International
Fertilizer Industry
Association

Slow- and Controlled-Release and Stabilized Fertilizers

An Option for Enhancing Nutrient Use Efficiency in Agriculture

M.E. Trenkel

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About the book and the author

About the book

This book is a revision of the IFA publication “Improving Fertilizer Use Efficiency: Controlled-Release and Stabilized Fertilizers in Agriculture” by the same author, published in 1997. It is intended for use by the fertilizer industry, policy makers and scientists. The main objectives of the book are to:

- Provide an up-to-date state of scientific knowledge on issues related to the development, production and use of slow- and controlled-release and stabilized fertilizers;
- Explain the importance of slow- and controlled-release and stabilized fertilizers to improve nutrient use efficiency;
- Present slow- and controlled-release and stabilized fertilizer products that are currently available;
- Assess the current market and prospects for slow- and controlled-release and stabilized fertilizers; and
- Discuss the policy and regulatory frameworks needed to maximize the benefits from using slow- and controlled-release and stabilized fertilizers.

This book is a contribution to IFA’s efforts to promote nutrient stewardship through the use of the right product(s) at the right rate, right time and right place (IFA, 2009).

About the author

Martin Trenkel is a German scientist. He is an accredited Agricultural Engineer from the Christian-Albrechts-University in Kiel, Germany, with plant nutrition and soil science as top subjects. He also holds a PhD degree in agriculture from the same University.

Martin Trenkel joined BASF Aktiengesellschaft in 1955 as an agricultural adviser overseas. He travelled extensively consulting and lecturing in the Middle East, Latin America, Africa, Europe and the Far East. From 1962 to 1968, he was based in Uruguay for the BASF Agricultural Division, coordinating BASF’s agricultural services in Latin America (fertilizers and plant protection). He retired in 1991, as the Director Fertilizer Product Management, in the Fertilizer Division of BASF.

Martin Trenkel has also served as:

- Chairman of the Technical Sub-Committee of the FAO/Fertilizer Industry Advisory Committee (FIAC) in Rome;
- Chairman of the FIAC 'Ad-hoc Working Party on Fertilizer Marketing and Credit' in Rome;

- Chairman of the Technical Committee of the Centre d'Etude de L'Azote in Zürich;
- Vice-Chairman of the Agricultural Committee of the International Fertilizer Industry Association (IFA) in Paris.

He has authored and co-authored several publications.

Since 1991, Martin Trenkel has been a consultant for the Food and Agriculture Organization of the United Nations (FAO), the European Fertilizer Manufacturers Association (EFMA) and the German Foundation for International Development (DSE), among others.

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Abbreviations, acronyms and symbols

(as used in the book)

Abbreviations

AI	Activity index
AM	2-Amino-4-chloro-6-methyl-pyramidine
AS	Ammonium sulphate
ASN	Ammonium sulphate nitrate
ATP	Adenosintriphosphate
ATS	Ammonium thiosulphate
BMP	Best management practice
CAN	Calcium ammonium nitrate
CDU	Cyclo diurea (condensation product of urea and acetaldehyde)
CEC	Cation exchange capacity
CLMP	4-chloro-3-methylpyrazole
CMP	1-carbamoyle-3-methylpyrazole
CRF	Controlled-release fertilizer
CRN	Controlled-release nitrogen
CRU	Controlled-release urea
CWI	Cold water insoluble
CWS	Cold water soluble
DAT	Days after transplanting
DCD	Dicyandiamide
DMPP	3,4-dimethylpyrazole phosphate
DMTU	Dimethylene triurea
ED	Efficiency design
ESN	‘Environmentally smart nitrogen’
EVA	Ethylene vinyl acetate
FBMP	Fertilizer best management practice
GHG	Greenhouse gas
HQ	Hydroquinone
HWI	Hot water insoluble
HWS	Hot water soluble
IBDU	Isobutylidene diurea
MDU	Methylene diurea
3-MP	3-methyl pyrazole
NBPT	N-(n-butyl) thiophosphoric triamide
NICU	Neem/Nimin-extract-coated urea

NK	Nitrogen-potassium
NP	Nitrogen-phosphorus
NPK	Nitrogen-phosphorus-potassium
2-NPT	N-(2-nitrophenyl) phosphoric acid triamide
NUE	Nutrient use efficiency
PAPR	Partially acidulated phosphate rock
PCF	Polymer- or resin-coated fertilizer
PCU	Polymer- or resin-coated urea
PE	Polyethylene
POCU	Polyolefin-coated urea
PPD/PPDA	Phenylphosphodiamidate
PSCF	Polymer-coated sulphur-coated fertilizer
PSCU	Polymer-coated sulphur-coated urea
SCF	Sulphur-coated fertilizer
SCU	Sulphur-coated urea
SNF	Stabilized nitrogen fertilizer
SRF	Slow-release fertilizer
TZ	1H-1,2,4-triazole
UAN	Urea ammonium nitrate (solution)
UF	Urea-formaldehyde

Acronyms

AAPFCO	Association of American Plant Food Control Officials
CEN	Comité Européen de Normalisation (European Standardization Committee)
EPA	Environmental Protection Agency (United States)
EU	European Union
FAO	Food and Agriculture Organization of the United Nations
IFA	International Fertilizer Industry Association
IFDC	International Fertilizer Development Centre
IPI	International Potash Institute
IRRI	International Rice Research Institute
JMAFF	Japanese Ministry of Agriculture, Forestry and Fishery
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RECRA	Resource Conservation and Recovery Act
TVA	Tennessee Valley Authority

Symbols

Al	Aluminium
B	Boron
C	Carbon
Ca	Calcium
$CaCO_3$	Calcium carbonate
$CaSO_4$	Calcium sulphate
CH_4	Methane
Cl	Chlorine
Cu	Copper
Fe	Iron
H^+	Proton
HCO_3	Bicarbonate
H_2O	Water
K	Potassium
KCl	Potassium chloride (also muriate of potash or MOP)
K_2O	Potash
K_2SO_4	Potassium sulphate (also sulphate of potash or SOP)
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
N	Nitrogen
NH_3	Ammonia
NH_4^+	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate
N_2	Dinitrogen
NO_X	Nitrogen oxides
N_2O	Nitrous oxide
O_2	Dioxygen
P	Phosphorous
S	Sulphur
SO_4^{2-}	Sulphate
Zn	Zinc

Introduction

The fertilizer industry faces a continuing challenge to improve its products to increase the efficiency of their use, particularly of nitrogenous fertilizers, and to minimize any possible adverse environmental impact. This is done either through improvement of fertilizers already in use, or through development of new specific fertilizer types (Maene, 1995; Trenkel *et al.*, 1988).

Improvement of fertilizers already in use is done through appropriate product design (Bröckel and Hahn, 2004). The product profile is determined by its chemical and physical properties, environmental safety and its stability against mechanical stress, hygrometry and temperature. With solid fertilizers new product design is mostly aimed at improving handling properties (reduction of dust formation and caking/hygroscopicity).

Increasing the efficiency of mineral nitrogen (N) fertilizers[1] use is not easy, because plants take up N normally as nitrate or ammonium ions, through their roots from the soil solution. However, ammonium-N, unlike nitrate-N[2], can be retained on soil constituents so that soil and plants compete for ammonium-N, either already available in the soil or applied (Amberger, 1996). This competition for nitrogen, with the exception of nitrate-N is the main problem when it is added as mineral fertilizer to feed plants. Only a certain proportion of the N is taken up, or can be taken up, and used by the growing plants.

Nitrogen use efficiency terms and calculations (IFA, 2007)

Partial factor productivity (kg product/kg N applied): crop yield per unit N applied.

Agronomic efficiency (kg product increase/kg N applied): crop yield increase per unit N applied.

Recovery efficiency ((fertilized crop N uptake – unfertilized crop N uptake)/N applied): increase in N uptake by the crop per unit N added, usually for the first crop following application and usually expressed as a percentage or fraction.

Removal efficiency (crop N removal/N applied): N removed by the harvested portion of the crop per unit N applied, usually expressed as a percentage or fraction.

Physiological efficiency (kg product increase/kg increase in fertilizer N taken up): crop yield increase per unit fertilizer N taken up.

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[1] *Globally, most N is applied as urea, which, chemically, is not a mineral but an organic compound. FAO, however, lists it traditionally as a '**mineral fertilizer**' in its publications and particularly its statistics. The FAO terminology is used here.*

[2] *Nitrate-N is not adsorbed on soil particles but is free in the soil solution and therefore available for plant uptake but also liable to leaching. Only vulcanic soils, e.g. trumao-soils, have a high adsorption-power for anions, including nitrate (Amberger, 2008b).*

Under practical conditions, nutrient use efficiency (NUE) can be considered as the amount of nutrients taken up from the soil by plants and crops within a certain period of time compared with the amount of nutrients available from the soil or applied during that same period of time. Improving NUE in agriculture has been a concern for decades (Dobermann, 2005), and numerous new technologies have been developed in recent years to achieve this. The types of fertilizers and their management in agriculture will be at the forefront of measures to improve the global N balance in the short- and long-term. The most important task for the future is to further improve NUE or, more precisely, N-use efficiency (Grant, 2005), because a significant share of the added fertilizer N is lost during the year of application. Finck (1992) gives the following indications of nutrient uptake from mineral fertilizers:

- The utilization rate of N in mineral fertilizers is about 50-60% in the first year.
- The utilization rate of P in mineral fertilizers is 10-25% (average 15%) in the first year. A further 1-2% per year will be taken up in the following decades.
- The utilization rate of K in mineral fertilizers is about 50-60% in the first year.

Because a considerable proportion of applied fertilizer-N is lost during the year of application, N application and crop management must be fine-tuned in order to maximize system-level NUE. However, it will require policies that favour increases in NUE at the field scale with emphasis on technologies that can achieve greater congruence between crop demand and N supply from all sources – including fertilizers, organic inputs, and indigenous soil N (Cassman *et al.*, 2002; Dobermann, 2005).

Farming practices, particularly fertilizer application methods must aim to support the crops in the competing soil-plant system, thereby, achieving the greatest possible nutrient uptake/use efficiency. This support includes:

- Promoting root growth by improving soil structure (good soil aeration, storage and supply of water), soil reaction (liming), humus content, storage capacity for soluble nutrients and mobility of nutrients (Amberger, 1996, 2006; Finck, 1992).
- Using soil and plant analyses for nutrients and constantly monitoring crop growth and development (Sturm *et al.*, 1994).
- Applying amounts of nutrients that correspond as precisely as possible to crop needs and growing conditions. This can be achieved by choosing the most suitable type and rate of plant nutrient/mineral fertilizer and the most appropriate application technique (for example fertilizer placement or band application into the root zone, split application, and so-called 'spoon-feeding').
- Taking measures to reduce possible losses of nutrients to the environment (Shaviv, 1993). Immobilization, denitrification, ammonia volatilization and leaching may occur especially with N.
- The fertilizer industry has been challenged to develop special types of fertilizers that avoid, or at least reduce, such losses (Joly, 1993). These special fertilizer types can be listed as:
    - Foliar fertilizers;
    - Slow- and controlled-release (coated/encapsulated) fertilizers with the release of nutrients over several months;

- Stabilized fertilizers (fertilizers associated with nitrification or urease inhibitors) delaying either the nitrification of ammonia or the ammonification of urea.

Nutrient use efficiency could be improved considerably through the use of foliar sprays, because any immobilization in or leaching from soil is avoided. However, with foliar sprays several applications are necessary because only limited amounts of nutrients can be applied at any one time because of leaf scorch and concentration problems. In practice, this makes it impossible to economically apply all the necessary nutrients via plant leaves (Amberger, 1996).

Another possible route of improving nutrient use efficiency is the use of so-called 'intelligent mineral fertilizers', particularly N fertilizers, which release the nutrients contained according to the plant's requirements, i.e. by application of slow- and controlled-release, or 'stabilized' N fertilizers, which 'hold' the nutrients until plants actually require them.

Shoji and Gandeza (1992) consider that an ideal fertilizer should have as a minimum the following three characteristics:

- A single application should supply enough nutrient throughout the entire growing season to meet plant demand for optimum growth;
- A maximum percentage recovery to achieve the largest return for the cost of the input; and
- Minimum detrimental effects on the soil, water and atmospheric environment.

Slow-, and particularly controlled-release and 'stabilized' fertilizers meet, to a significant extent, these requirements for an ideal fertilizer. Polyolefin-coated urea (POCU) for rice with sigmoidal release (first produced by Chissoasahi) has enabled a single basal application and co-situs placement (Fujita and Shoji, 1999; Shoji and Takahashi, 1999).

Though slow- and controlled-release and stabilized fertilizers can contribute to improved NUE and minimize negative environmental effects it must be remembered that errors in field and crop management cannot be compensated for by the use of these special fertilizer types. They should always be part of 'good agricultural or best management practices (BMPs)'.

1. Definitions of slow- and controlled-release fertilizers and nitrification and urease inhibitors

The Association of American Plant Food Control Officials (AAPFCO) has published the following general definitions (Official Publication 57):

- **Slow- or controlled-release fertilizer**: A fertilizer containing a plant nutrient in a form which delays its availability for plant uptake and use after application, or which extends its availability to the plant significantly longer than a reference 'rapidly available nutrient fertilizer' such as ammonium nitrate or urea, ammonium phosphate or potassium chloride. Such delay of initial availability or extended time of continued availability may occur by a variety of mechanisms. These include controlled water solubility of the material by semi-permeable coatings, occlusion, protein materials, or other chemical forms, by slow hydrolysis of water-soluble low molecular weight compounds, or by other unknown means.
- **Stabilized nitrogen fertilizer:** A fertilizer to which a nitrogen stabilizer has been added. A nitrogen stabilizer is a substance added to a fertilizer which extends the time the nitrogen component of the fertilizer remains in the soil in the urea-N or ammoniacal-N form.
- **Nitrification inhibitor:** A substance that inhibits the biological oxidation of ammoniacal-N to nitrate-N.
- **Urease inhibitor:** A substance that inhibits hydrolytic action on urea by the enzyme urease.

1.1. Slow- and controlled-release fertilizers

According to AAPFCO (1997): There is no official differentiation between slow-release and controlled-release fertilizers.

