

Nitrate fertilizer

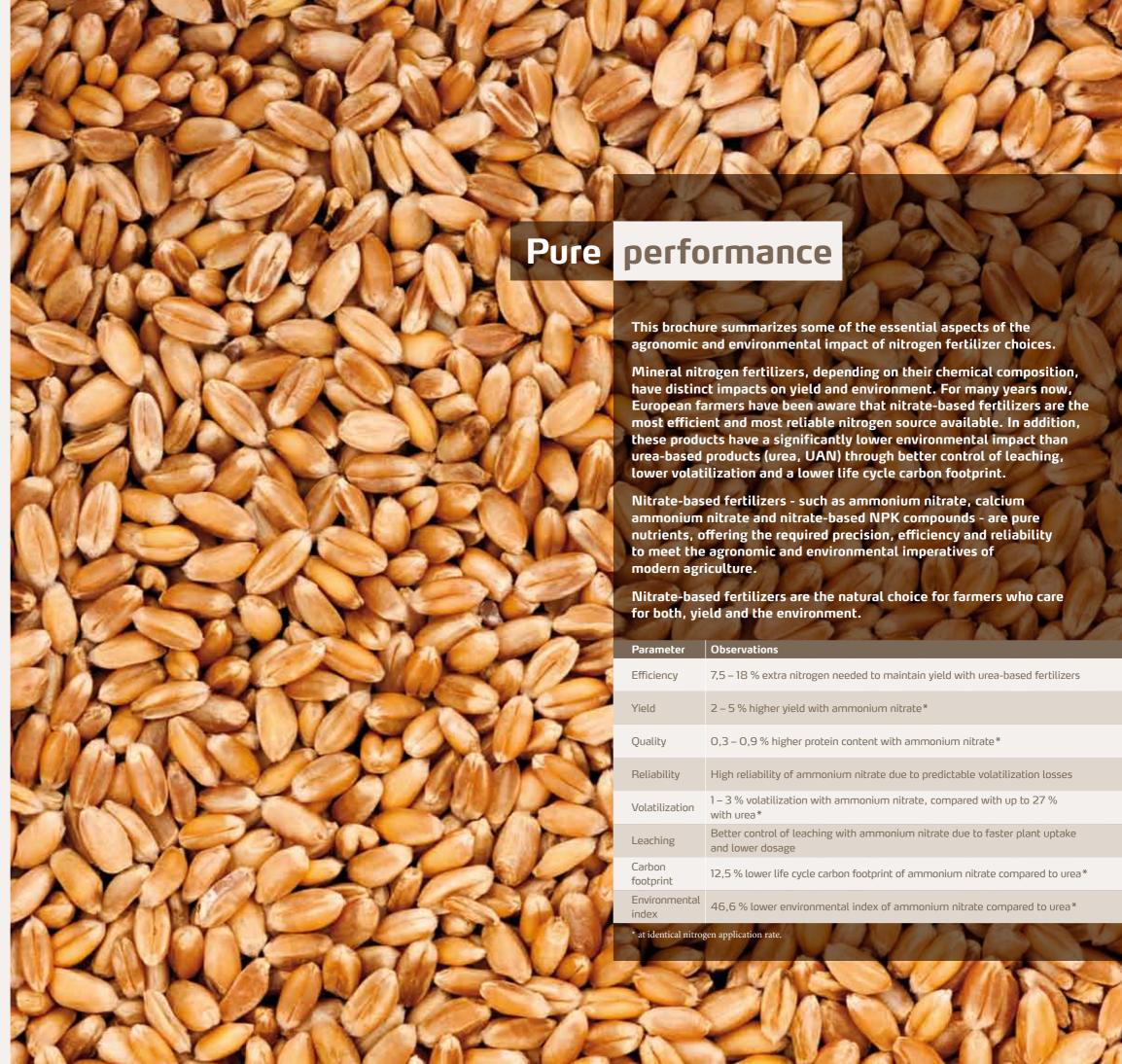
Optimizing yield, preserving the environment.





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Feeding the world, protecting nature

An expanding world population and the dawning environmental crisis are putting agriculture under a whole new light. How can food security and environmental protection be reconciled? What is the role of mineral fertilizers? How to weight agronomic performance versus environmental burden? Yara, as a knowledge leader in plant nutrition, responds to questions regarding the best choice of mineral fertilizers.

