Brochure/Collateral

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Limus®
The best urea protection for optimal plant nutrition

Technical Brochure

The Chemical Company
The best ideas in agriculture always land on fertile soil: Limus®

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Nutrient concentration (mg/kg shoot dry matter)

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>100,000</td>
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<tr>
<td>P</td>
<td>10,000</td>
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<td>K</td>
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<td>Ca</td>
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<td>Mn</td>
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<td>Zn</td>
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<td>Cu</td>
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</tr>
<tr>
<td>Mo</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>0.01</td>
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</table>

Macronutrients and Micronutrients

Data from Maschner (2012)

Figure 1: The 14 plant nutrients and average concentrations in the shoot for adequate growth

Nitrogen: the engine of plant growth

Using energy from the sun, a plant produces carbohydrates from CO₂ and water. All chemical elements essential to the plant’s nutrition and productivity are either mineral or non-mineral plant nutrients.

The plant uses minerals to produce protein, fat, enzymes, phytohormones and vitamins. Non-mineral nutrients include carbon, hydrogen and oxygen. Mineral nutrients are divided into classifications of macronutrients and micronutrients that reflect the quantity absorbed by the plant, see figure 1.

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’s 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.
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 nitrogen 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 (dung, manure, slurry). Significant ammonia losses also occur after the application of urea-containing fertilizers.

In high concentrations, ammonia gas is toxic for humans and animals. Studies show that in 2006, increased health costs associated with ammonia emissions were an estimated 36 B US$. In addition, the pungent odor is unpleasant.

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

As a nitrogen-containing gas, ammonia can be carried great distances by the wind. Rain precipitation then often injects ammonia into natural ecosystems where it acts as a nitrogen fertilizer and has the undesired effect of boosting growth. While some plant species have a stronger reaction to nitrogen fertilization and grow better, other plants are impaired in their development. In areas where the soil has a low nutrient content, this can lead to grasses taking over and suppressing the development of rare flowering plants. In short, ammonia, has a substantially negative impact on biodiversity.

Nitrogen cycle in the soil

There are two large nitrogen pools in the soil: organically bound nitrogen (95%), which is not 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 can 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, gaseous combinations form that escape into the atmosphere (e.g., nitrous oxide losses).

Once ammonia enters the soil, it is nitrified relatively quickly, depending on temperature on some days. This goes hand in hand with soil acidification, which under extreme conditions can lead to the release of toxic heavy 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.

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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. In humid conditions, leached nitrates translate into a significant cost for the grower.

From a toxicological perspective, threshold values have been set worldwide for groundwater levels (to avoid a transformation into nitrite in case that the water is polluted by bacteria or a transformation in the human body).

Excessive nitrate concentrations are suspected of causing the following illnesses: cyanosis in newborns, stomach and intestinal cancer as a result of nitrosamine formation, and goiter. Conversely, numerous studies show that nitrate boosts the body’s immune system and effectively prevents numerous diseases.

Nitrate is the preferred form of nitrogen for plants, which is why nitrate in surface water bodies stimulates water plant and algae growth to the point of algal bloom. As algae and/or water plants decay, the resulting oxygen depletion (oxygen is consumed in the decomposition of organic substances from dead algae and plants) 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$_2$. Nitrous oxide losses in the soil — most often only a few grams or kilograms — may represent a cost 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.

This convention was implemented in Europe in the context of the NEC Directive (National Emission Ceiling), along with emission ceilings per EU member states. An additional and much more significant reduction of these emissions 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.

Nitrous oxide
The reduction of nitrous oxide emissions is 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).
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 cannot be 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 3: Formation of NH₃ with increase in pH at the site of formation

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

Figure 4: Importance of different types of nitrogen fertilizers in selected countries