According to Shaviv (2005): "The term controlled-release fertilizer (CRF) became acceptable when applied to fertilizers in which the factors dominating the rate, pattern and duration of release are well known and controllable during CRF preparation." Slow-release fertilizers (SRFs) involve the release of the nutrient at a slower rate than is usual but the rate, pattern and duration of release are not well controlled. Trenkel (1997) noted that it became common practice to denote microbially decomposable nitrogen products, such as urea-formaldehyde, as 'SRFs'.

Shaviv (2005) proposed the following classification of slow- and controlled-release fertilizers:

- **Organic-N low-solubility compounds.** These can be further divided into biologically decomposing compounds usually based on urea-aldehyde condensation products, such as urea-formaldehyde (UF), and chemically (mainly) decomposing compounds, such as isobutylidene-diurea (IBDU).

- **Fertilizers in which a physical barrier controls the release.** The fertilizer can be as tablets or granules coated by hydrophobic polymers or as matrices in which the soluble active material is dispersed in a continuum that restricts the dissolution of the fertilizer. The coated fertilizers can be further divided into fertilizers with organic polymer-coatings - that are either thermoplastic or resins - and fertilizers coated with inorganic materials such as sulphur or mineral-based coatings.

  The materials used for preparation of matrices can also be subdivided into hydrophobic materials such as polyolefines, rubber, etc., and gel-forming polymers (sometimes called 'hydrogels'), which are hydrophilic in nature and reduce the dissolution of the soluble fertilizer due to their high water retention (swelling). In general, the use of matrices is less common in practice than the use of coated fertilizers. Gel-based matrices are still being developed (Shavit *et al.*, 1995).
- **Inorganic low-solubility compounds.** Fertilizers such as metal ammonium phosphates (e.g. magnesium ammonium phosphate ($MgNH_4PO_4$)), and partially acidulated phosphate rock (PAPR), are typical of this type of SRFs. The biologically and microbially decomposed N products, such as UF, are commonly referred to in the trade as slow-release fertilizers and coated or encapsulated/occluded products as controlled-release fertilizers. Definitions are also discussed by Zhang *et al.* (2005).

In practice, the main difference between the two types of fertilizer is that for slow-release fertilizers the nutrient release pattern is fully dependent on soil and climatic conditions and it cannot be predicted (or *only v*ery roughly). With controlled-release fertilizers, the release pattern, quantity and time can be predicted within certain limits.

The classification of 'sulphur-coated urea (SCU)' is subject to debate. The release pattern can differ considerably between different batches of fertilizer depending on the percentage of granules with damaged coatings. If the coatings are badly damaged (sometimes denoted as 'burst') the nutrients may be released immediately after contact with water in the soil (Goertz, 1995; Shaviv, 2005). Consequently, SCU should be classified as a 'slow-release fertilizer'.

The European Standardization Committee (CEN) Task Force on Slow-Release Fertilizers made the following proposals (Kloth, 1996):

- **Release**: The transformation of a chemical substance into a plant-available form (e.g. dissolution, hydrolysis, degradation, etc.);
- **Slow-release**: The release rate of a nutrient from the fertilizer must be slower than that from a fertilizer in which the nutrient is readily available for plant uptake. For example, for a slow-release nitrogen fertilizer, the release rate/plant response must be less than that from an application of urea, or ammonium or nitrate solution;
- **Declaration**: A fertilizer may be described as slow-release if the nutrient or nutrients declared as slow-release meet, under defined conditions – including at a temperature of 25°C – each of the following three criteria:
  - no more than 15% released in 24 hours,
  - no more than 75% released in 28 days,
  - at least about 75% released at the stated release time.

1.2. Nitrification inhibitors

Nitrification inhibitors delay the bacterial oxidation of the ammonium ion (NH_4^+) by depressing over a certain period of time (four to ten weeks) the activity of *Nitrosomonas* bacteria in the soil. These bacteria transform ammonium ions into nitrite (NO_2^-), which is further transformed into nitrate (NO_3^-) by *Nitrobacter* and *Nitrosolobus* bacteria. The objective of using nitrification inhibitors is to control the loss of nitrate by leaching or the production of nitrous oxide (N_2O) by denitrification from the topsoil by keeping N in the ammonium form longer and thus increasing N-use efficiency. Furthermore, nitrification inhibitors – by delaying the conversion of ammonium to nitrate – avoid undesirable high nitrate levels in plants used for human and animal nutrition. Inhibiting nitrification, however, will not prevent mineral N from entering water bodies by direct N application of fertilizers and by runoff (Edmeades, 2004).

There is some confusion concerning the terms nitrogen stabilizers, nitrification inhibitors, urease inhibitors and stabilized fertilizers. The terms nitrogen stabilizers and nitrification inhibitors have been used interchangeably. Strictly speaking stabilized fertilizers are only those to which a nitrogen stabilizer has been added during production (nitrification inhibitor and/or urease inhibitor = substances which when added to the fertilizer extend the time that the nitrogen component of the fertilizer remains in the soil in the urea or ammoniacal form). According to AAFPCO (1994), stabilized nitrogen fertilizers are fertilizers to which a nitrogen stabilizer has been added.

1.3. Urease inhibitors

Urease inhibitors prevent or suppress over a certain period of time the transformation of amide-N in urea to ammonium hydroxide and ammonium through the hydrolytic action of the enzyme urease. By slowing down the rate at which urea is hydrolyzed in the soil, volatilization losses of ammonia to the air (as well as further leaching losses of nitrate) is either reduced or avoided. Thus, the efficiency of urea and of N fertilizers containing urea (e.g. urea ammonium nitrate solution), is increased and any adverse environmental impact from their use is decreased.

Though nitrification and urease inhibitors are recognized as nitrogen stabilizers (AAPFCO), nitrification inhibitors in some publications are designated as slow- or controlled-release fertilizers. Because all plants are able to take up ammonium as well as nitrate this designation is incorrect (see also section 4.2).

2. Development and manufacture of slow- and controlled-release fertilizers and nitrification and urease inhibitors

2.1. Slow- and controlled-release fertilizers

Slowing the release of plant nutrients from fertilizers can be achieved by different methods and the resulting products are known as slow- or controlled-release fertilizers. With controlled-release fertilizers, the principal method is to cover a conventional soluble fertilizer with a protective coating (encapsulation) of a water-insoluble, semi-permeable or impermeable-with-pores material. This controls water penetration and thus the rate of dissolution, and ideally synchronizes nutrient release with the plants' needs.

The most important manufactured materials are:

- Materials releasing nutrients through either microbial decomposition of low solubility compounds with a complex/high molecular weight chemical structure, e.g. organic-N low-solubility compounds, such as urea-aldehyde condensation products (e.g. urea-formaldehyde – UF), or chemically decomposable compounds (e.g. isobutyledene-diurea – IBDU) (Shaviv, 2005).
- Materials releasing nutrients through a physical barrier, e.g. fertilizers coated with inorganic materials such as sulphur or mineral-based coatings and fertilizers coated with an organic polymer.
- Materials releasing nutrients incorporated into a matrix, which itself may be coated, including gel-based matrices, which are still under development (Shavit *et al.*, 1995; Shaviv, 2005). In practice, however, matrices are only used in exceptional cases.
- Materials releasing nutrients in delayed form due to a small surface-to-volume ratio (super-granules, briquettes, tablets, spikes, plant food sticks, etc.).

Other materials classified in a broader sense as slow-release fertilizers, are not discussed here. They include:

- organic substances, e.g. crop residues, manure, slurry, composts, heat-dried or sun-dried sewage sludge (biosolids), etc.;
- organic or organic-mineral fertilizers, e.g. meat and bone meal, hoof and horn meal, rapeseed meal, treated leather meal, etc.;
- inorganic compounds, metal-ammonium phosphates (struvites, e.g. magnesium ammonium phosphates ($MgNH_4PO_4$)), and partially acidulated phosphate rock (PAPR).

An introduction into the production principles, classification and conceptual models of nutrient release from coated fertilizers is given by Shaviv *et al.* (2003a, 2003b). Effects of coating materials on nutrient release are also discussed by Yang *et al.* (2007). When sulphur-coated urea (SCU) is coated with a polymer, the initial release rate of the N from the polymer-sulphur-coated urea (PSCU) can be reduced and the duration of nutrient release prolonged.

An excellent introduction and overview of the principles and innovation of coated/controlled-release fertilizers is given by Fujita and Shoji (1999) with reference to Meister®, the controlled-release fertilizer of Chissoasahi Fertilizer Co., which has the same history of development as Nutricote®.

A compilation of the various complicated technical coating processes (patents) is given by Goertz (1993) in '*The O.M. Scott and Sons Company*'. Further details on manufacturing processes mainly used in Japan are given by Shoji and Gandeza (1992); Fujita *et al.* (1977*)*, and on the Reactive Layers Coating (RLC™) process[3] by Pursell (1995). Models of controlled-release fertilizers developed in Israel are described by Lupu (1996), Reiss (1996) and Shavit *et al.* (1994).

The much more complex manufacturing processes and high-cost coating materials for exclusively polymer-coated fertilizers as compared to conventional fertilizers are reflected in significantly higher product costs. This has also favoured the production of polymer-coated, sulphur-coated urea/fertilizers (PCSCU/PCSCF) which, since 2000, have become the largest group of slow-release or controlled-release fertilizers.

2.2. Nitrification and urease inhibitors

The development of nitrification and urease inhibitors is both very time-consuming and expensive because these products have special characteristics.

- They must not have any unfavourable side effects on soil fertility;
- They should not degrade to toxic substances in the soil;
- They should not be toxic to plants, animals and man;
- They should fit into the complex production systems of the producers to be economically viable and environmentally acceptable;
- They should be stable during production, storage, transport, and use;
- Their cost should be acceptable to farmers;
- In the case of urease inhibitors, they should be compatible with urea and urea-containing fertilizers;
- Finally, the registration process, which is required before these materials can be used in agriculture, will take several years.

Despite these difficulties, thousands of chemical substances have been tested for their nitrification and urease inhibiting efficiency, but only a very few have proved to be of agronomic and environmental relevance.

2.2.1. Nitrification inhibitors

Comprehensive research has been carried out in the development of nitrification inhibitors, and a large number of chemicals have been found to have nitrification

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[3] *Process developed by Pursell Technologies Inc. United States Patent Nos. 4,711,659 – 4,804,403 – 4,969,947 – 5,374,292 and 5,547,486.*

inhibiting properties including several plant protection products (Winley and San Clemente, 1971), e.g. the fungicide Etridiazole (5-ethoxy-3-(trichloromethyl)-1,2,4-thiodiazole) and various natural products in plant residues (Bremner and McCarty, 1993). However, most of these substances have an insufficient period of activity, or are phytotoxic, or have an undesirable impact on the environment. Only a limited number of substances have met the numerous requirements and agronomic, economic and environmental criteria that a nitrification inhibitor has to fulfil to be marketable.

Several N compounds – some of which have very satisfactory nitrification inhibiting characteristics – have not gained practical and commercial importance as nitrification inhibitors (McCarty, 1999; McCarty and Bremner, 1989; Dressel, 1995). The same applies to S compounds, to urea derivatives (Jung and Dressel, 1978) and to acetylene which is difficult to apply even in encapsulated form, and its derivatives.

Table 1. Some patented nitrification inhibitors (adapted from Frye, 2005).

Chemical name	Common name	Developer	Inhibition by day 14 (%)
2-chloro-6-(trichloromethyl-pyridine)	Nitrapyrin	Dow Chemical	82
4-amino-1,2,4-6-triazole-HCl	ATC	Ishihada Industries	78
2,4-diamino-6-trichloro-methyltriazine	CI-1580	American Cyanamid	65
Dicyandiamide	DCD	Showa Denko	53
Thiourea	TU	Nitto Ryuso	41
1-mercapto-1,2,4-triazole	MT	Nippon	32
2-amino-4-chloro-6-methyl-pyramidine	AM	Mitsui Toatsu	31

To the list in Table 1 should be added:

- 3,4-dimethylpyrazole phosphate (DMPP), from BASF
- 1-amide-2-thiourea (ASU), from Nitto Chemical Ind.
- Ammoniumthiosulphate (ATS)
- 1H-1,2,4-triazole (HPLC)
- 5-ethylene oxide-3-trichloro-methly1,2,4-thiodiazole (Terrazole), from Olin Mathieson
- 3-methylpyrazole (3-MP)
- 1-carbamoyle-3-methyl-pyrazole (CMP)
- Neem

A comprehensive study listed 64 selected chemical compounds that have been tested as nitrification inhibitors (Subbarao *et al.*, 2006). Recently introduced N stabilizers in the United States are given by Landels (2010a).

Of the producers of nitrification inhibitors worldwide, the following hold production patents at present: BASF (Germany), Dow Agro Sciences (USA) and SKW Piesteritz (Germany).

Table 2. Commonly used nitrification inhibitors in agriculture (Subbarao *et al.*, 2006).

Name (chemical, trademark)	Solubility in water (g/l)	Relative volatility	Mode of application
2-chloro-6-(trichloromethyl) pyridine (Nitrapyrin; N-serve)	0.04 (at 20°C)	High	Suitable with anhydrous ammonia for soil injection
2-amino-4-chloro methyl pyrimidine	1.25 (at 20°C)	High	Coatings on solid nitrogen fertilizers
Dicyandiamide (DCD), cyanoguanidine	23.0 (at 13°C)	Low	Blend with urea or other solid nitrogen fertilizers
DMPP		Low	Blend with urea or other solid nitrogen fertilizers

2.2.2. Urease inhibitors

Thousands of chemicals have been evaluated as soil urease inhibitors (Kiss and Simihaian, 2002). However, only a few of the many compounds tested meet the necessary requirements of being non toxic, effective at low concentration, stable and compatible with urea (solid and solutions), degradable in the soil and inexpensive. They can be classified according to their structures and their assumed interaction with the enzyme urease (Watson, 2000, 2005).

Four main classes of urease inhibitors have been proposed:

- reagents which interact with the sulphydryl groups (sulphydryl reagents),
- hydroxamates,
- agricultural crop protection chemicals, and
- structural analogues of urea and related compounds.