Farming tomorrow

During the past half-century, the "green revolution" tripled food production while world population grew steeply from 3 to 6 billion people. With world population expected to grow to some 8.5 billion people by 2030, food production will need to increase by more than 50% [ref. 1]. Since land suitable for conversion to agriculture is dwindling, optimizing yield from existing agricultural surface is a necessity.

European agriculture is one of the most efficient worldwide. Nevertheless, the European Union has emerged as the world's largest importer of agricultural commodities. The net imports exceed exports by 65 million

tons with an increase of 40% over the last decade. The agricultural surface outside the European Union required for producing these imports amounts to almost 35 million hectares (approximately the size of Germany!) [ref. 2].

Further progress in yield and productivity are required to meet the challenges of the 21st century. Mineral fertilizers are key to an efficient use of arable land. They help to assure food security on a global scale, protect pristine forests and grassland from conversion and thus can contribute to mitigating climate change.

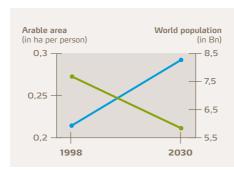


FIGURE 1: The world population is increasing but available arable land is limited. Using agricultural land efficiently is a vital necessity. [ref. 1]

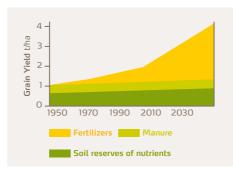


FIGURE 2: The growing world food supply increasingly relies on mineral fertilizers. [ref. 3]

Mineral sources of nitrogen

European farmers traditionally rely on ammonium nitrate as the most efficient source of nitrogen. However, other sources such as urea and UAN are also considered. Different sources of mineral nitrogen do not interact the same way with the soil. These differences need to be taken into account when evaluating agronomic and environmental performances.

Nitrogen - a source of life

Nitrogen is a vital element for plant life. It stimulates root growth and photosynthesis, as well as uptake of other nutrients. However, 99 % of the nitrogen on earth is stored in the atmosphere and less than 1 % is available in the earth's crust. The nitrogen molecules (N_2) in the atmosphere are chemically inactive and cannot be easily absorbed by plants.

The small amount of reactive nitrogen in the soil limits biomass production in natural ecosystems. Agriculture further depletes reactive nitrogen from the soil. Nitrogen is absorbed during plant growth and then exported from the fields by harvesting. It needs to be restored by organic or mineral

sources of nitrogen. Fertilizers, whether applied as manure or as mineral nitrogen, are therefore a key element of sustainable agriculture

Lack of nitrogen results in declining soil fertility, low yields and low crop quality. On the other hand, excess amounts of nitrogen in the soil may move into the ground water, euthrophicate surface water or escape to the atmosphere, causing pollution and climate warming.

Mineral fertilizers

This brochure evaluates the efficiency and side effects of the principle mineral sources of nitrogen being used in Europe:

- Ammonium nitrate (AN) contains nitrogen as NH₄⁺ (ammonium) and as NO₃⁻ (nitrate) in equal portions. Calcium ammonium nitrate (CAN) contains in addition dolomite or limestone.
- Urea contains nitrogen in its amide (NH₂) form.
- Urea ammonium nitrate (UAN) is an aqueous solution of urea and ammonium nitrate.

Conclusions for specialty produces, such as NPKs or sulphur containing products, even if not specifically mentioned, can be easily derived from general observations.

PRODUCT	NITROGEN CONTENT				
	nitrate-N (NO ₃ -)	Nitrification	ammonium-N (NH ₄ +)	Hydrolysis	amide-N (NH ₂)
Calcium Ammonium Nitrate	50 %		50 %		
Ammonium Nitrate	50 %		50 %		
UAN	25 %		25 %		50 %
Urea					100 %

TABLE 1: Common forms of mineral fertilizers contain nitrogen as nitrate, ammonium or amide in different proportions. Only nitrate is easily taken up by plants. Ammonium and amide is transformed into nitrate by hydrolysis and nitrification.

