection of urea provides for longer storage time and greater flexibility along the transportation chain under a wide range of temperature and humidity conditions.

Plant compatibility of Limus®

Tolerance tests with a variety of crops have shown that Limus® does not result in plant damage. However, any damage caused by the application of urea-containing fertilizers will not be undone by the addition of Limus®.

On very light soils, urea applied during sowing may impair the emergence of small-seed crops (e.g. sugar beet). Adding Limus® to urea-containing fertilizers will mitigate these detrimental effects.

Figure 11: AI concentration on urea during 12 months storage period (bulk storage, 20 °C) of Limus® (2 L Limus® formulation/tonne urea) and Competitor (3 L/tonne urea); upper and lower limits (% AI related to urea) for Limus® and NBPT according to EU fertilizer directive (2003/2003)

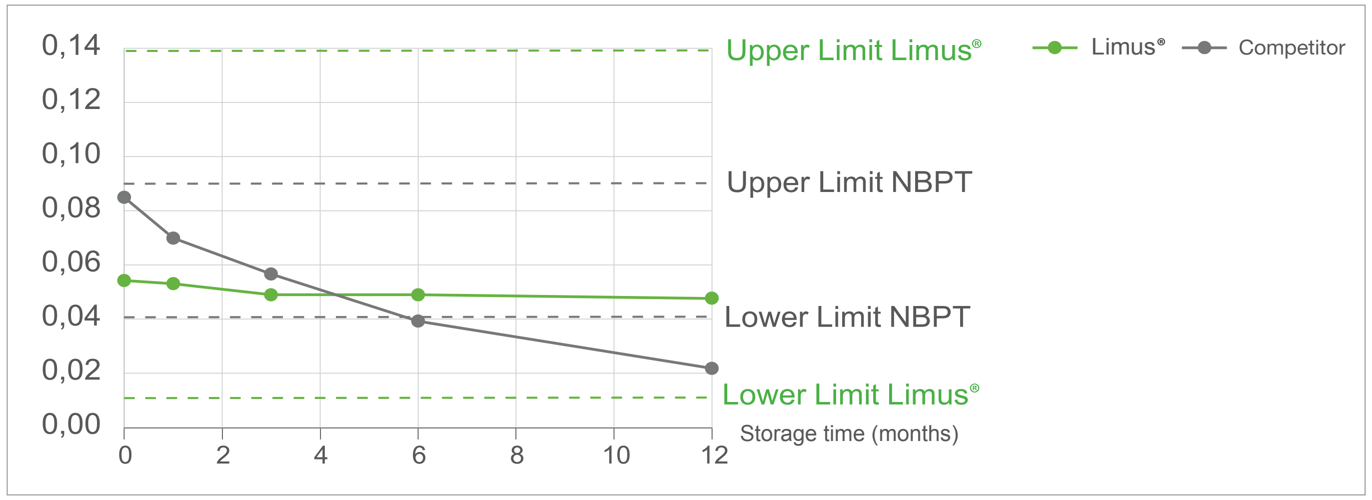


Figure 12: Limus® formulation with BASF polymer technology

Parameters	Competitor 1	Competitor 2	Limus®
Stability of active ingredient in the formulation	+++	+/-	+++
Crystallization	+/-	+++	+++
Viscosity	++	+/-	++
Drying time	++	++	+++
Stability of active ingredient on urea	+/-	++	+++

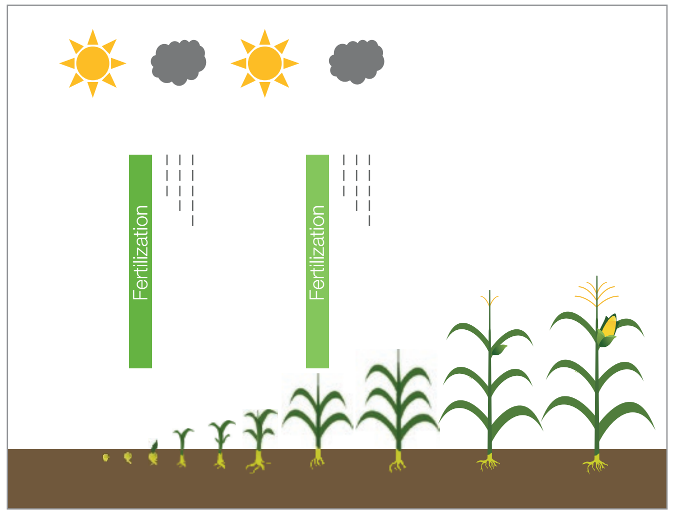
Limus® is a significant step forward in handling and storage of stabilized fertilizers

Application Flexibility

Application flexibility without Limus®

Standard urea should be applied right in advance of rainfall to reduce ammonia losses. Additional fertilizer application at later growth stages might be necessary to compensate for losses.