N-(n-Butyl) thiophosphoric triamide (NBPT), phenylphosphorodiamidate (PPD/PPDA), and hydroquinone are probably the most thoroughly studied urease inhibitors (Kiss and Simihaian, 2002). Research and practical testing has also been carried out with N-(2-nitrophenyl) phosphoric acid triamide (2-NPT) and ammonium thiosulphate (ATS). The organo-phosphorus compounds are structural analogues of urea and are some of the most effective inhibitors of urease activity, blocking the active site of the enzyme (Watson, 2005).

Of the producers of urease inhibitors worldwide, the following hold production patents at present: Agrotain International (originally assigned to Freeport McMoRan Resource Partners and IMC-Agrico) and SKW Piesteritz. Further research with a number of compounds resulting from patent applications for new urease inhibitors is mainly conducted in Germany, India and the United States.

3. Characteristics and types of slow- and controlled-release fertilizers and nitrification and urease inhibitors

3.1. Characteristics of slow- and controlled-release fertilizers

In addition to the competition between soil and plant roots for available nutrients in the soil-plant system, there are further complex interactions between plant roots and soil micro-organisms: chemical and physical reactions on and within soil particles and soil conditions conducive to losses of plant nutrients that affect nutrient availability. Most of the transformations that nutrients undergo in the soil/soil solution are concentration-dependent (Shaviv, 2005). Any surplus of plant nutrients in the soil not taken up by plants can undergo three types of processes/reaction that decrease their availability to plants (Shaviv, 2005). These are:

- microbial – e.g. nitrification, denitrification, immobilization;
- chemical – e.g. exchange, fixation, precipitation, hydrolysis;
- physical – e.g. leaching, run-off, volatilization.

Fertilizer best management practices (FBMPs) for the application of plant nutrients should always aim to avoid a surplus of plant-available nutrients in the soil. This will increase nutrient-use efficiency and minimise unfavourable effects on the environment. However, it must be remembered that the root system of most arable crops only explores 20-25% of the available soil volume in any one year. Consequently, the quantity of plant-available nutrients in soil will not only depend on the stage of growth and nutrient demand, but also on the rate of delivery of plant nutrients to the root by mass flow and diffusion.

The application of conventional N fertilizers, especially when applied on only one occasion, results in too large amounts in the early growth stages and too little at later stages. According to Liao *et al.* (2006), proper fertilization seeks to ‘cutting off peak and filling up valley’ in the supply of nutrients. With seasonal crops, the uptake of macronutrients is generally ‘sigmoidal’ (S-shaped) (Shoji and Kanno, 1994).

Matching nutrient demand with availability from fertilizers is shown diagrammatically in Figure 2 (Lammel, 2005). However, when Lammel claims that any excess nutrients should remain in the soil for the next crop, he probably refers to phosphate and, to a lesser extent, potash. With mineral N any surplus remaining in soil at harvest is likely to be lost by leaching and denitrification.

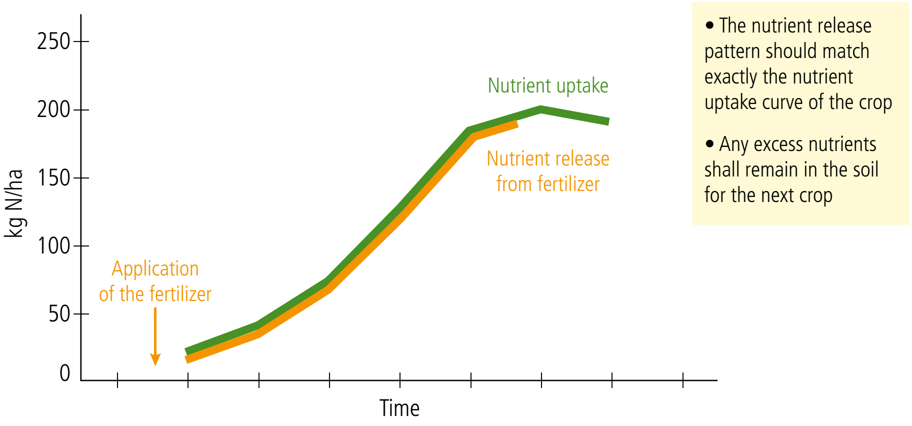

Figure 1. The 'ideal fertilizer': the nutrient release is synchronized with the crop's nutrient requirements (Adapted from Lammel, 2005).

Based on Figure 2, the ideal fertilizer should release nutrients in a sigmoidal pattern for optimal plant nutrition and reduction in nutrient losses by processes that compete with the plant's nutrient requirements. Shaviv (2005) and Shoji and Takahashi(1999) state that a sigmoidal pattern of nutrient supply will provide optimal nutrition for plant growth and reduce losses by processes competing with the plant for nutrients.

Lammel (2005) claims that a sigmoidal pattern of nutrient supply can be obtained by a so-called 'enhanced-efficiency fertilization concept', i.e. applying N fertilizer during plant growth in several split applications (Figure 2).

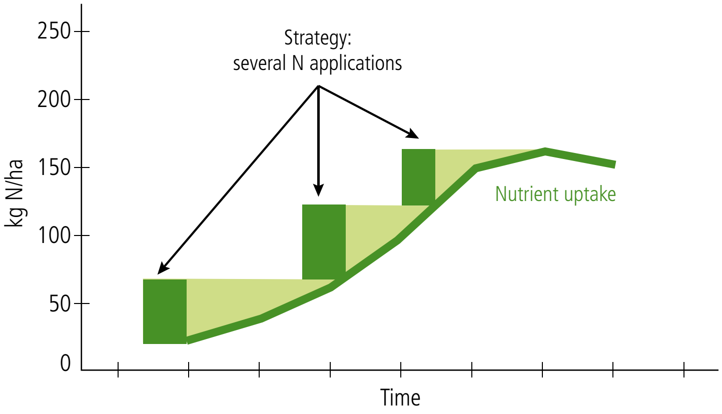

Figure 2. Enhanced-efficiency fertilization concept: fertilizer application in several N dressings (Adapted from Lammel, 2005).

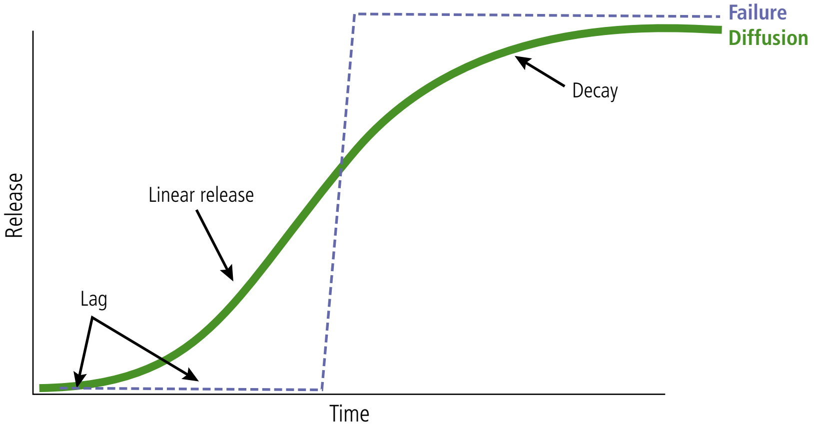

Figure 3. Release from a single coated urea granule: diffusion vs. failure* (Adapted from Shaviv, 2005).
(*) 'Failure' means the complete absence of slow-release.

There is no doubt that, in intensive farming systems (e.g. in European countries), applying the enhanced-efficiency fertilization concept, can lead to very high nutrient/nitrogen use efficiency, thus reducing any negative environmental impact. The cost of applying N in such a way, including plant analysis for precise split application rates, may be comparable or even more profitable than where slow- or controlled-release fertilizers or fertilizers stabilized with urease or nitrification inhibitors are used. However, there are some drawbacks to using a split appication system. It is more labour-intensive, it requires extra applications, with an energy cost, reduces on-farm labour flexibility, is predominantly dependent on weather and field conditions, trafficability in the field may be restricted or impossible, and there is the risk of missing the 'window of opportunity for fertilizer application' (Grant, 2005). Also depending on the type of agriculture, some farmers prefer one application of controlled-release fertilizers instead of several split applications of conventional fertilizers. For example, in Japan Shoji (2005) demonstrates how the development of controlled-release fertilizers led to the innovation of agro-technologies for various field crops including new concepts of fertilizer application.

Drawbacks of split applications (Grant, 2005)

- Multiple applications increase cost, fuel consumption, traffic and labour
    - Economic, environmental and societal effects
- Surface application may be inefficient
    - Volatilization and immobilization
    - Remaining on soil surface
    - Lack of foliar uptake
- In-soil applications may damage crop
- Risk of missing window of application

Synchronization between supply and uptake can, in practice, be met using slow- or preferably controlled-release fertilizers. However, to find the 'optimum' slow- or controlled-release fertilizer, it is necessary to predict the rate of nutrient release. A conceptual model for nutrient release from coated fertilizers is given by Shaviv (2005) and Shoji and Takahashi (1999); see also Hara (2000) and Wang *et al.* (2005). Fertilizers coated with hydrophobic materials, especially polymer-coated types, provide reasonable/good control over the rate of release (Zhang, 2000). Polymer-coated controlled-release fertilizers are less sensitive to soil conditions (Salman *et al.*, 1990). The pattern of temporal release from coated fertilizers ranges from parabolic release (with or without 'burst'), to linear release, to sigmoidal release. The linear and sigmoidal release patterns synchronize better with nutrient uptake by plants than does the parabolic release (Shaviv, 1996, 2001, 2005). The test methods used in Japan and in China are given in Annexes I and II.

The release of urea from sulphur-coated urea (SCU) usually follows a parabolic pattern. However, if there are cracks in the coating, SCU will immediately release one third or more of its urea sometimes denoted as 'burst', when it comes into contact with water (Shaviv, 2005), and about one third may be released long after it is needed by the plant (the 'lock-off' effect) (Goertz, 1995; Jiang *et al.*, 2005; Shaviv, 2001, 2005). To improve the attrition resistance of SCU, it is preferable to use a double coating with sulphur and a polymer (Yang *et al.*, 2006).

Manufactured slow- and controlled-release fertilizers can be classified into linear and sigmoidal release types (Shoji and Gandeza, 1992) and a good explanation of the release of nutrients is given by Fujita and Shoji (1999) using Meister® (coated/encapsulated urea) as a model. Examples of linear-release formulations are. 20, 30, 40, 50, 70, 100 (Meister® 15) 140, 180 and 270, and for sigmoidal-release formulations, S30, S40, S60, S80, S100, S120, S160, S200 and SS100 days during which 80% of the nutrients are released at 25°C. For example, Meister®-7 (urea) shows linear release and requires 70 days to release 80% of the nutrient in water at 20°C, whereas Meister®-S7 (urea) has a lag period of 35 days, and it needs 35 days to release 80% of the nutrient in water at 20°C (Fujita and Shoji, 1999). A sigmoidal release indicates that the release of nutrients only starts after a certain lag time, i.e. a given number of days after application; SS100 has a longer lag time (70 days) than S100 (45), the most common type of Meister®. These lag times are in response to requests by farmers.

In Japan, farmers can obtain information on the nitrogen release patterns and placement of sigmoidal-release formulations from fertilizer producers, agricultural co-operatives and agricultural research institutes. All have a database of many crops grown with Meister® or software to link nutrient release to soil temperature (Tachibana, 2008; Figure 4). Polyolefin-coated compound fertilizer (NPK) named Nutricote® is produced by Chissoasahi using the same production patents as Meister® (Shoji and Gandeza, 1992). They also have both linear and sigmoidal release patterns and with a wide range of longevity (40 to 360 days at 25°C) and varying contents of macronutrients.

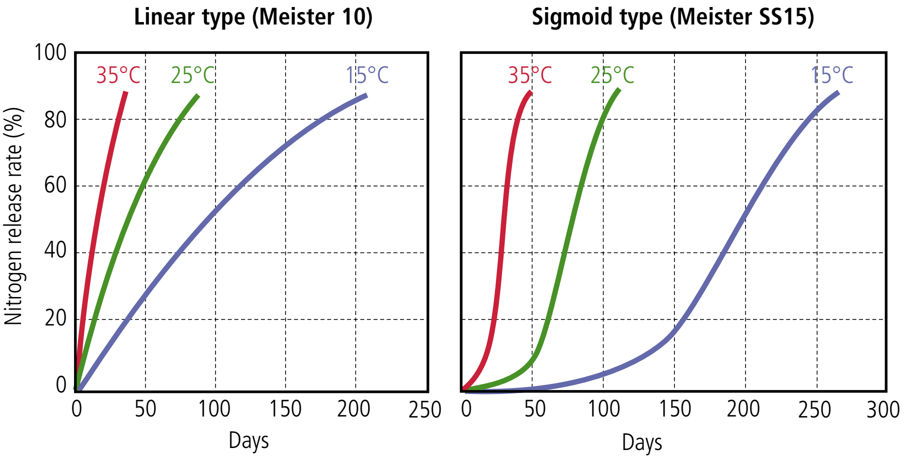

Figure 4. The effect of temperature on the release rate of Meister® (Adapted from Chissoasahi, 2005).

The formulation for Nutricote® is decided according to the release rate of nitrogen, which is usually present in the largest concentration. The annual production of Nutricote® (approx. 30 000 tonnes) is used mainly for horticultural crops and tea plants in Japan and for ornamental trees and flowers in the United States.

Fujita *et al.* (1983) showed that various release rates and duration of release from Meister® can be produced by varying the ratio of ethylene vinyl acetate (EVA) to polyethylene (PE) in the coating resin. For example, the number of days required to release 80% of N (urea) from Meister® in water at 25°C is 1300 days, if the fertilizer particles are coated with 100% PE. The release duration is 98 days if the particles are coated with blended material of 50% PE and 50% EVA.

Slow- and controlled-release fertilizers may contain only N or K, NP or NK (with different forms of K), NPK or NPK plus secondary nutrients and/or different micronutrients. The longevity of these products can range from 20 days to 18 months (Shoji and Gandeza, 1992).