Nitrogen transformations in the soil

Nitrogen undergoes transformations in the soil, depending on the chemical composition of the nitrogen applied. While nitrate is taken up directly by plants, ammonium and urea need to be first transformed into nitrate. Transformation losses are lowest with nitrate and highest with urea.

- Application of fertilizers, containing mineral nitrogen as urea, ammonium, nitrate or a mix.
 Organic fertilizers and manure contain mostly complex organic nitrogen compounds and ammonium.
- 2 Uptake of nitrate is rapid due to the high particle mobility. Most plants therefore prefer nitrate over ammonium.
- 3 **Uptake of ammonium** is slower than nitrate. Ammonium is bound to clay particles in the soil and roots have to reach it. Most of the ammonium is therefore nitrified before it is taken-up by plants.
- 4 **Nitrification** by soil bacteria converts ammonium into nitrate in between a few days and a few weeks. Nitrous oxide and nitric oxide are lost to the atmosphere during the process.

- (5) **Denitrification** is favoured by lack of oxygen (water logging). Soil bacteria convert nitrate and nitrite into gaseous nitrous oxide, nitric oxide and nitrogen. These are lost to the atmosphere.
- (6) Immobilization transforms mineral nitrogen into soil organic matter. Activity of soil microbes is mainly stimulated by ammonium. Immobilized nitrogen it is not immediately available for plant uptake, but needs to be mineralized first.
- **Mineralization** of soil organic matter (and manure) releases ammonium into the soil.
- 7 **Hydrolysis of Urea** by soil enzymes converts urea into ammonium and CO₂ gas. Depending on temperature, hydrolysis takes a day to a week. The soil pH around the urea granules strongly increases during the process, favouring ammonia volatilization.
- (8) Ammonia volatilization occurs when ammonium is converted to ammonia and lost to the atmosphere. A high soil pH level favours conversion of ammonium to ammonia. If conversion takes place at the soil surface, losses are highest. These two conditions are met when urea is spread and not immediately incomprated.
- Leaching of nitrate occurs mainly in winter when rainfall washes residual and mineralized nitrates below the root zone. Accurate fertilization prevents leaching during the growth period.

CO ₂	carbon dioxide (gas)
CO(NH ₂) ₂	urea
NH ₃	ammonia (gas)
NH ₄ ⁺	ammonium
NO ₃	nitrate
NO ₂ -	nitrite
NO	nitric oxide (gas)
N ₂ O	Nitrous oxide (gas)
N ₂	nitrogen (gas)

$N_2O + NO + N_2$ $N_2O + NO$ CO NH. IIRFA ΑN 1 Application 1 Application 8 Volatilization 2 Uptake 3 Uptake 4 Nitrification NO₂ CO (NH. 5 Denitrification 7 Hydrolysis 6 Immobilization NITRATE AMMONIUM 9 Leaching NO₃

Nitrogen from nitrate

Nitrate (NO₃) is easily absorbed by plants at high rates. Unlike urea or ammonium, it is immediately available as a nutrient. Nitrate is highly mobile in the soil and reaches the plant roots quickly. Applying nitrogen as ammonium nitrate or calcium ammonium nitrate therefore provides an instant nutrient supply.

The negative charge of nitrate carries along positively charged nutrients such as magnesium, calcium and potassium.

It is important to note that essentially all the nitrogen in the soil, whether it was applied as urea, ammonium or nitrate, ends up as nitrate before plants take it up. If nitrate is applied directly, losses from the transformation of urea to ammonium and from ammonium to nitrate are avoided.

Nitrogen from ammonium

Ammonium (NH₄*) is directly absorbed by plants at low rates. The positively charged ion fixes to soil minerals and is less mobile than nitrate (NO₃·). Plant roots therefore need to grow towards the ammonium. Most of the ammonium is transformed into nitrate by soil microbes. This nitrification process depends on temperature and takes between one and several weeks. Another part of the ammonium is immobilized by soil microbes and released only over longer periods of time, thus building up soil organic matter.

Nitrogen from urea

Plant roots do not directly absorb the ureic form of nitrogen in significant quantities. Urea needs to be first hydrolysed to ammonium by soil enzymes, which takes between a day and a week, depending on temperature. Moisture is required for hydrolysis.

