

Knowledge grows

# Nitrate Based Fertilizers

Optimizing yield, preserving the environment.



### Contents

Feeding the world, protecting nature	2
Farming tomorrow	2
Mineral Sources of nitrogen	3
Nitrogen - a source of life	3
Mineral fertilizers	3
Nitrogen transformations in the soil	4
Nitrogen from nitrate	5
Nitrogen from ammonium	5
Nitrogen from urea	5
Ensuring optimum yield	6
Optimizing yield and quality	6
Enhacing fertilizer efficiency	6
Reducing soil acidifcation	7
Preserving the Environment	8
Optimizing fertilizer production	9
Improving fertilizer application	9
Mitigating climate change	10
Controlling leaching	11
Assessing overall environmental performance	12
References	13





### Pure Performance

This brochure summarizes some of the essential aspects of the agronomic and environmental impact of nitrogen fertilizer choices.

Mineral nitrogen fertilizers, depending on their chemical composition, have distinct impacts on yield and environment. For many years now, European farmers have been aware that nitrate-based fertilizers are the most efficient and most reliable nitrogen source available. In addition, these products have a significantly lower environmental impact than urea-based products (urea, UAN) through better control of leaching, lower volatilization and a lower life cycle carbon footprint.

Nitrate-based fertilizer - such as ammonium nitrate, calcium nitrate

and nitrate based water soluble NPK - are pure nutrients, offering the required precision, efficiency and reliability to meet the agronomic and environmental imperatives of modern agriculture.

Nitrate-based fertilizers are the natural choice for farmers who care for both, yield and the environment.

©Yara | 1

Parameter	Observations
Efficiency	Nitrate moves more freely in the soil solution than ammonium, making it easier to get into the roots.
Yield	5 – 8 % higher yield with ammonium nitrate*
Quality	Better quality, with less BER and less disease
Reliability	High reliability of ammonium nitrate and calcium nitrate on the losses and plant uptake
Acidification	Less acidification compare to urea "
Volatilization	No lost as ammonia gas in moist alkaline soils
Leaching	Better control of leaching with ammonium nitrate due to faster plant uptake and lower dosage
Carbon footprint	12,5 % lower life cycle carbon footprint of ammonium nitrate compared to urea $^{st}$
Environmental index	46,6 % lower environmental index of ammonium nitrate compared to urea*



### 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]





### Mineral Sources of Nitrogen

European farmers traditionally rely on nitrate form (Ammonium nitrate and calcium 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:

- Ammonium nitrate (AN) contains nitrogen as NH<sub>4</sub><sup>+</sup> (ammonium) and as NO<sub>3</sub><sup>-</sup> (nitrate) in equal portions. Calcium ammonium nitrate (CAN) contains in addition dolomite or limestone.
- Urea contains nitrogen in its amide (NH<sub>2</sub>) form.
- Urea ammonium nitrate (UAN) is an aqueous solution of urea and ammonium nitrate.
- Ammonium sulfate contains nitrogen as NH<sub>4</sub><sup>+</sup> (ammonium) 100%.

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

PRODUCT	NITROGEN CONTENT					
	Nitrate-N (NO <sub>3</sub> -) <	Nitrification	Ammonium-N (NH4 <sup>+</sup> )	Hydroly	/sis Amide-N (NH <sub>2</sub> )	
Calcium nitrate	100%					
Ammonium nitrate	50%		50%			
UAN	25%		25%		50%	
Urea					100%	
Ammonium sulfate			100%			

Table 1: Common forms of mineral fertilizer 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.

- 1 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 CO<sub>2</sub> 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 incorporated.
- (9) 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 <sub>2</sub>	carbon dioxide (gas)
CO(NH <sub>2</sub> ) <sub>2</sub>	urea
NH <sub>3</sub>	ammonia (gas)
$NH_4^+$	ammonium
NO <sub>3</sub> -	nitrate
NO <sub>2</sub> -	nitrite
NO	nitric oxide (gas)
N <sub>2</sub> O	Nitrous oxide (gas)
N <sub>2</sub>	nitrogen (gas)



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.



#### Nitrogen from nitrate

Nitrate (NO<sub>3</sub><sup>-</sup>) is easily absorbed by plants at high rates. Unlike urea or ammonium, it isimmediately available as a nutrient. Nitrate is highly mobile in the soil and reaches the plant roots quickly. Applying nitrogen as ammonium nitrate or calcium 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  $(NH_4^+)$  is directly absorbed by plants at low rates. The positively charged ion fixes to soil minerals and is less mobile than nitrate  $(NO_3^-)$ . 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 shortterm alkalinization in the immediate vicinity of the urea grain applied. It shifts the natural balance between  $NH_4^+$  and  $NH_3$  to the latter form, resulting in volatilization losses. These losses are the main reason for the lower N-efficiency observed with urea.

After urea converted into ammonium, 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  $NH_3$  rather than  $NH_4$  formation and susequent volatilization and acidification.

	рН 4	Impact of N Form on pH in the rhizosphere - vizualised with a pH indicator
	рН 5	Ammonium acidifies the
<b>ANNI Ö</b>	рН 6	rhizosphere, where the crop is most sensitive to acidify, while nitrate increases rhizosphere oH.
	рН 7	F

### **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 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 these 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.

#### 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.

Fertigation with split application is considered best agricultural practice under most conditions. Fertilizers offering a predictable release of plantavailable nitrogen are best suited for split application. This is the case for ammonium nitrate and calcium 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<sup>™</sup> is a tool to measure plant nitrogen needs on spot and adjust fertilizer nitrogen applications correspondingly.