The majority of coated fertilizers have been used in horticulture, in part due to the steady increase in container-grown plants, and for high-value vegetable crops. However, some producers offer specific products for use in agriculture and horticulture: e.g. Aglukon with its Agroblen® and Agromaster®, Compo with Basacote® and Haifa Chemicals with Agricote Power™. Chissoasahi has supplied ‘Naebako-makase’ and ‘Ikubyou-makase’ for single basal nutrient application in rice nurseries or horticultural crops. Haifa has developed three major polymer-coated fertilizer products for agricultural crops: Cote-N™ and Coted-N Mix™ for arable crops and Multigro® for cash crops and fruit trees. Agricote Power offers enhanced-efficiency of nutrient use, which enables application rates to be reduced by up to 50%. It is specifically recommended on light soils where conventional fertilizers are easily leached, and in rainy areas when rainfall accelerates nutrient leaching (Achilea *et al.*, 2005; Raban, 2005). Since 2000, Agrium has succeeded, based on a large-scale production and an excellent promotion, to introduce a polymer-coated fertilizer (ESN) specifically targeting maize, winter wheat and forage crops.

Important features of controlled-release fertilizers (Shaviv, 2005)
- Release pattern: shape, lag, lock off;
- Release duration;
- Differential release between N, P and K;
- Effect of temperature on release;
- Effect of the medium/environmental conditions on release.

3.1.1. Slow- and controlled-release fertilizers available for application

The two most important groups of slow- and controlled-release fertilizers, according to their production process are:
- condensation products of urea-aldehydes (slow-release fertilizers), and
- coated or encapsulated fertilizers (controlled-release fertilizers).
- Supergranules and others are of lesser or only regional importance.

3.1.1.1. Condensation products of urea and aldehydes/nitrogen reaction products

Among the nitrogen reaction products designed mainly for use on professional turf, in nurseries, greenhouses, on lawns and for gardens and landscaping, three types have gained practical importance (Goertz, 1993; Hähndel, 1986; Shaviv, 2005):
- urea-formaldehyde (UF),
- urea-isobutyraldehyde/isobutylidene diurea (IBDU®), and
- urea-alcetaldehyde/cyclo diurea (CDU®).[4]

In the past, urea-aldehyde reaction products, such as UF, IBDU®, and CDU®, had the largest share of the slow-release fertilizer market, currently however, the polymer-coated / polymer-sulphur-coated products have taken the lead; mainly due to increased production capacity by Kingenta (China) and Agrium/Hanfeng (Canada/China).

3.1.1.2. Urea-formaldehyde (UF) - 38% N

UF-based products were the first group to be developed for the slow release of nitrogen. As early as 1924, Badische Anilin- & Soda-Fabrik (now BASF) in Germany acquired the first patent (DRP 431 585) for UF-based fertilizers (BASF, 1965). In the United States, UF was patented in 1947 for use as a fertilizer. Commercial production began in 1955. At present, several types of UF fertilizer products are manufactured as solids and liquids, the latter as both solutions and suspensions in water (Goertz, 1993).

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[4] *CDU – Cyclo DiUrea is a registered trademark of Chissoasahi Fertilizer Co. Within the Fertilizer Regulations of the European Union this substance is produced by a different production process and is called crotonylidene diurea (BASF SE production process based on crotonaldehyde and urea), it is a branched chain molecule rather than a a cyclic molecule.*

Urea-formaldehyde is formed by the reaction of formaldehyde with excess urea under controlled conditions, pH, temperature, mole proportion, reaction time, etc., resulting in a mixture of methylene ureas with different long-chain polymers.

Table 3. Urea-formaldehyde solubility (Detrick, 1995).

Fractions		
Cold water soluble (CWS)	Cold water insoluble (CWI[1])	
	Hot water soluble (HWS)	Hot water insoluble (HWI)
(I)	(II)	(III)
	The Activity Index (AI) is only concerned with cold water insolubility	

[1] appears as "W.I.N." on United States Labels.

The main problem is to produce condensation-oligomers with the desired proportion of different methylene ureas because this influences the release of nitrogen. The nitrogen use efficiency of a UF fertilizer is determined by the Activity Index (AI) related to the relative proportions of three fractions, which are:

- **Fraction I**: cold water soluble (CWS, 25°C) containing residual urea, methylene diurea (MDU), dimethylene triurea (DMTU) and other soluble reaction products. The N of Fraction I is slowly available, depending on soil temperature (AAPFCO 73, N-29 and N-30).
- **Fraction II**: hot water soluble (HWS, 100°C), containing methylene ureas of intermediate chain lengths, the N is slow-acting.
- **Fraction III**: hot water insoluble (HWI), containing methylene ureas of longer chain lengths, the N is extremely slow-acting or non-available.

The release pattern of nitrogen from UF fertilizers is a multi-step process (dissolution and decomposition). In general, some proportion of the N is released slowly (Fraction I); this is followed by a more gradual release over a period of several (3-4) months (Fraction II) depending on the product type. However, the release pattern is also influenced by the soil temperature and moisture, as well as by soil organisms and their activity.

Previous UF formulations had an AI of about 40 to 50, however, more recent formulations have values of 55 to 65. The Association of American Plant Food and Control Officials (AAPFCO) has set a minimum AI of 40 with at least 60% of the nitrogen as cold water insoluble nitrogen (CWI N) and a total nitrogen content of at least 35%. Unreacted urea nitrogen content is usually less than 15% of total nitrogen.

In general, UF fertilizers show a significant slow release of nitrogen with a good compatibility with most crops. Because of its low solubility it will not scorch vegetation or impare germination. Because it is more effective at higher temperatures, it is widely used in warmer climates (in the Mediterranean region in Europe and in the southern and southwestern regions of the United States).

3.1.1.3. Isobutylidene diurea (IBDU®) – 32% N

Isobutylidene diurea is formed as a condensation product by a reaction of isobutyraldehyde with urea. In contrast to the condensation of urea with formaldehyde, which results in a number of different polymer chain lengths, the reaction of urea with isobutyraldehyde results in a single oligomer. To obtain the optimal proportion of IBDU, it is important that the reaction is stopped by neutralization at the point at which it is yielding most IBDU. The theoretical nitrogen content is 32.18%. The AAPFCO (1995) definition of IBDU requires a minimum of 30% nitrogen, 90% of which is cold water insoluble prior to grinding. The release mechanism functions by gradual hydrolysis of the sparingly water insoluble IBDU to urea, which is transformed by soil bacteria initially to ammonium ions and then to nitrate.

The rate of nitrogen release is a function of particle size (the finer the particle size the more rapid the release), moisture, temperature and pH. Based on agronomic response and safety margin, IBDU is good for turf, but phytotoxicity has sometimes been observed with greenhouse crops. It is preferably applied at lower temperatures.

3.1.1.4. Cyclo diurea (CDU®) – 32.5% N

Cyclo diurea was first patented as a slow-release fertilizer in 1959. The Chisso Corporation developed an economic, continuous industrial process to produce CDU from acetaldehyde and urea in 1962. CDU is produced in Japan using the Chissoasahi process (acetaldehyde + urea) but, in Germany, BASF use crotonaldehyde + urea. The molecule has a cyclic structure and is formed by the acid-catalyzed reaction of urea and acetaldehyde. CDU decomposes by both hydrolysis and microbial processes in the soil, and temperature, soil moisture and biological activity affect the rate of release. The degradation is slower than that of IBDU, even in acid soils. As with IBDU, the particle size of CDU greatly influences the rate of N release and the agronomic performance is similar to that of IBDU. In Japan and in Europe, its main use is on turf and in speciality agriculture, typically formulated into granulated NPK fertilizers. In Europe, CDU-containing fertilizers are exclusively used for pot and container plants.

3.1.2. Coated/encapsulated slow- and controlled-release fertilizers

These are conventional soluble fertilizer materials with rapidly plant-available nutrients, which after granulation, prilling or crystallization are given a protective, water-insoluble coating to control water penetration and thus dissolution rate, nutrient release and duration of release. AAPFCO (1995) defined them as 'products containing sources of water soluble nutrients, the release of which in the soil is controlled by a coating applied to the fertilizer'.

There are three main groups of coated/encapsulated fertilizers, based on the following coating materials:

- sulphur,
- sulphur plus polymers, including wax polymeric materials, and
- polymeric/polyolefin materials.

Melamine (1,2,5-triazine-2,4,6-triamine) – 66% N

Melamine is produced worldwide in large quantities (about 600,000 t per year), because it is the basic raw material for the production of various melamine resins (laminates, glues, adhesives, water repellents, fire retardents, etc.).

Because of its chemical structure, it is very slowly soluble and it was tested as slow-release N fertilizer by the Tennessee Valley Authority (TVA) in the USA, some decades ago. In the early 1980s, the former Melamine Chemicals Inc. (Louisiana, USA) tentatively developed an urea-melamine fertilizer (Super 60) and carried out some trials on rice to test its delayed nitrogen release ('time release' fertilizer system). However, the results were inconclusive, and the product was never commercialized. Melamine Chemicals also carried out tests to increase the crush strength of urea granules/prills by adding melamine (US-Patent 1977).

No information is available as to whether melamine spike and stake fertilizers, which in the USA had been offered in the seventies/early eighties as controlled-release fertilizers for use on house plants and ornamental shrubs and trees, has ever had wider use.

There is no data available about the decomposition of melamine in the soil (hydrolitic decomposition). Melamine is non-hazardous, non-toxic and non-allergic; it has no acute or chronic toxic effects on human health. There is no scientific data demonstrating that the use of melamine as N fertilizer (whether conventional or slow-release) has ever led to toxic effects on animals or men[1].

In the USA, EPA has banned any use of melamine-based fertilizers. There is also no registration for use of melamine-based fertilizers in Western Europe (Hähndel, 2009)[2].

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[1] *The latest concerns about melamine had nothing to do with its possible use as slow-release fertilizer. They were because some baby-milk powder producers in China replaced protein substances by melamine. The calculation of the protein content, based on the Kjeldahl method for total N was correct, however, the babies became ill or even died from protein deficiency and with too large a direct intake of melamine blocking the kidney system.*

[2] *This is confirmed by a worldwide melamine survey by IFA among its urea producing members to investigate whether there is hard evidence of possible use of melamine as a fertilizer. The survey of 80 companies in 50 countries in late November 2008 covered 98% of the world's urea production. The 30 companies that replied confirmed that they had no knowledge about the current use of melamine in commodity fertilizers. The response equated to 84% of the world production of urea.*

Agents/materials mainly used for coating are:

- sulphur;
- polymers (e.g. polyvinylidenchlorid (PVDC)-based copolymers, gel-forming polymers, polyolefine, polyethylene, ethylene-vinyl-acetate, polyesters, urea formaldehyde resin, alkyd-type resins, polyurethane-like resins,etc.);
- fatty acid salts (e.g. calcium-stereate);
- latex[5], rubber, guar gum, petroleum derived anti-caking agents, wax;

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[5] *The word 'latex' originally meant an emulsion of natural rubber, such as that obtained by cutting the bark of rubber trees. However, in chemistry, all colloidal dispersions of polymers in an aqueous media are called latex.*

- calcium and magnesium phosphates, magnesium oxide, magnesium ammonium phosphate and magnesium potassium phosphate;
- phosphogypsum, phosphate rock, attapulgite clay;
- peat (encapsulating within peat pellets: organo-mineral fertilizers);
- neemcake/'nimin'-extract (extract from neemcake).

The polymeric material used by each manufacturer mainly depends on its chemical and physical properties, cost, availability and whether or not there exists a patent. In comparison to urea reaction products, coated fertilizers, particularly those coated with a multi-layer coating of sulphur and a polymeric material, may be favoured economically.

Total fertilizer cost can be decreased by blending coated/encapsulated fertilizers with conventional fertilizers in different ratios. For example, Agrium (2007) recommends combining ESN with conventional fertilizers, the ratio and application rate mainly depending on the growth stage of the crop. Coated/encapsulated fertilizers offer flexibility in determining the nutrient release pattern (Fujita *et al.*, 1983; Shoji and Takahashi, 1999). They also permit the controlled release of nutrients other than nitrogen. Nyborg *et al.* (1995) found in greenhouse and field tests that slowing the release of fertilizer P into the soil by coating fertilizer granules (polymer coating) can markedly increase P recovery by the crop in the year of application and improve yield.

Another speciality product is the combination of a coated fertilizer with a nitrification inhibitor as produced by Chissoasahi (Dd Meister®). In the first step, urea is coated with Dd = DCD (dicyandiamide). Then a second coating with polyolefin is applied to obtain a controlled release of N and DCD; with either a linear or a sigmoidal release pattern. The longevity is 40, 70 and 140 days with the linear type, and 60 days (30 day lag time and 30 day release time) with the sigmoidal type (always with 80% release at 25°C).

3.1.2.1. Sulphur-coated urea (SCU)

The Tennessee Valley Authority (TVA), Alabama developed the basic production process for SCU in 1961. Within the group of coated, slow-release fertilizers, SCU is currently the most important. The sulphur coating may be considered to be an impermeable membrane that slowly degrades through microbial, chemical and physical processes. The concentration of nitrogen and its rate of release varies with the thickness of the coating in relation to the granule or prill size; it is also influenced by the purity of the urea used (El Sheltawi, 1982)[6].

There are four main reasons favouring the combination of urea and sulphur:

- Urea has 46% N and after coating with sulphur, SCU still contains about 30-40% N;
- Urea is prone to leaching and/or to ammonia losses by volatilization; by covering the urea granules with an impermeable sulphur membrane such losses are significantly reduced;
- Sulphur melts at about 156°C;

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[6] *Sulphur coating is not used for potassium nitrate or other fertilizers with a large nitrate content, because of explosive hazard. However, encapsulation according to the Reactive Layers Coating (RLC) process of Pursell Technologies, is possible without risk.*

- Sulphur is a valuable plant nutrient and its application is becoming more important because environmental regulations are decreasing sulphur emmissions to the atmosphere and hence, deposition on to soil.

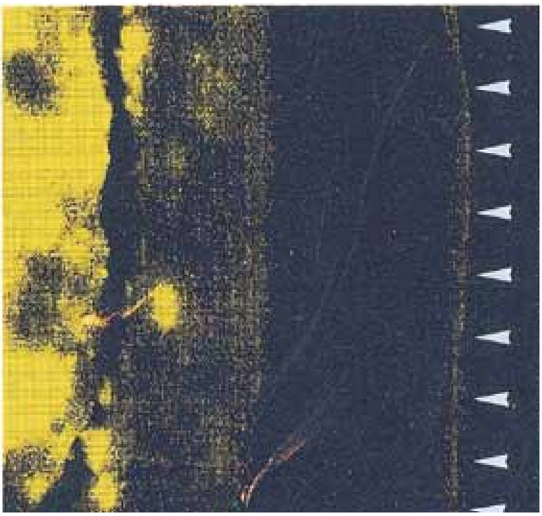

Figure 5. Electron micrograph of a cross-section of a slow-release fertilizer granule showing the distribution of sulphur (10 µm) (Photo: BASF SE).