The ammonium generated by hydrolysis does not, however, behave exactly as the ammonium from ammonium nitrate. Hydrolysis of urea results in a short-term alkalinization in the immediate vicinity of the urea grain applied. It shifts the natural balance between $\mathrm{NH_4}^*$ and $\mathrm{NH_3}$ to the latter form, resulting in volatilization losses. These losses are the main reason for the lower N-efficiency observed with urea. This is also the reason why urea, whenever possible, should be incorporated into the soil immediately upon application

In the long term, urea, as well as other sources of nitrogen, has an acidifying effect on the soil.

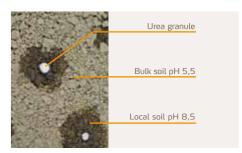


FIGURE 4: Hydrolysis of urea leads to local alkalinazation, resulting in NH₃ rather than NH₄ formation and susequent volatilization.

FIGURE 3: Transformation of urea, ammonium and nitrate in the soil. Urea suffers the highest transformation losses, nitrate the lowest. UAN, a 50/50% mix of ammonium nitrate and urea, undergoes the same transformations and losses as its components.



France

In France, Arvalis and Yara conducted 122 field trials between 1987 and 2004 with winter wheat on various soil types. At an average optimum N rate of 183 kg / ha, ammonium nitrate produced 0,26 t more yield and 0,75 points higher protein content than UAN. An additional 27 kg N / ha (15 %) from UAN was needed to reach economic optimum. [ref. 4]

Germany

In Germany, Yara conducted conducted 55 fields trials between 2004 and 2010 with winter cereals and various soil types. At an average optimum N rate of 210 kg / ha, calcium ammonium nitrate produced 2 % more yield and 0,23 points higher protein content than urea. An additional 15 kg N / ha (7,1 %) from urea was needed to reach economic optimum. [ref. 5]

For more detailed information as well as information on other crops, please contact Yara.

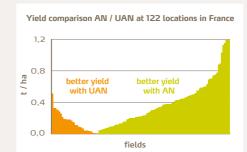


FIGURE 5: Out of 122 fields fertilized at N-opt in France, 75 % produced a better yield with ammonium nitrate and 25 % produced a better yield with UAN. [ref. 4]

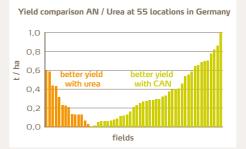


FIGURE 7: Out of 55 fields fertilized at N-opt in Germany, 75 % produced a better yield with calcium ammonium nitrate and 25 % produced a better yield with urea. [ref. 5]

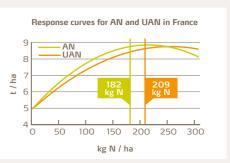


FIGURE 6: The N response curves for the trials indicate that on average an additional 27 kg of nitrogen would have been needed with UAN to reach economic optimum. [ref. 4]

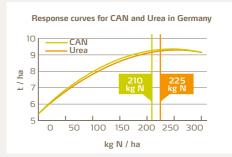


FIGURE 8: The N response curves for the trials indicate that on average an additional 15 kg of nitrogen would have been needed with urea to reach economic optimum. [ref. 5]

Ensuring optimum yield

The golden rule in fertilizer use remains simple: apply the right amount of nitrogen at the right time. Fertilizers with a reliable nitrogen release profile and precise application characteristics reduce losses and improve plant uptake.

In field studies, calcium ammonium nitrate and ammonium nitrate have consistently returned higher yield and better crop quality than urea and UAN. Best Farming Practice and precision farming tools can further enhance fertilizer efficiency.

Optimizing yield and quality

Different mineral sources of nitrogen have different effects on yield and crop quality. This has been well known by European farmers for decades. The different performance of mineral nitrogen sources is mainly due to losses, especially volatilization but also leaching. Some of theses losses are aggravated by a mismatch between nitrogen supply and plant uptake. Scorching of leaves can also impact yield. Most of the underperformance observed with Urea and UAN can be compensated by higher nitrogen dosage, though on the cost of increased environmental burden.