Figure 13: Application options without Limus®



Application flexibility with Limus®

Limus® stabilized urea can be applied independent of weather conditions. Limus® mitigates the risks of unpredictable losses from drought.

Figure 14: Application flexibility with Limus®

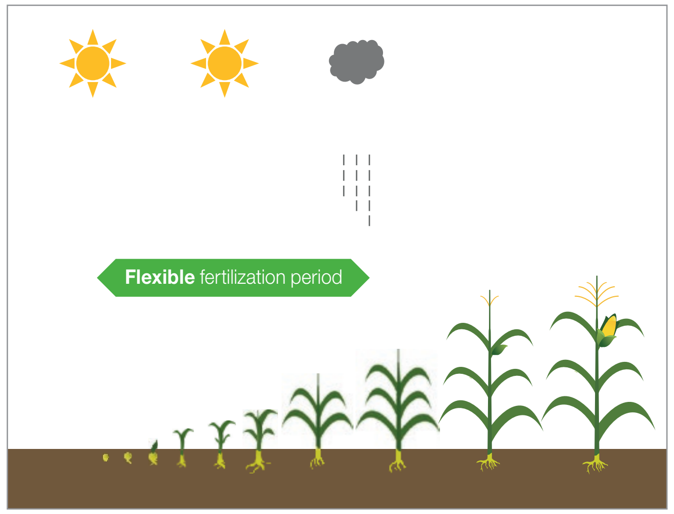
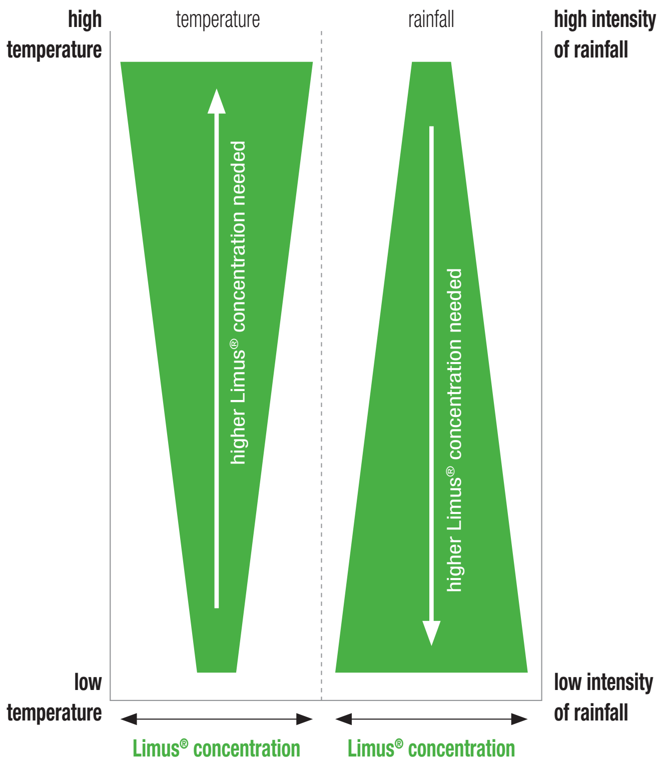


Figure 15: Recommended Limus® concentration on urea and UAN under various environmental conditions; reduction of ammonia losses by more than 80 % of fertilized nitrogen



Recommendations for application

Limus® may be added to all types of urea-containing fertilizers, and these fertilizers can be used on all types of crops.

However, urea itself may cause leaf damage; therefore, application to vegetable crops is generally not recommended. This also applies to urea-containing fertilizers treated with Limus®.

Recommended application concentrations

All urea-containing fertilizers can be treated with Limus®. Recommended Limus® concentrations are calculated to exceed the average statistical intervals between rainfalls. They also account for the effects of various soil characteristics and temperatures.

Limus® is mixed with the fertilizer prior to fertilizer application. The Limus®-treated fertilizer should be stored separately from other fertilizing products (e.g., phosphate-containing fertilizers, potassium-containing fertilizers). Cover the product pile to maintain high fertilizer quality.

Key benefits of Limus®

- Limus®, a multi-patented novel urease inhibitor with two active ingredients reduces nitrogen losses from volatilization of urea fertilizers.
- Developed on the basis of BASF's know how in fertilizers and agriculture, Limus® is about 40% more effective than single AI (NBPT) by blocking the activity of a broader variety of urease enzymes.
- Limus® keeps nitrogen available during critical crop growth stages for more consistent yields while improving the environmental footprint of urea-based fertilizers.
- Limus® helps to provide more application flexibility independent from weather conditions.
- Limus® is a benchmark in formulation stability, storage and transportation of treated urea.
- Limus® enables players in the nitrogen industry to position themselves as leading partners committed to sustainable agriculture.

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