Manufacture of SCU consists of preheating urea granules (71-82°C) which are then sprayed with molten sulphur (143°C) in a rotating coating drum to coat each granule. Any pores and cracks in the coating are sealed by adding a wax sealant or polymeric paraffin oil (2 to 3% of total weight). Finally, a conditioner (2 to 3% of total weight) is applied to obtain a free flowing and dust-free product with good handling and storage characteristics. Currently manufactured products contain 30 to 42% N and 6 to 30% S, plus various sealants and conditioners. However, SCU is not attrition-resistant due to the nature of the sulphur coating.

Nutrient release from SCU particles is directly affected by the thickness and quality of the coating. The dissolution of urea into the soil solution follows microbial and hydrolytic degradation of the protective sulphur coating, and the presence of micropores and imperfections, i.e. cracks and incomplete sulphur coverage. Typically, there are three types of coatings: damaged coating with cracks, damaged coating with cracks sealed with wax, and perfect coating. SCU fertilizers may contain more than one third of granules with damaged coating and about one third of perfectly coated granules. Therefore, one third or even more of the urea may be released immediately after contact with water (so-called 'burst'), and one third may be released long after it is required by the plant (so-called 'lock-off' effect) (Goertz, 1995; Shaviv, 2001, 2005).

Traditionally, the quality of SCU is characterized by the rate of N release into the soil solution within seven days. The seven-day dissolution rate method developed by TVA makes it possible to generate a leaching profile for SCU but, unfortunately, the results do not correlate reliably with the release pattern under actual field conditions (Goertz, 1995; Hall, 1996). Currently, SCU fertilizers have dissolution values of about 40 to 60%. 'SCU-30' designates a product with a nitrogen release of 30% within seven days under prescribed conditions. With such a high dissolution rate, a rapid initial effect on the crop is to be expected. In fact, there have been repeated claims of a too-rapid release of nitrogen (Wilson, 1988).

3.1.2.2. Polymer coating of sulphur-coated urea (PSCU)

The disadvantages of the irregular nutrient release from SCU have led to the development of so-called hybrid coatings with sulphur and a thin polymer-coating (thermoplastic or resin) containing about 38.5 - 42% N, 11 - 15% S and less than 2% polymer sealant. The quality of a polymer-coated fertilizer is thus combined with the lower cost of sulphur-coating (Detrick, 1992, 1995, 1997; Van Peer, 1996; Zhang *et al.*, 1994). Although products with a hybrid coating have shown better release characteristics than SCU, they still have certain 'burst' and 'lock-off' characteristics (Goertz 1995; Shaviv 2005). Examples of hybrid-coating products are: Lesco Poly Plus® PSCU 39N, Agrium (Pursell) TriKote®[7] PSCU 39-42N and Scott Poly-S® PSCU 38.5-40N).

3.1.2.3. Polymer-coated/encapsulated controlled-release fertilizers

Standard SCU and PSCU have dominated the market for several years. However, the horticultural and garden-lawn markets in particular require a more sophisticated nitrogen release pattern. Thus, many new controlled-release fertilizers with modified coatings have been developed (Detrick, 1997; Fujita 1993, 1996a, 1996b, 1997; Fujita and Shoji, 1999; Fujita *et al.*, 1983, 1989, 1990a, 1990b, 1992; Jeffreys, 1995; Kloth, 1989; Shaviv, 2001, 2005; Thompson and Kelch, 1992).

Polymer coatings may either be semi-permeable or impermeable membranes with tiny pores. The main problems in the production of polymer-coated fertilizers are the choice of the coating material and the process used to apply it (Fujita and Shoji, 1999; Goertz, 1993; Hähndel, 1986; Moore, 1993; Pursell, 1992, 1994, 1995). The nutrient release through a polymer membrane is not significantly affected by soil properties, such as pH, salinity, texture, microbial activity, redox-potential, ionic strength of the soil solution, but rather by temperature and moisture permeability of the polymer coating. Thus, it is possible to predict the nutrient release from polymer-coated fertilizers for a given period of time much more reliably than, for instance, from SCU (Fujita and Shoji, 1999; Shaviv, 2005; Shoji and Gandeza, 1992).

According to Hauck (1985), nutrient release from Osmocote (an alkyd-resin-coated fertilizer) follows water entering the microscopic pores in the coating. This increases the osmotic pressure within the pore, which is enlarged and nutrients are released through the enlarged micropore. The alkyd-resin-type coating makes it possible to satisfactorily control the release rate and timing. Polyurethane-like coatings also provide a good control over rate and duration of release. The rate of nutrient release from a polymer-coated product, can – to a reliable extent – be controlled by varying the type and the

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[7] *Pursell Trikote® PSCU process under the United States Patent No. 5,599,374 of Feb. 4,1997.*

thickness of the coating, as well as by changing the ratio of different coating materials (Detrick, 1992; Goertz, 1993, 1995; Fujita, 1993; Fujita and Shoji, 1999; Fujita *et al.*, 1989, 1990a; Pursell, 1992,1994; Shaviv, 2005). The moisture permeability of the capsule can be controlled by changing the composition of the polymeric coating material used. For instance, with the Chissoasahi process, the ratio of ethylene-vinyl-acetate (EVA – high moisture permeability) to polyethylene (PE – low moisture permeability) is changed. The nutrient release pattern is then determined by a water-leaching test at 25°C: T-180 indicates, that 80% of the nutrients are released over 180 days at 25°C in water (Fujita and Shoji, 1999).

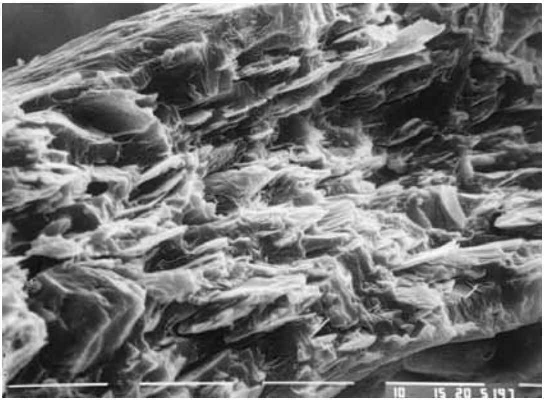


Figure 6. Electron micrograph cross-section of the polyolefine coating of a controlled-release fertilizer (Meister®). Diameter of granule approximately 2-3 mm; thickness of the polyolefine film 50-60μm (Photo: Chissoasahi, 2007).

Polymer-coated fertilizer technologies vary greatly between producers depending on the choice of the coating material and the coating process. The Pursell Reactive Layers Coating (RLC™) uses polymer technology, while (Polyon®) uses a polyurethane as does Haifa (Multicote®) and Aglukon (Plantacote®). Chissoasahi polymer technology (Meister®, Nutricote®) is a polyethylene; while Scotts polymer technology (Osmocote®) is an alkyd-resin. The quantity of coating material used for polymer coatings of conventional soluble fertilizers depends on the geometric parameters of the basic core material (granule size to surface area, roundness, etc.) and the longevity target. In general, the coating material represents 3-4% (RLC™) to 15% (conventional coating with polymers) of the total weight of the finished product. For example, the capsule or coating film of Meister® (encapsulated urea) is 50 to 60 μm in thickness and approximately 10% in weight (Fujita and Shoji, 1999).

The longer the need to supply the nutrients, the smaller is the amount released per unit of time. The producers indicate the period of release, e.g. 70, 140, up to 400 days release at constant 25°C. However, if the polymer-coated fertilizers are not straight nitrogen but NPK fertilizers, particularly when containing secondary and micronutrients, the rate of release of the different nutrients, N, P, K, S, Ca, Mg and micronutrients, are generally

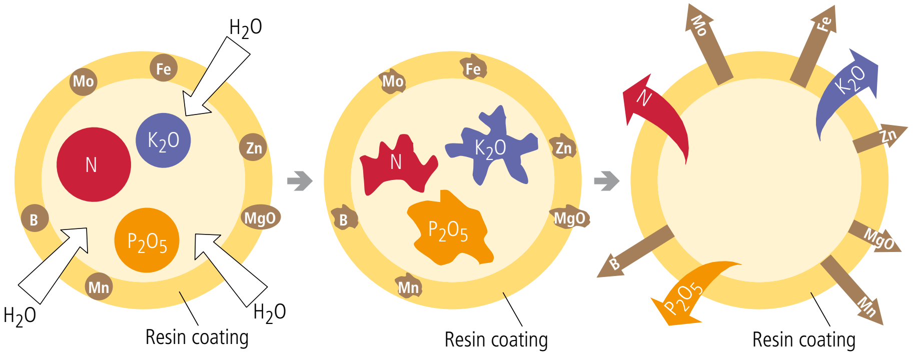


Figure 7. Mode of action of a coated/encapsulated controlled-release fertilizer (Basacote®) (Adapted from Hähndel, BASF, 1997).

not stated (Figure 17.). Apparently, it is very difficult to determine exactly the release mechanism, particularly for secondary and micronutrients.

The problem is that, in order to guarantee the longevity of nutrient release from a polymer-coated product, there should be no (or an extremely slow) bio-degradation, chemical-degradation or mechanical destruction of the coating during the period of nutrient release. Only after the nutrient supply of the product has ceased should microbial attack and mechanical destruction of the empty shell occur (Kloth, 1996). Some polymer-coated fertilizers still present a problem with the persistence in the soil of the synthetic material used for encapsulation; there is much research on this topic (Kolybaba *et al.*, 2003). Agrium indicates that the polymer coating of their polymer-coated urea (ESN) degrades in a two-step process to CO_2, ammonia and water. Coating material made from a photo-degradative polymer is easily decomposed by photochemical process in the soil (Fujita, 1996a; Sakai *et al.*, 2003).

Recently, 'UBER', a new type of controlled-release fertilizer without a polymer coating has been developed by Chissoasahi (Sakamoto *et al.*, 2003, 2007). It is produced using CDU and two additives that control the pattern and rate of nutrient release. Three formulations are available with short to long release patterns. It is mainly used for high-value plants and is especially helpful for 'eco-farmers' practicing environment-friendly farming because it has no polymer coating.

3.1.2.4. Partly polymer-encapsulated controlled-release fertilizers/mixtures of encapsulated and non-encapsulated N, NP or NPK fertilizers.

Another possibility to combine the advantage of controlled-release nutrient supply with the lower cost of conventional fertilizers, is to mix polymer-coated and non-coated granules of the same fertilizer type (for example in a ratio of 1:1) (Hähndel, 1997). In Germany, an NPK fertilizer (with a minimum content of 3% N, 5% P_2O_5, 5% K_2O), of which only 50% of the granules are polymer-coated, has been registered under German fertilizer law (Kluge and Embert, 1996). In 1997, a similar NPK fertilizer type was

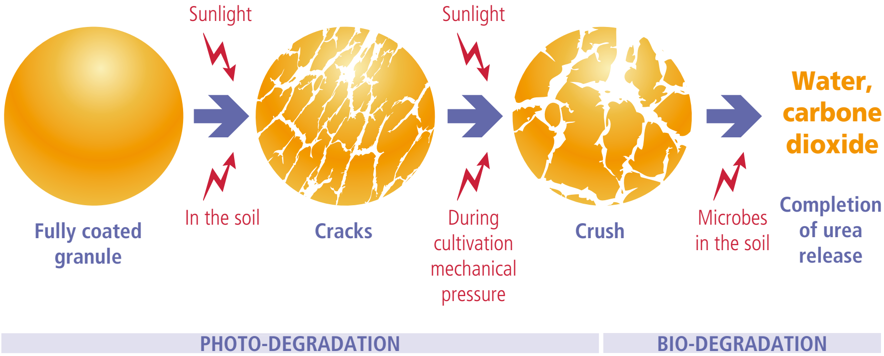


Figure 8. Decomposition model of the coating polymer of Meister® (Adapted from Chissoasahi, 2007).

registered with only 25% polymer-coated granules, offering a greater flexibility in use and further improved economy. Such mixtures of encapsulated and non-encapsulated granules or prills are also used in Japan.

3.1.2.5. Neem- or 'nimin'-coated urea

The Indian neem tree *(Azadirachta indica)* has a number of traditional uses, based on the insect repellent and bacteriostatic properties that are contained in various tissues. The press cake from the production of neem oil has a controlled-release and nitrification-inhibiting effect, aside from other possible uses. It is therefore frequently recommended to add neem cake to urea to form NCU (neem-coated urea) or NICU (nimin-coated urea; nimin = extract from neem cake) to improve nitrogen use efficiency and to reduce losses (Wichmann, 1997). Though Budhar *et al.* (1991), De *et al.* (1992), Geethadevi *et al.* (1991), Jena *et al.* (1993), Kumar and Thakur (1993) and Singh and Singh (1994) obtained promising results when comparing NCU with prilled urea for rice (See 3.2.2.8.), the use of NCU or NICU is apparently not practiced to any extent by farmers, neither in India where the tree originates, nor in other tropical countries to which it has been brought in the past. The main reason might be the difficulty of obtaining sufficient quantities of neem cake at the village level, the additional labour for blending or the lack of a mechanical process for blending. Whatever the reason, no attempt has been made to develop the technology to coat urea with neem on a wider commercial scale (Suri, 1995). Recently, Laijawala (2010) has again drawn the attention to neem as a possible nitrification inhibitor, showing particularly that neem oil-coated urea significantly reduces ammonia volatilization.

3.1.2.6. Supergranules and others

This group of fertilizer products has been given special attention, particularly in tropical and subtropical regions. Supergranules are conventional soluble fertilizers formulated in a compacted form, with a relatively small surface-to-volume ratio. This results in a slow or relatively slow release of nutrients into the soil solution. Some of these special formulations also contain UF or IBDU®. In Western Europe such supergranules, briquettes, tablets or sticks are mostly used for fertilizing trees and shrubs, pot plants and some vegetables. In tropical regions, their preferred use is in irrigated rice (Geethadevi *et al.*, 1991; Gour *et al.*, 1990; Raju *et al.*, 1989).