United Kingdom

The most extensive study comparing different forms of nitrogen fertilizers was performed on behalf of the UK government between 2003 and 2005 (Department for Environment, Food and Rural Affaires, Defra) (ref. 6). Besides quantitative differences, the study highlighted the variability of results observed with urea and UAN. The required nitrogen application rates can therefore not be predicted with the same reliability as with ammonium nitrate.



FIGURE 9: To maintain the same yield, significantly more nitrogen was needed from urea and UAN than from ammonium nitrate. [ref. 6]

	Urea	UAN
Lost yield at identical nitrogen application rates	0,31 t/ha	0,39 t/ha
Lost protein at identical nitrogen application rates	0,3 points	0,5 points
Required extra nitrogen to maintain yield	14 %	18 %

TABLE 2: Urea and UAN resulted in underperformance compared to ammonium nitrate on cereals in the UK. [ref. 6]

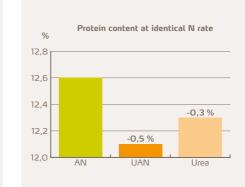


FIGURE 10: Protein content was significantly lower on fields fertilzed with urea or UAN than with ammonium nitrate. [ref. 6]

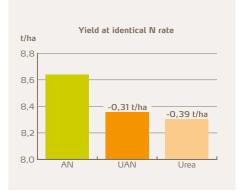


FIGURE 11: Yield was also significantly lower with urea and UAN than with ammonium nitrate. [ref. 6]

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Enhancing fertilizer efficiency

Matching fertilizer application with plant needs

Nitrogen needs to be available in sufficient quantities so that it does not limit growth and yield. However, excess amounts of nitrogen beyond short-term plant needs may be lost to the environment or result in luxury consumption. Matching nitrogen availability precisely to current plant needs and actual soil nutrient supply maximizes yield, minimizes environmental impact and optimizes profit.

Split application is considered best agricultural practice under most conditions. Fertilizers offering a predictable release of plant-available nitrogen are best suited for split application. This is the case for ammonium nitrate and calcium ammonium nitrate, but generally not for urea. Hydrolysis of urea and volatilization losses heavily depend on climatic conditions after spreading, especially on rainfall. They cannot be predicted reliably, resulting in either under- or oversupply of nitrogen. The Defra study has highlighted the unreliability of urea, finding volatilization losses that varied from 2 to 58 % of applied nitrogen!

Balanced nutrition is another prerequisite of economic fertilizer use. Insufficient supply of Phosphorus, Potassium or Sulphur can diminish nitrogen use efficiency. Frequent soil sampling provides data on actual supply of nutrients from the soil and fertilizer needs.

The Yara N-Tester™ is a tool to measure plant nitrogen needs on spot and adjust fertilizer nitrogen applications correspondingly.

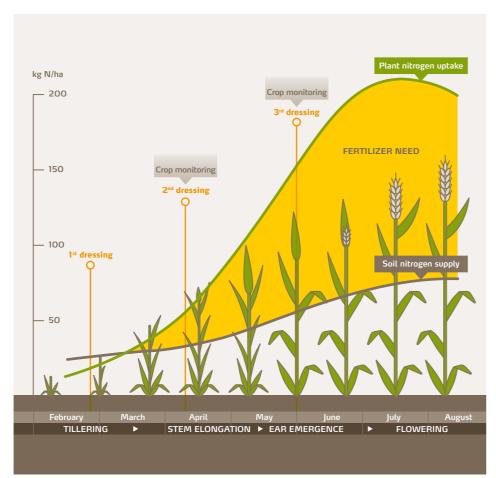


FIGURE 12: Split application of ammonium nitrate with winter wheat. The actual fertilizer need depends on both, soil nitrogen supply and plant need. Tools such as Yara N-Tester or N-Sensor facilitate crop monitoring and help to ajust split applications accurately. [ref. 5]

Reducing fertilizer input by sensor controlled spreading

Precision farming tools can further enhance spreading accuracy. The Yara N-Sensor™ offers farmers real-time control over fertilizer application and GPS based accounting of nutrient supply. The plant nitrogen need is measured continuously during spreading. The Yara N-Sensor™, when being used for spreading homogeneous nitrate fertilizers, guarantees highest yield with lowest nitrogen input. More than a hundred field trials have compared the N-Sensor to common farming practice, demonstrating an increase in protein content by O,2-1,2 %, an increase in yield by 7 % and a cut in nitrogen input by 12 %. [ref. 7]

Ensuring spreading precision

Even spreading assures optimum nutrient supply. Ammonium nitrate, due to a higher bulk density and lower nitrogen concentration, offers more homogeneous spreading characteristics than urea. Wind can further degrade spreading homogeneity with urea, resulting in significant local over- or undersupply.