## Fertigation: Matching the fertilizer application with plant needs

This provides:

- Ĥigher efficiency of applied fertilizers;
- Allow to reduce the applied quantity traditionally



#### 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 nitrate, leading to further savings in cost and time for lime application.

With nitrate form you avoid the soil acidification:



Nitrate is immediately available:

- No lock up by soil microbes or fixation to soil particles.
- Quick yield response
- Enhanced stress-tolerance with nitrate nutrition

Nitrate is non-toxic to plant cells.

 Nitrates can be stored in cells, whereas ammonium/ammonia can not accumulate and require energy for detoxification

Figure 7: The lime demand of (calcium) ammonium nitrate is significantly lower than for urea. [ref. 9]





Figure 8: The Yara N-Tester is a handheld tool that provides immediate information on actual nitrogen need.

### Preserving the Environment

Ammonium nitrate and calcium 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 N<sub>2</sub>O, a powerful greenhouse gas.

Yara has developed proprietary catalyst technology to abate most of the  $N_2O$  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  $CO_2$ -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.

## 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.



Figure 11: Energy consumption of European fertilizer production plants has decreased over time and is today near the theoretical optimum. [ref. 10]







## 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<sub>2</sub> 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  $CO_2$ - equivalents ( $CO_2$ -eqv). For example 1 kg  $N_2O$  corresponds to 296 kg  $CO_2$ -eqv, as  $N_2O$  has a 296 times stronger effect on the climate than  $CO_2$ . The resulting figure is called "carbon footprint".

Different fertilizer types have different carbon footprints. Urea emits less CO<sub>2</sub> during production than ammonium nitrate. Upon spreading, this difference is reversed since urea releases the CO<sub>2</sub> contained in its molecule. Urea also releases more  $N_2O$  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.





#### 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 13: 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. 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 and calcium 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 with good irrigation management
- 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 14: 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]





### References

#### Literature

[ref. 1] Food and Agriculture Organization of the United Nations (2003): World Agriculture towards 2015/2030.

[ref. 2] Von Witzke H., Noleppa, S. (2010): EU agricultural production and trade: can more efficiency prevent

increasing 'land-grabbing' outside of Europe? Humboldt Universität zu Berlin.

[ref. 3] Adapted from Kaarstad, O. (1997): Fertilizer's significance for cereal production and cereal yields from 1950 to 1995. In: International symposium on fertilization and the environment (Mortwedt, J. and Shaviv, A.; Eds.). Haifa, Israel, April 1997.

[ref. 4] Lesouder C., Taureau J. (1997): Fertilisation azotée, formes et modes d'actions. Perspectives Agricoles N° 221.

[ref. 5] Yara International, Research Centre Hanninghof, Germany

[ref. 6] Dampney P., Dyer C., Goodlass G., Chambers B. (2006): Component report for DEFRA project NT2605/

WP1a. Crop Responses.

[ref. 7] Agricon: www.agricon.de/produkte/yara-n-sensor/sensorvergleich

[ref. 8] Stamm R. (2006): Streufehler bei Seitenwind. DLZ Agrarmagazin 10:2006

[ref. 9] Sluijsmans C.M.J. (1970): Influence of fertilizer upon liming status of the soil. J. Plant Nutr. Soil Sci., 126.

[ref. 10] Adapted from Anundskas, A. (2000): Technical improvements in mineral nitrogen fertilizer production. In: Harvesting energy with fertilizers. European Fertilizer Manufacturers Association.

[ref. 11] Pachauri R., Reisinger A. (2007): Climate Change 2007. Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. IPCC, Geneva, Switzerland. [ref. 12] European Fertilizer Manufacturers Association (EFMA), Annual Report 2008, Industry Benchmarks.

[ref. 13] Dampney P., Chadwick D., Smith K., Bhogal A. (2004): Report for DEFRA project NT2603. The behaviour of some different fertiliser-N materials.

[ref. 14] Chadwick D., Misselbrook T., Gilhespy S., Williams J., Bhogal A., Sagoo L., Nicholson F., Webb J., Anthony S., Chambers B. (2005): Component report for Defra project NT2605/WP1b. Ammonia Emissions and crop N use efficiency. [ref. 15] EMEP/CORINAIR Technical Report No. 16/2007

[ref. 16] Adapted from Brentrup, F. (2010). Yara International, Research Centre Hanninghof, Germany.

[ref. 17] Baumgärtel G., Engels T., Kuhlmann H. (1989): Wie kann man die ordnungsgemäße N-Düngung überprüfen? DLG-Mitteilungen 9, 472-474.

[ref. 18] Adapted from: Brentrup F., Küsters J., Lammel J., Barraclough P., Kuhlmann H. (2004): Environmental impact assessment of agricultural production systems using the life cycle assessment (LCA) methodology II.

The application to N fertilizer use in winter wheat production systems. Europ. J. Agronomy 20, 265-279.

This will need changing to reflect the revised figures

For further information contact: Yara International ASA Postboks 343, Skøyen O213 Oslo Norway www.yara.com

© 2015 Yara. All rights reserved. Yara International April 2015

#### About Yara

Yara's knowledge, products and solutions grow farmers and industrial customers' businesses profitably and responsibly, while nurturing and protecting the earth's resources, food and environment.

Our fertilizers, crop nutrition programs and technologies increase yields, improve produce quality, and reduce environmental impact from agricultural practices. Our industrial and environmental solutions reduce emissions and improve air quality from industry and transportation, and serve as key ingredients in the production of a wide range of goods.

Founded in 1905 to solve emerging famine in Europe, Yara today has a global presence with more than 12,000 employees and sales to more than 150 countries. www.yara.com