3.1.2.7. Controlled-release fertilizers in a matrix

In these products, the fertilizer particles are incorporated throughout the carrier matrix. However, to achieve the desired slow-release effect, a large quantity (up to 40%) of carrier material is required. Consequently, only low-grade fertilizer formulations are possible (e.g. NPK 10-10-10 or NPK 5-15-10). In general, the carrier material is a mix of molten waxes, surfactants and polyethylene glycols (polymeric matrices; styrenebutadiene rubber formulations and some others).

3.2. Characteristics of nitrification inhibitors

3.2.1. General

The importance of a specific plant nutrient is characterized by the fact that its functions cannot be replaced by any other nutrient. The outstanding position of nitrogen (N) within plant nutrients is its role in the formation of proteins and proteides, chlorophyll and other important compounds, such as phytohormones. The plant's requirement for N is greater than that of any other nutrient, with the exception of potassium (K). Plants can take up carbon (C) in the form of CO_2 through the leaves, but not N and thus they

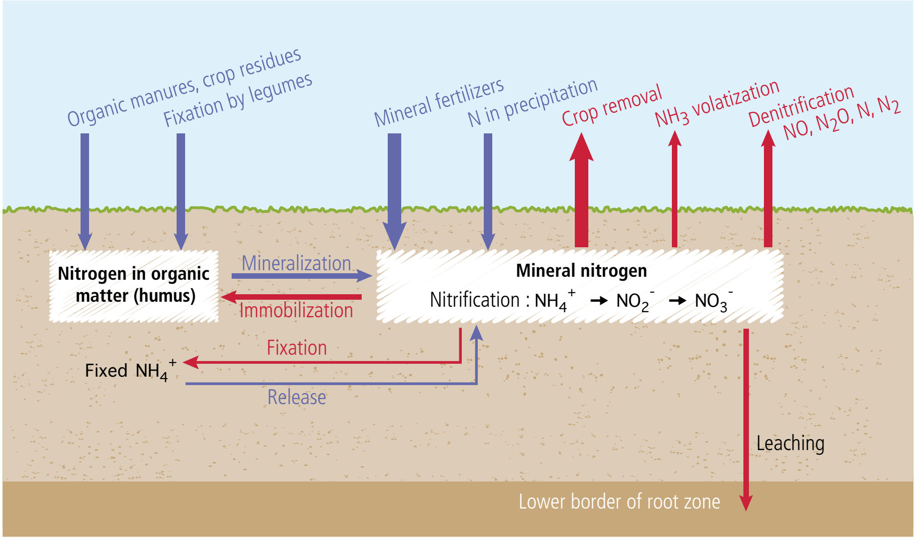
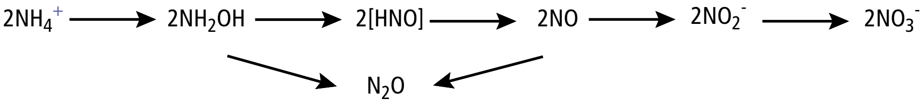


Figure 9. Simplified N cycle (Adapted from Zerulla, 2008).

cannot make use of the enormous stock of N in the air. Plants can take up N only after transformation of gaseous N into ammonium and nitrate (Amberger, 1996).

In soil about 90% of the N is in organic forms; only a small part is in inorganic forms such as ammonium (NH_4^+) or nitrate (NO_3^-). The ammonium ion but not nitrate is adsorbed at the surface of soil particles, thus nitrate is very mobile and prone to leaching. Ammonium in soil is oxidized first to nitrite (NO_2^-) and then to nitrate by bacteria:



$$2NH_4^+ \longrightarrow 2NH_2OH \longrightarrow 2[HNO] \longrightarrow 2NO \longrightarrow 2NO_2^- \longrightarrow 2NO_3^-$$

$$N_2O$$

Nitrosomonas spp are responsible for the transformation to nitrite and *Nitrobacter and Nitrosolobus spp.* for the conversion to nitrate (Amberger 1996, 2006). The process is known as nitrification.

$$2NO_2^- + O_2 \xrightarrow[\text{Nitrosolobus}]{\text{Nitrobacter}} 2NO_3^-$$

The process of ammonium oxidation/ammonia monooxygenase has been investigated by McCarty (1999).

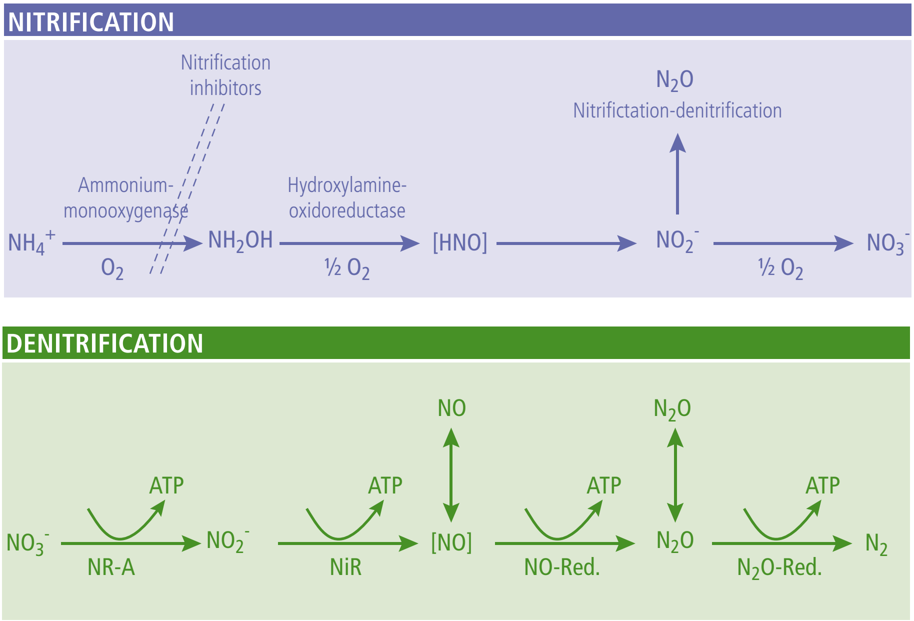


Figure 10. Nitrification/denitrification (Adapted from Weiske *et al.*, 2001a).

Because nitrate is present in the soil solution, it is easily taken up by plant roots. It may, however, be lost to surface water or leached into deeper soil horizons where there are no plant roots and thus it will be lost to ground water. These losses can contribute to high nitrate levels in drinking water and eutrophication of surface waters (Frye, 2005). In addition, particularly in soils saturated with water and at high temperatures, denitrification (the transformation of nitrate to N_2 and the production of nitrous oxide N_2O, a potent greenhouse gas) and nitrogen oxides (NO_X) will be favoured. Del Prado *et al.* (2006) defined these gases as by-products or intermediate products of microbial nitrification and denitrification processes. They studied the importance of several factors (soil moisture, fertilizer type and temperature) on nitrous oxide and nitrogen oxides (NO_x) emissions, concluding that the water content of the soil is the most important factor controlling their formation. Some loss of nitrous oxide from the soil is unavoidable due to the N transformations by microorganisms. Though long-term organic fertilization with manure and slurry is of special significance for nitrous oxide emissions, short-term emissions are influenced by mineral N fertilizer use. All such losses, whether by leaching or by gaseous emissions, do not contribute to crop production, are detrimental to the environment, and represent a considerable economic loss to the farmer. These losses can be reduced by choosing an appropriate fertilizing strategy and the use of nitrification inhibitors (Linzmeier *et al.,* 2001a). The effects of different nitrification inhibitors (or controlled-release fertilizers) are variable, depending on the actual test conditions.

Halvorson and Del Grosso (2010) have found that using ESN results in reduced N_2O fluxes. However, significant results have only been obtained in no-till crop rotations with maize (a reduction of 49%); whereas results with conventional tilled maize have been negligible. They also reported a significant reduction of N_2O fluxes using Super U (urea with incorporated Agrotain Plus) in no-till maize crops (51%).

Nitrification inhibitors, when added to N fertilizers and applied to the soil, delay the transformation of ammonium to nitrite by inhibiting or at least by slowing the action of *Nitrosomonas spp*. (Farm Chemicals Handbook, 1996; Sturm *et al.*, 1994; Zacherl and Amberger, 1990). Ammonium ions will stay adsorbed to soil particles and be protected against leaching, but available for plants, because they are also capable of taking up ammonium. Moreover, nitrification inhibitors favour the partial ammonium nutrition of plants. Plants use energy for the incorporation of ammonium into amino acids but more energy is needed if they first have to reduce nitrate to ammonium (Amberger, 2008b). The possible direct use of ammonium within protein metabolism has a positive effect on the synthesis of polyamines, cytokinins and gibberellins (Pasda *et al.,* 2001b). An additional advantage of ammonium nutrition is an improved uptake of P. When plant roots take up ammonium ions, protons (H^+) are excreted for charge equilibration in the roots. Thus, the pH of the rhizosphere is decreased (up to two pH units), resulting in P mobilization (Curl and Truelove, 1986). The same is valid for the mobility and uptake of some micronutrients (Marschner, 1986). The effect on phosphate and micronutrients mobilization is intensified by the addition of a nitrification inhibitor, which extends the ammonium phase in the soil, resulting in greater P and Zn uptake (Amberger, 1991b; Amberger, 1992; Rothmeier and Amberger, 1983). However, P uptake will only be

Table 4. Inhibition of N_2O emissions after use of different nitrification inhibitors (Snyder, 2007) .

Nitrification inhibitor or coating	Fertilizer	Crop	N_2O reduction (%)	Length of monitoring	Reference cited in Weiske, 2006
Nitrapyrin	ammonium sulphate	soil only; lab study[1]	93	30 days	Bremer & Blackmer, 1978
Nitrapyrin	urea	soil only; lab study[1]	96	30 days	Bremer & Blackmer, 1978
Nitrapyrin	urea	corn	40-65	100 days	Bronson *et al.*, 1992
Calcium carbide	urea	corn	33-82	100 days	Bronson *et al*, 1992
DCD	liquid manure	pasture grass	50-88	14 days	De Kein & van Logtestijn, 1994
DCD	ammonium sulphate	pasture grass	40-92	64 days	Skiba *et al.*, 1993
DCD	urea	spring barley	82-95[5]	90 days	Delgado & Mosier, 1996
POCU[2]	urea	spring barley	35-71[5]	90 days	Delgado & Mosier, 1996
DCS[3]	ammonium sulphate	pasture grass	62	64 days	Skiba *et al.*, 1993
DMPP[4]	ammonium sulphate nitrate	spring barley, corn and winter wheat	51	3 years	Weiske *et al.*, 2006

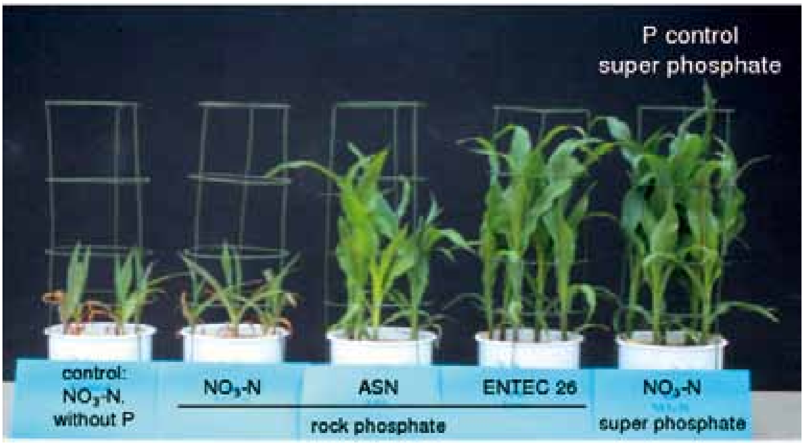
[1] Conditions set to measure emissions during nitrification only
[2] POCU = polyolefin coadted urea
[3] DCS = N (2,5 dichlorphenyl) succinic acid monoamide
[4] DMPP = 3,4-dimethylpyrazole phosphate
[5] Interpretation varies due to relatively large baseline emission

improved if the P fertilizer has been incorporated directly into the rhizosphere zone by band application. Rahmatullah *et al.* (2006) showed that applying ASN + DMPP improved the uptake of P when P was applied as phosphate rock. This effect was not observed in the bulk soil, but only in the rhizosphere.

Ammonium, retained on clay minerals by ion exchange, is sparingly mobile; nitrate being mobile is much more readily leached from the soil (Amberger, 1993a; Scheffer, 1991, 1994; Schweiger, 1991; Zerulla, 1991; Zerulla and Knittel, H., 1991a). Because leaching losses of nitrate depend on the concentration in the soil solution (Shaviv 2005), addition of a nitrification inhibitor to N fertilizers will decrease the concentration of nitrate in the soil solution and minimize nitrate leaching and denitrification losses.

Table 5. Characteristics of NH_4^+ and NO_3^- in the soil (Pasda, 2008).

Characteristics	NH_4^+	NO_3^-
adsorption by soil particles	yes	no
leaching	no	yes
nitrification	fast	–
denitrification	–	possible



Picture 1. Effect of ASN + DMPP (Entec 26) and phosphate rock in maize grown in a sub-soil with very low P content (Rahmatullah *et al.*, 2006). (Photo: Institute of Plant Nutrition, University Giessen, Germany)

In addition, several investigations have shown that using nitrification inhibitors not only decreases nitrate-N leaching and nitrous oxide emissions, but there is suppression of methane (CH_4) emissions (Bronson and Mosier, 1993, 1994; Bronson *et al.*, 1992; Bundesrat, 1996; Klasse, 1991; 1993; Kumar *et al.*, 2000; Schweiger, 1991). These are important positive environmental aspects of using nitrification inhibitors.

Reduced losses of N not only protect the environment, but they also increase N use efficiency, resulting in larger yields on a more consistent basis.

Farmers may reduce N losses to a certain extent by using fertilizer best management practices (FBMPs). However, further improvements may be possible by using N fertilizers amended with a nitrification inhibitor, particularly in environmentally sensitive areas (Ministère de l'environnement, 1994). This is recommended not only on arable fields, but also on grassland.