<table>
<thead>
<tr>
<th>Consumption</th>
<th>Western and Central Europe</th>
<th>Brazil</th>
<th>China</th>
<th>India</th>
<th>United States</th>
<th>World</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>2011 — % of total N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ammonium sulphate</td>
<td>2.8</td>
<td>12.4</td>
<td>0.9</td>
<td>0.6</td>
<td>2.4</td>
<td>3.1</td>
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<td>Urea</td>
<td>19.6</td>
<td>51.0</td>
<td>66.7</td>
<td>78.6</td>
<td>21.5</td>
<td>55.4</td>
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<tr>
<td>AN/CAN</td>
<td>45.0</td>
<td>17.4</td>
<td>0.3</td>
<td>0.2</td>
<td>2.2</td>
<td>9.3</td>
</tr>
<tr>
<td>Nitrogen solutions</td>
<td>11.5</td>
<td></td>
<td></td>
<td></td>
<td>28.3</td>
<td>52.2</td>
</tr>
<tr>
<td>Other N straight</td>
<td>4.6</td>
<td>17.3</td>
<td>0.1</td>
<td>3.2</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>Ammonium phosphate (N)</td>
<td>2.0</td>
<td>11.2</td>
<td>8.6</td>
<td>10.8</td>
<td>5.5</td>
<td>7.0</td>
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<tr>
<td>Compound fertilizer (NPK)</td>
<td>14.4</td>
<td>8.0</td>
<td>6.2</td>
<td>9.8</td>
<td>8.4</td>
<td>9.6</td>
</tr>
<tr>
<td>total N (1000 t N)</td>
<td>10445.3</td>
<td>3614.3</td>
<td>34100.0</td>
<td>17300.2</td>
<td>12243.9</td>
<td>108406.0</td>
</tr>
</tbody>
</table>

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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 NH₃ and NH₄ is shift to the side of NH₃ (red arrow in figure 3, page 11) and emissions appear.

The conversion rate and resulting ammonia losses, depends 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).

These gaseous losses can be avoided if the urea is washed in with rain or irrigation or incorporated into the soil. However, this is not possible under most circumstances (winter crops, grasslands, lack of irrigation, drylands, etc.).

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 carbamic acid and ammonia 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 100%.

Figure 6: Effect of UI — A UI inhibits the activity of the enzyme urease for a certain period of time

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.
Gets the full potential for farmers: Limus®

Introducing 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. What sets Limus® apart is the combination of its two active ingredients, which complement and strengthen each other synergistically. A patented new formulation enables efficient application and offers more flexibility with regard to storage, mixing with urea-based fertilizers and fertilizer application.

Figure 7: Two active ingredients = NxPT (3:1) (synergistic effect)

- N-Butyl-thiophosphoric triamide NBPT
- N-Propyl-thiophosphoric triamide NPPT

State: liquid as single formulation
Combines with urea, resulting in light orange granules

Reducing ammonia losses (see figure 8) allows the applied urea nitrogen to work more efficiently and enhance nitrogen nutrition. This often leads to higher yields (see figure 9) or nitrogen fertilizer savings, as well as a reduced environmental pollutant load related to fertilization.

Figure 8: Gaseous NH₃-N losses from fertilized urea and urea + Limus® resp. after 14 d under lab conditions depending on different European soils (D, F, I, E)

As shown in the figure above, Limus® significantly reduces the ammonia losses from urea (reduction of NH₃-N losses between 71 and 98%).

Figure 9: Yield difference of urea plus Limus® vs. urea only

- average yield increase (%) of urea plus Limus® (n=56 in 2013)

Better nitrogen availability and use efficiency for more consistent and improved yield potential.
The Limus® mode of action

Limus® blocks urease activity in the soil. Urease is an extracellular enzyme produced by plants and microbes. It enters the soil through execution 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.

Limus® works by binding to the active site, blocking the urea from doing so. This prevents urea hydrolysis and reduces ammonia formation.

Figure 10: Mode of action of urease inhibitors

Figure 11: How Limus® works (Dual A.I.)

Urease inhibitors in general bind to urease, thus preventing conversion to ammonia

The characteristics of urease enzymes vary based on origin and soil properties. Limus® is a composition two different urease inhibitors that combined are more effective than a single inhibitor.
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 supplemented 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.

Crop tolerance to 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.

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.

Figure 12: Comparison of Uf formulations — stability on urea after 4 weeks at 40 °C in the lab

- Competitor 1
- Competitor 2
- Limus®
Recommended for best results

**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 supplemented 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. Precipitation and irrigation cause urea to leach into the soil profile, which generally prevents further ammonia losses.

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.

**Figure 14: Recommended Limus® concentration on urea and UAN under various environmental conditions; reduction of ammonia losses by more than 80% of fertilized nitrogen**