A study, conducted in Germany, compared the spreading loss of urea to calcium ammonium nitrate. The results are shown in the charts below. Even with a spreading width of only 21 meters, a mild breeze of 4 m/s resulted in 26 % variation of application rate with urea, whereas it was only 6 % with CAN! A spreading inaccuracy of 26 % is typically associated to yield losses of 2 % for winter wheat. Larger spreading width result in even higher losses. Lower spreading width increases work load and reduces strike force. [ref. 8]

Reducing soil acidification

Nitrogen fertilizers can have an acidifying effect on certain soils, which needs to be corrected by liming. Applying fertilizers with high nitrogen efficiency reduces acidification and liming requirements. Fertilizers such as calcium ammonium nitrate contain limestone or dolomite, leading to further savings in cost and time for lime application.

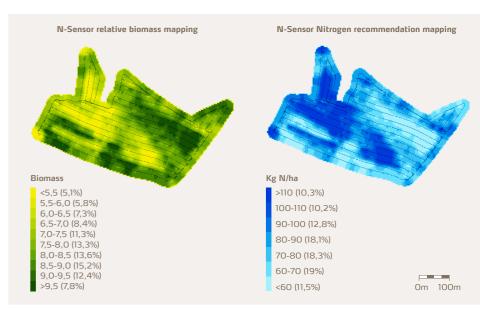


FIGURE 14: The Yara N-Sensor™ automatically applies optimum nitrogen rates (blue) based on real time mapping of biomass and chlorophyll (green), avoiding both, over- and underfertilization. Winter wheat, Germany, [ref. 5]

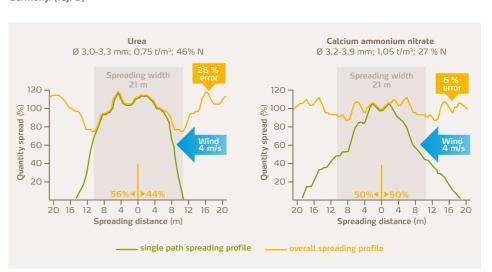


FIGURE 13: Spreading errors, and therefore losses, are significantly higher with urea than with CAN. Even with a spreading width of only 21 m, a light breeze of 4 m/s causes a significant spreading error of 26% with urea. [ref. 8]

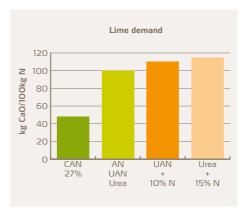


FIGURE 15: The lime demand of (calcium) ammonium nitrate is significantly lower than for urea. [ref. 9]



FIGURE 16: The Yara N-Tester is a handheld tool that provides immediate information on actual nitrogen need.

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Preserving the environment

Ammonium nitrate and calcium ammonium nitrate are pure nutrients that have demonstrated clear environmental advantages over urea and UAN:

- Lower life cycle carbon footprint, including production and application
- Lower ammonia volatilization, even if it is not incorporated into the soil
- Lower aggregated environmental index



Optimizing fertilizer production

Fertilizers are produced by extracting nitrogen from the atmosphere. The process requires energy and thus releases CO_2 , contributing to global warming. Due to continuous improvements, European fertilizer plants are today operating near the theoretical energy minimum and Yara plants are among the best in the world.

In addition to CO_2 , fertilizer production also releases $\mathrm{N}_2\mathrm{O}$, a powerful green house gas. Yara has developed proprietary catalyst technology to abate most of the $\mathrm{N}_2\mathrm{O}$ released during production. As a forerunner in the industry, Yara is sharing its catalyst technology with other fertilizer producers around the world.

The climate impact of fertilizers can be measured by its carbon footprint. It is expressed as kg CO₂-eqv per kg nitrogen produced. However, to understand the true climate impact of a product, lifecycle analysis needs to be performed, including all steps from production to application. A detailed comparison of the respective life cycle carbon footprints for different fertilizer types are given in the next section.