3.2.2. Types of nitrification inhibitors available for application

Although hundreds of chemicals have been tested only very few have gained practical importance as nitrification inhibitors (Kiss and Simihaian, 2002). Nitrapyrin, DCD, DMPP, Triazol, 3-MP and 2-amino-4-chloro-6-methyl-pyrimidine (AM) are the main compounds now used in agriculture. Some other compounds have restricted use in certain regions.

3.2.2.1. DCD - dicyandiamide (about 67% N), combinations of DCD with 1H-1,2,4-triazole and 1H-1,2,4-triazol + 3-methyl-pyrazol

Dicyandiamide (DCD - $H_4C_2N_4$), as a technical product, is produced from calcium cyanamide by several manufacturers in China, Germany, Japan and Norway. Its possible use in agriculture was tested as early as 1917, not as a nitrification inhibitor, but as an N fertilizer in comparison to calcium cyanamide (Linter, 1917).

DCD is produced in the form of non-volatile, white or colorless crystals from calcium cyanamide, water and carbon dioxide (CO_2). DCD has a wide range of industrial uses (ODDA, 1995). It is very soluble in water and contains at least 65% N (AAPFCO, 1985). It can be incorporated into any ammonium-containing solid, liquid or suspension fertilizer. For incorporation of DCD into anhydrous ammonia, special highpressure equipment is necessary (Rajbanshi *et al.,* 1992).

With an oral lethal dose (LD_{50}) of >10,000 mg/kg in female rats, it is practically non-toxic. The Ames Test with DCD did not reveal any mutagenic activity. Furthermore, long-term studies have shown that DCD is not carcinogenic. The Official Institute for Public Health of the Federal Republic of Germany has confirmed that there is no risk to human health from DCD and its residues (Roll, 1991; Zerulla, 2008).

In the soil, DCD is decomposed in part abiotically and in part biotically by specific enzymes, and converted via guanylurea and guanidine to urea (Amberger, 1989, 1991a, 2008a; Hallinger, 1992; Hauser and Haselwander, 1990; Rajbanshi, 1993; Vilsmeier, 1991a and 1991b) and, finally, to ammonia (NH_3) and CO_2. According to Weiske *et al.* (2001c) DCD is mineralized more rapidly than DMPP.

Following extensive use in Western Europe and Japan, DCD was introduced into the United States by SKW Trostberg in 1984, and officially approved by the EPA as a nitrification inhibitor in the late 1990s and so defined by AAPFCO in 2000 (Official Publication AAPFCO, No. 54, 2001).

In the soil, DCD has a bacteriostatic effect on *Nitrosomonas*, i.e. the bacteria are not killed but their activity is depressed or inhibited for a certain period of time. Even several applications have only led to a depressive effect on *Nitrosomonas* (Sturm *et al.,* 1994). Depending on the amount of mineral N applied and the moisture and temperature of the soil, the ammonium-N in fertilizer or in slurry/urine excreta is stabilized for several weeks (4 to 10) through the nitrification inhibiting effect of DCD. A disadvantage of DCD has been that, for technical incorporation into conventional ammonium-containing fertilizers (AS, ASN, UAN), a relatively large quantity of about 5-10% DCD-N relative to the total N content has to be used (BASF, 1991, 1993; Wozniak, 1997; Zerulla, 1996). There is also the problem of rather quick hydrolytic decomposition, particularly with repeated applications (Rajbanshi, 1993; Rajbanshi *et al.,* 1992).

To reduce the application rate and maintain full activity, combinations of DCD with other nitrification inhibitors have been developed, such as with 3-methyl pyrazole (DCD + 3-MP), and 1H-1,2,4-triazole (DCD + TZ, 10:1, w/w) (Weber *et al.,* 2004a), some showing a synergistic effect (Michel *et al.,* 2004). For incorporation into slurries, a mixture of TZ + 3-MP is offered in liquid form (SKW Piesteritz).

Compared with the application of conventional N fertilizers, there are larger amounts of ammonium and significantly less nitrate found in the soil solution when the N fertilizer was amended with DCD + TZ or with a combination of TZ + 3-MP. In a 19-year lysimeter study when ASN and CAN were amended with DCD nitrate leaching deceased and crop yields increased (Gutser, 1999a). The benefits of using DCD +TZ are greater on light textured soils and with excess rainfall within the 4-8 weeks following application (Amberger, 1993a, 1993b, 2006; Klasse, 1991; Zerulla and Knittel, 1991a, 1991b). The effect of DCD + TZ on reducing nitrous oxide emissions is significant (Kumar *et al.,* 2000; Schuster *et al.,* 2005; Weiske *et al.,* 2001a). A significant reduction of nitrous oxide emissions was also obtained in laboratory and field experiments when using this mixture (Michel *et al.,* 2004; Weber *et al.,* 2004a; Wozniak *et al.,* 2001).

Table 6. Average nitrate contents of drainage water (Auenlehm/Südweyhe) in mg N/l (Scheffer, 1994).

Year	CAN[1]	Alzon[2]	Without N
1984/85	18.8	15.1	-
1985/86	28.7	20.2	25.2
1986/87	18.4	8.6	6.2
1987/88	20.1	7.9	3.2
1988/89	12.8	2.2	0.1
1989/90	24.8	16.9	9.3
1990/91	11.2	8.8	5.4
1991/92	6.5	2.4	2.0

[1] CAN = calcium ammonium nitrate
[2] Alzon = ammonium sulphate nitrate (ASN) stabilized with DCD

Types of fertilizers amended with DCD (Didin®) and new nitrification inhibitors distributed in Western Europe by SKW Piesteritz are:

- Alzon® 46: 46% total N, urea with a mixture of DCD and TZ;
- Alzon® liquid: UAN solution with 28% total N, and a mixture of TZ and 3-MP;
- Alzon® liquid S: 24% total N and 3% water soluble sulphur (S), and a mixture of TZ and 3-MP;
- Piadin®: N stabilizer for organic fertilizers, liquid formulation of TZ and 3-MP.

Piadin® can be mixed directly with slurry before spreading or it may be spread (also in combination with plant protection products) immediately before spreading slurry or on to crop residues.

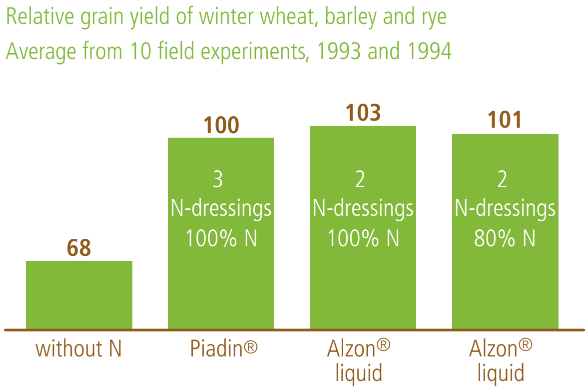


Figure 11. Stabilized fluid fertilizers on winter cereals (Adapted from Wozniak, 1997).

Recently, DCD has been used on grass pastures where it is said to increase yield and grass quality (Moir *et al.*, 2007) and to significantly decrease nitrate leaching (Di and Cameron, 2007). The use of DCD on grassland and with slurry in Western Europe has been replaced by a special liquid formulation of TZ + 3-MP (by SKW Piesteritz). Outside Europe, DCD is still applied with slurry or on grassland (slurry/urine, excreta/urine, excreta or urine patches) to reduce nitrate leaching, e.g. as Eco-N^{TM} of Ravensdown Fertilizer in New Zealand. DCD formulated as a fine-particle suspension can be applied as a spray through traditional agrochemical applicators (Di and Cameron, 2002, 2004). The application rate is 10kg DCD/ha applied with 100–150 litres of water twice a year, in late autumn and in early spring (Di and Cameron, 2005).

In Japan, Chissoasahi has for many years sold an NPK fertilizer combined with DCD under the name of 'Yodel' for the production of high quality tea leaves. In addition the company has developed a controlled-release fertilizer with DCD (Dd-Meister®), combining the nitrification inhibiting effect with that of controlled N release (Tachibana, 2007).

3.2.2.2. DMPP – 3,4-dimethylpyrazole phosphate

DMPP is a rather new nitrification inhibitor, developed in 1995 by BASF, which is marketed since 1999 by Compo under the trade name Entec®. According to European legislation, DMPP is classified as a new chemical substance and, as such, it has been subject to extensive toxicology and ecotoxigology tests (Zerulla *et al.*, 2001a). To date, none of these investigations has revealed toxic and ecotoxic side effects (Andreae, 1999; Roll, 1999). The various toxicology tests, necessary for the registration of a nitrification inhibitor, as a new chemical substance, are in the meantime regulated within the EU by REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals), the following listing may give an impression of the toxicological research work that is required.

Registration of DMPP in Germany/Europe (Pasda, 2008)

Information necessary for registration according to the Chemical Substance Act (base set)

- Acute toxicity (orally);
- Acute toxicity (inhalation);
- Skin and eye irritation;
- Skin sensitization;
- Carcerogenicity and mutagenicity;
- Teratogenicity;
- Subacute toxicity;
- Acute toxicity for fish and daphnia;
- Growth inhibition on algae;
- Bacterial inhibition;
- Degradation (biotic, antibiotic);
- Adsorption/desorption.

DMPP is registered in several European and South American countries, in Australia and New Zealand. Its oral lethal dose (LD_{50}) in rats ranges from 300 to 2,000 mg/kg (ATC-method). It is non-mutagenic (Ames Test) and it does not irritate the skin. In contrast to 3-MP, DMPP has no teratogenic effect.

DMPP is produced as a white to greyish powder. It can be used on solid or liquid fertilizers, or in slurry. Application rates of 0.5 to 1.5 kg/ha are sufficient to achieve optimal nitrification inhibition (Zerulla *et al.*, 2001a). It causes no phytotoxic damage and leaves no residues within plants. In soil and plants it decomposes by the destruction of the pyrazol-ring (Fettweis *et al.*, 1999a, 1999b, 2001) without affecting aquaric organisms and soil life (Andreae, 1999). DMPP may reduce significantly nitrate leaching without being leached itself. The significant reduction of N leaching through the use of DMPP has been shown in model studies (Wissemeyer *et al.*, 1999) and field experiments on different soil types. The adsorption of DMPP to inorganic soil surfaces is supposed to play a major role in its efficiency (Barth *et al.*, 2001).

Table 7. Nitrate leaching after application of different nitrification inhibitors on Ruchheim soil growing spinach (pot trial) (Zerulla *et al.*, 2001a).

Irrigation before sampling (mm)	Sampling date DAF	ASN	ASN+DMPP[1]	ASN+DCD[2]
			(% of fertilized N)	
20	7	10.7 a	4.5 b	12.1 a
10	18	8.3 a	2.6 b	3.5 b
10	22	2.7 a	0.5 b	0.5 b
Σ40	Σ	21.7 a	7.6 b	16.1 ab

[1] 1.6% according to the NH_4^+-N content of the basic fertilizer ASN (18.5% NH_4^+-N, 7.5% NO_3^--N)
[2] 13% according to the NH_4^+-N content of the basic fertilizer ASN (18.5% NH_4^+-N, 7.5% NO_3^--N)
Values in a row followed by the same letter do not differ significantly (Duncan's test, 5% level).
DAF = Days after fertilization.

Compared to other nitrification inhibitors, DMPP has two specific characteristics:

- Its rate of application is substantially less than that of e.g. DCD (Zerulla *et al.*, 2001a);
- Its mobility within the soil is rather low, compared to that of ammonium (Fettweis *et al.*, 2001; Gutser, 1999b; Linzmeier *et al.*, 2001a).

Table 8. Effect of DMPP on the amount of ammonium-N and nitrate-N in soil incubated at different temperatures (Zerulla *et al.*, 2001a).

Temperature	DAT	ASN		ASN+DMPP[1]	
		NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N
		mg/pot			
5°C	7	4.7	3.2	5.2	2.6
5°C	21	3.9	3.3	3.1	2.5
5°C	42	2.8	3.6	4.3	3.1
5°C	63	2.9	5.0	3.7	2.9
5°C	91	1.8	7.3	4.8	4.0
5°C	140	0	9.1	4.1	4.1
10°C	7	5.6	2.6	6.6	2.6
10°C	21	4.1	5.2	5.1	3.2
10°C	42	2.4	7.2	4.6	4.3
10°C	63	0.9	7.1	3.8	4.1
10°C	91	0	8.9	3.6	4.6
20°C	7	2.5	7.1	4.9	3.8
20°C	21	0	10.2	4.4	5.1
20°C	42	0	11.9	2.9	9.5
20°C	63	0	10.9	0.6	10.9
20°C	91	0	11.7	0	10.2

[1] 1% according to the NH_4^+-N content of the basic fertilizer ASN (18.5% NH_4^+-N, 7.5% NO_3^--N)
DAT = Days after treatment.

A further advantage of nitrification inhibitors is their apparent efficiency at higher temperatures, which boost transformation of ammonium to nitrate. Bañuls *et al.* (2000b) and Serna *et al.* (2000) have studied N fertilizer use efficiency, the reduction of nitrate leaching and the behaviour of DMPP under different irrigation systems. These studies have been carried out with two-year-old Valencia orange plants in 14-l pots under greenhouse conditions. From July to December, temperatures ranged from 16 to 20°C at night and 26 to 32°C during the day. During the summer, the maximum temperature was maintained at 32°C or below using evaporative coolers. The results showed that, even under South European summer temperatures, DMPP can stabilize ammonium and can significantly delay nitrate leaching for several weeks. Satisfactory efficiency of DMPP under high temperature (25°C) was also found by Azam *et al.* (2001) in an experiment under laboratory conditions.

Of particular importance is the significant reduction of nitrous oxide (N_2O) emissions when using DMPP (Linzmeier *et al.,* 2001a), apparently without any negative effect on methane (CH_4) oxidation in the soil (Weiske *et al.,* 2001b; Zerulla *et al.,* 2001a). In a two-year field trial (Weiske *et al.,* 2001a) there was a reduction in nitrous oxide emissions of 49% compared to 70 and 30% reduction with nitrapyrin and DCD, respectively, reported by Bronson *et al.* (1992). However, the extent of any reduction fluctuates widely depending on the specific conditions during the investigation. The positive effect of DMPP on reducing nitrous oxide emissions from grassland (slurry injection plots) has been studied by Dittert *et al.* (2001). Recent studies have been made by Menéndez *et al.* (2006) with cattle slurry on a mixed clover-ryegrass sward treated with ASN + DMPP, and by Merino *et al.* (2005) on grassland after cattle slurry applications.