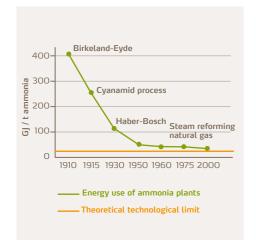


FIGURE 17: Energy consumption of European fertilizer production plants has decreased over time and is today near the theoretical optimum. [ref. 10]

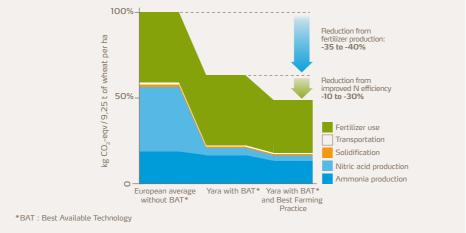


FIGURE 18: Yara has reduced the carbon footprint of nitrate fertilizer production by 35 - 40%. Enhancing N efficiency in fertilizer use can contribute by another 10 - 30%. [ref. 11] [ref. 12]

Improving fertilizer application

The undesirable environmental effects of fertilizer application, whether from mineral or organic sources, are not caused by any fundamental properties of these elements but as a result of lost nitrogen. Where such losses are kept small, the negative effects on the environment are also minimal.

Reducing volatilization

Ammonia can be lost upon spreading of fertilizers. The European emission inventory estimated that 94% of all NH₃ emissions are caused by agriculture. Most of these emissions are from organic sources but about 20% derive from mineral nitrogen fertilizers.

Ammonia volatilization is a direct loss of nitrogen, and therefore money. Volatilized ammonia also represents a significant environmental burden. Volatilized ammonia travels beyond national borders, causing acidification and eutrophication of land and water. This is the reason why the UN/ECE Gothenburg Protocol and the EU National Emissions Ceiling Directive have been implemented, to control ammonia emissions at a national level, whatever their source.

It has long been known that urea or UAN cause higher volatilization losses than ammonium nitrate or calcium ammonium nitrate. Ammonia losses from urea can be reduced by incorporation into the soil upon spreading. However, this is only practicable for spring sown crops. Losses from grasslands are generally considered to be greater than those from arable soils, as fertilisers are typically surface spread and the grass matt has a high urease activity and low absorption capacity.

Volatilization losses [% N]	Arable land		Grassland	
	EMEP	Defra	EMEP	Defra
(Calcium) ammonium nitrate	0,6 %	3 (-3-10) %	1,6 %	2 (-4 -13) %
UAN	6 %	14 (8-17) %	12 %	N.A.
Urea	11,5 %	22 (2-43) %	23 %	27 (10-58) %

TABLE 3: Average ammonia emissions per kg of nitrogen applied for different fertilizer types. The table includes data from the official European Emission Inventory EMEP as well as the Defra study. In all cases, volatilization losses are significantly higher with urea and UAN than with (calcium) ammonium nitrate. [ref. 13] [ref. 14] [ref. 15]

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Mitigating climate change

Production, transportation and use of mineral fertilizers contribute directly and indirectly to greenhouse gas (GHG) emissions, notably carbon dioxide (CO_2) and nitrous oxide (N_2O). At the same time, fertilizers enhance agricultural productivity and stimulate CO_2 uptake by the crop. They increase yield and reduce the necessity to cultivate new land, thus avoiding GHG emissions from land use change (land use change alone accounts for $20\,\%$ of global of GHG emissions).

Life-cycle analysis of fertilizers determines GHG emissions and absorptions in fertilizer production, transportation and storage, as well as during application and crop growth, i.e. throughout every stage of the 'life' of a fertilizer. This provides a better understanding of what can and shall be done to improve the overall carbon balance. To make different GHGs comparable, they are converted into $\rm CO_2$ - equivalents ($\rm CO_2$ -eqv). For example 1 kg $\rm N_2O$ corresponds to 296 kg $\rm CO_2$ -eqv, as $\rm N_2O$ has a 296 times stronger effect on the climate than $\rm CO_2$. The resulting figure is called "carbon footprint".

Different fertilizer types have different carbon footprints. Urea emits less CO_2 during production than ammonium nitrate. Upon spreading, this difference is reversed since urea releases the CO_2 contained in its molecule. Urea also releases more $\mathrm{N}_2\mathrm{O}$

during farming. The life cycle carbon footprint is therefore higher for urea than it is for ammonium nitrate. In addition, volatilization losses of urea and lower N-efficiency need to be compensated by a higher dosage of roughly 15 %, adding up to the carbon footprint.

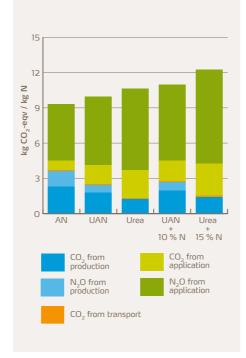


FIGURE 19: The life cycle carbon footprint for ammonium nitrate is lower than for urea and UAN. When conpensating the lower efficiency of urea and UAN by higher dosage, the difference is even more marked. [ref. 16]

Controlling leaching

Elevated nitrate concentrations in ground and surface water are undesirable. The EU Nitrates Directive of 1991 has set the tolerable limit to 50 mg/l. Nitrate leaching is independent from the source of nitrogen. It can be caused by mineral fertilizers, organic manure or even soil organic matter.

Nitrate leaching occurs when the soil is saturated with water and nitrate is washed beyond the root zone by percolating rainfall or irrigation. Nitrate is not bound to soil particles and remains in the soil solution, where it moves freely with the soil water. Ammonium is mainly bound to clay particles in the soil and thus less prone to leaching. Urea is rapidly transformed into ammonium and nitrate through hydrolysis. In addition, the urea molecule is very mobile and can be washed directly to the subsoil by heavy rainfall upon application.

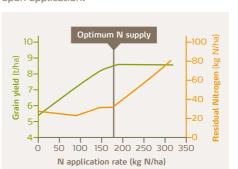


FIGURE 20: The residual nitrogen in the soil after harvesting, and thus the risk of leaching, is not increasing for application rates below optimum N supply. [ref. 17]

Most loss of nitrate to water occurs during winter. The overall objective is therefore to minimize soil nitrate concentrations at the end of the vegetation period. For winter cereals, nitrogen application up to the economic optimum rate does not significantly increase soil nitrate concentration after harvest. The optimum nitrogen application rate also minimizes residual nitrogen.

Leaching can be avoided by best agricultural practices:

- Determine soil nitrogen contents by frequent sampling and analysis
- Split nitrogen applications to assure rapid take-up by plants
- Use fertilizers with a quick, predictable nitrogen release such as ammonium nitrate
- Whenever possible, adjust nitrogen application to real needs by use of precision farming tools
- Allow for a deep and extensive root system as to utilize nitrogen more efficiently
- Keep a porous soil structure
- Absorb residual nitrogen by catch and cover crops
- Ensure balanced nutrition such that available nitrogen can be taken-up

Assessing overall environmental performance

The different environmental effects of fertilizer production and application (land use, eutrophication of land and water, global warming and acidification) can be aggregated into the so-called environmental index EcoX. The index measures the environmental burden based on a life cycle analysis. All burdens are then compared to European targets, weighted and added. The higher the resulting figure, the higher the environmental burden. Ammonium nitrate offers the lowest environmental index.

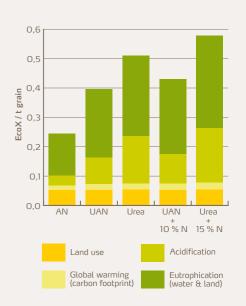


FIGURE 21: Environmental index EcoX for an average of 15 field trials in the UK with winter wheat at a rate of 160 kg N/ha. The EcoX of Urea is almost two times higher than that of ammonium nitrate. [ref. 18]



Knowledge grows

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About Yara

Yara International ASA is an international company headquartered in Oslo, Norway. Yara specializes in plant nutrition as well as products for environmental and industrial applications. As the world's largest supplier of mineral fertilizers for more than a century, we help to provide food and renewable energy for a growing world population.

With our long experience and deep knowledge in the production and application of plant nutrients, we believe that mineral fertilizers play an essential role in environmentally and economically sustainable agriculture.

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