DMPP has been tested in various crops throughout Europe, for example in 136 field trials with agricultural and horticultural crops (Pasda *et al.,* 2001a). Nitrogen fertilizers amended with DMPP significantly enhanced fertilizer N-use efficiency. In a number of field trials, this enhanced N-use efficiency resulted in a 7 to 16% increase in yield, depending on the crop grown (Zerulla *et al.,* 2001b). Furthermore, the DMPP–amended N fertilizers offer the advantage of reducing the conventional N fertilization rate or of producing a higher yield with the same amount of N and a better crop quality (Zerulla *et al.,* 2001a). Using DMPP leads to a significant saving in on-farm labour, because the same yield is achieved with fewer N applications. Application of a high N rate with DMPP at an early growth stage does not promote excessive plant growth, which could affect water and nutrient supply and/or lead to lodging (Pasda *et al.,* 2001a, 2001b).

Linzmeier *et al.* (2001b) also recommend simplified fertilizer strategies with stabilized N fertilizers, e.g. fewer applications, larger applications at earlier growth stages, that can result in the dual benefit of increased yield and a reduced risk of nitrate losses. Also their use can lead to a reduction in the demand for labour because fewer applications are required and there is greater flexibility in their timing. For example, two applications of an N fertilizer with DMPP instead of three applications without DMPP, or only one N application + DMPP early in growth instead of two or even three dressings without the nitrification inhibitor (Ebertseder and Kurpjuweit, 1999). Improved yields have been obtained in both agricultural and horticultural crops (Pasda *et al.,* 2001a). Savings on labour costs were also reported by Casar *et al.* (2007a) in an experiment with broccoli (*Brassica oleracea* L.).

DMPP distributed under the trade name Entec® is incorporated in several N, NP, NK and NPK fertilizers (with 0.8% DMPP in relation to the total N content of the fertilizer), such as:

- Entec 46 = amide nitrogen; 46% amide-N
- Entec 26 = ammonium sulphate nitrate; 26% N (7.5% NO_3^-–N + 18.5% NH_4^+-N + 13% S)
- Entec 22 (+6+12) = 7.2% NO_3^--N + 14.8% NH_4^+-N + 6% MgO + 12% S

Table 9. Yield results from fertilizer + DMPP for different agricultural and horticultural crops (Pasda *et al.*, 2001b).

Trait	Vegetable class	Crop	Without N fertilization	N1			N2		
				Without DMPP 1 N application or 2 N applications or at seeding (radish only)	With DMPP 1 N application or 2 N applications or at seeding (radish only)	Without DMPP 1 N application or after emergence (radish only)	Without DMPP 1 N application or 2 N applications or at seeding (radish only)	With DMPP 1 N application or 2 N applications or at seeding (radish only)	Without DMPP 1 N application or after emergence (radish only)
Marketable yield (t/ha)	Directly sown vegetables	Carrots	87.5 a	89.3 a	94.2 b	–	–	–	–
		Lambs lettuce	2.3 a	3.98 b	5.9 c	–	4.2 b	6.6 d	–
		Spinach	6.7 a	21.6 c	19.2 b	–	23.5 d	21.0 c	–
		Onions	59.7 a	75.5 de	74.4 cd	76.0 de	73.0 bc	72.0 b	77.0 e
		Radish	11.4 a	25.6 b	30.2 c	29.6 c	29.9 c	32.1 c	28.6 bc
	Transplanted vegetables	Lettuce	4.9 a	32.3 b	33.7 b	–	37.8 c	37.1 c	–
		Cauliflower	10.0 a	34.8 b	38.1 bc	40.0 c	36.6 b	37.6 bc	40.2 c
		Leek	36.4 a	44.8 b	45.7 b	46.5 b	44.8 b	48.2 c	45.3 b
		Celeriac	43.2 a	71.8 bc	74.0 cd	70.1 b	71.4 b	77.8 e	74.4 d
NO_3^- concentration (mg/kg in fresh matter)	Directly sown vegetables	Spinach	98 a	1284 a	758 b	–	2128 b	1578 c	–
		Radish	693 a	1250 b	1216 b	1423 b	1313 b	1326 b	1400 b
	Transplanted vegetables	Lettuce	395 a	639 bc	603 b	–	893 d	785 cd	–
		Cauliflower	23 a	119 b	128 b	103 b	185 b	128 b	117 b
		Leek	48 a	72 ab	92 b	73 ab	101 b	72 ab	61 ab
		Celeriac	228 a	384 bc	338 ab	455 bc	514 c	448 bc	319 ab
General appearance[1]	Directly-sown vegetables	Onions	5.0 a	7.4 b	7.7 d	7.5 bc	7.6 cd	7.7 d	7.6 cd
		Radish	5.0 a	7.3 b	7.3 b	7.6 bc	7.7 bc	8.3 d	7.8 c
	Transplanted vegetables	Cauliflower	5.0 a	7.2 b	7.6 de	7.7 de	7.3 bc	7.5 cd	7.8 e
		Celeriac	5.0 a	6.5 b	6.9 d	6.9 d	6.7 c	7.0 d	7.0 d

[1] Rating: 1 very poor, 10 very good

Values in a row followed by the same letter do not differ significantly (Duncan's test, 5% level).

- Entec 25 + 15 = 11% NO_3^--N + 14% NH_4^+-N + 15% P_2O_5
- Entec Nitroka 12+0+18(+6+10) = 5.2% NO_3^--N + 6.8% NH_4^+-N + 18% K_2O + 6% MgO + 10% S
- Entec 24+8+7(+2) = 10.5% NO_3^--N + 13.5% NH_4^+-N + 8% P_2O_5 + 7% K_2O + 2% S
- Entec liquid = N fertilizer solution with DMPP; 21% N, thereof 5% NO_3^--N, 5% NH_4^+-N and 11% amide-N

Although the composition of Entec liquid is like that of an N solution, the recommended application rate of 10 l/ha for use with cattle slurry indicates that it is the presence of the active substance which is important. Fertilizers containing Entec, besides offering all the advantages of nitrification inhibitors, contain a small proportion of nitrate-N and a larger proportion of ammonium-N. Thus, the immediate nutritional needs of young plants are met and the ammonium content is protected through DMPP. The larger initial uptake of ammonium is beneficial for the energy balance within plants.

3.2.2.3. Nitrapyrin - 2-chloro-6-(trichloromethyl) pyridine and related chlorinated pyridines such as 4,6-dichloro-2-trichloromethylpyridine

Nitrapyrin belongs to the group of organic chlorine compounds and is produced exclusively by Dow Chemical in the United States and distributed by Dow Agro Sciences under the trade name N-Serve®. It was first registered in 1974 and was the first nitrification inhibitor to be approved by the Environmental Protection Agency (EPA) (Harrell, 1995). There are three crops for which N-Serve is labelled for use: maize, sorghum and wheat, the greatest use being in maize (Dow Agro Sciences, 2007).

Nitrapyrin has a very selective effect on *Nitrosomonas*. In contrast to DCD and 1-carbamoyle-3-methylpyrazole (CMP), it has some bactericidal effect, i.e. the *Nitrosomonas* bacteria are not only depressed or inhibited in their activity for a certain period, but part of the population in treated soils is killed (Huffman, 1996; *Sturm et al.*, 1994; Zerulla, 1996). The oral toxicity (LD_{50}) with N-Serve 24® is 2,140 mg/kg in female rats.

In soil and plants nitrapyrin is rapidly degraded by both chemical and biological processes into 6-chloropicolinic acid, the only significant chemical residue from its use, and, further, to N, Cl, CO_2 and H_2O. Decomposition is normally complete in 30 days or less in warm soils that are conducive to crop growth. However, nitrapyrin is very persistent in cool soils, thus providing excellent activity from fall or winter applications. When applied to warm soils measurable activity against *Nitrosomonas* is normally 6 to 8 weeks, but activity can last for 30 weeks or longer when applied to cool soils in the late fall or winter. Regular fertilizer rates can be reduced when amended with nitrapyrin, however, applying the normal rate may lead to higher yields.

Nitrapyrin can be added to any ammonium fertilizer such as ammonium sulphate, ammonium nitrate, urea, urea ammonium nitrate (UAN) solutions, anhydrous ammonia and also animal manures (slurry). However, the technical incorporation of nitrapyrin into conventional N fertilizers is difficult due to its high vapor pressure. Decreasing the vapor pressure reduces its nitrification inhibiting efficiency. Whatever type of ammonium-containing fertilizer is applied in combination with N-Serve®, the material has to be incorporated into a band or zone in the soil at a depth of at least 5-10

Picture 2. N fertilization of maize. Maize on the left received a commercial rate of anhydrous ammonia applied in spring prior to planting. Maize on the right received the same N rate plus nitrapyrin (N-Serve®). Note the difference in firing, caused by N deficiency, where the nitrification inhibitor was not used (Photo: J. Huffman).

cm during or immediately after the nitrogen fertilizer application. This is the reason why, in the United States, it is mainly applied by injection into the soil in combination with anhydrous ammonia. The recommended application rate is 1.4 to 5.6 l/ha.

With certain precautions, other possible application methods are: at planting use row or band injection, post-plant sidedress or split application on maize with knife injection, high pressure coulter injection, or application during cultivation. Research in Kentucky (Frye *et al.,* 1981) showed that nitrapyrin was also effective when sprayed directly onto urea or ammonium nitrate granules, which were surface-applied to the soil in no-tillage maize systems. The immediate proximity of nitrapyrin and ammonium in the soil at the sites of potential nitrification may facilitate its effectiveness in inhibiting nitrification even when surface-applied (Frye *et al.*, 1981).

Table 10. Grain yield of no-tillage maize as affected by nitrapyrin in Kentucky (Frye, 2005).

Nitrogen rate (kg/ha)	0	90	135	180
	Yield (t/ha)			
Without nitrapyrin[1]	3.41	5.96	5.13	7.45
With nitrapyrin[1]	–	7.91	8.29	7.73

[1] Nitrapyrin sprayed directly onto granular ammonium nitrate at rate of 0.56 kg/ha and surface-applied broadcast.

The active ingredient is formulated as a liquid product: N-Serve 24®-N stabilizer with two pounds active ingredients per gallon (240 g/l), for use with anhydrous ammonia, liquid fertilizers, liquid manure and urea.

For mixing nitrapyrin/N-Serve, two methods are recommended: (i) the premix method, recommended for use with liquid manure and (ii) the sequential method, recommended for use with liquid fertilizer.

A new nitrogen stabilizer called Instinct™ contains nitrapyrin as the active ingredient. It is labelled for use with urea ammonium nitrate (UAN) for spring application and for use with spring and fall applications of liquid manure. It is produced as an encapsulated formulation, which prevents evaporation losses of nitrapyrin for up to ten days when applied on the soil surface. During this period it may be incorporated mechanically or by 10-15 mm of rain (Dow AgroSciences, 2009; Ferguson, 2010; Schwab and Murdoch, 2010).

3.2.2.4. Ammonium-thiosulphate (ATS)

Ammonium-thiosulphate [$(NH_4)_2S_2O_3$] as a solid contains about 19% N and 43% S. Normally as a fertilizer it is used as an aqueous solution (60%) containing 12% N and 26% S. It is an excellent sulphur source for plants. However, ATS also inhibits nitrification and was classified as a nitrification inhibitor in 2000 by AAPFCO. It is mainly used in combination with DCD to reduce the amount of DCD required. ATS has also been tested as a urease inhibitor but it does not have the efficiency of NBPT and thus has little, if any, potential value for decreasing ammonia volatilization from urea fertilizers.

3.2.2.5. 1H-1,2,4-triazole

In practice, triazole is applied only in combination with other nitrification inhibitors such as DCD or 3-MP. When triazole is used, the quantity of DCD can be substantially reduced, the hazardous side effects of 3-MP can be reduced, and the tolerance of plants to triazole can be improved when used with DCD. The main advantage, however, is a significant synergistic effect with other inhibitors (Michel *et al.*, 2004).

3.2.2.6. 3-methylpyrazole (3-MP)

Since the late 1960s, CMP and its main metabolite 3-MP, have been widely tested in Eastern Europe and the Former Soviet Union where it is called KMP. As with nitrapyrin, CMP had to be incorporated into the soil during or immediately after application. Apparently, this product has never been marketed and used in agriculture. One exception is the inhibitor 3-MP, which is used in combination with other nitrification inhibitors (e.g. triazole) added to UAN (Wozniak, 1997).

3.2.2.7. 2-amino-4-chloro-6-methyl-pyrimidine (AM)

AM is a highly volatile substance, soluble in water and in anhydrous ammonia. Unfortunately, only limited field tests have been carried out to test its effectiveness as a nitrification inhibitor.

Nitrification inhibitors used in Japan

In Japan, in addition to DCD, guanyl thiourea (ASU) and N-2,5-dichlorophenyl succinanilic acid (DCS) are used. Of sporadic use are: 2-amino-4-chloro-6-methyl-pyrimidine (AM), 2-mercapto-benzothiazole (MBT), sulfany-amidothiazole (ST) and 4-amino-1,2,4-triazole (ATC) (Tachibana, 2007).

3.2.2.8. Neem- or 'nimin'-coated urea

The efficiency of neem or nimin, when applied to rice in the form of neem- or 'nimin'-coated urea, has been tested by Ketkar (1974), Gour *et al.* (1990), Tomar and Verma (1990), Yadav *et al.* (1990), Vyas *et al.* (1991), Joseph and Prasad (1993), and Vimala and Subramanian (1994). The results are contradictory (See chapter 3.1.2.5.)

3.3. Characteristics of urease inhibitors

3.3.1. General

The use of urease inhibitors should be part of fertilizer best management practices (FBMPs) as should the use of nitrification inhibitors. In world agriculture, urea is the most widely used N fertilizer, particularly in the tropics. Of the world total of 100.9 million metric tonnes (Mt) of N used in 2007/08, about 53.9 Mt (approximately 53.4%) were as amide-N in the form of urea (not including UAN and other fertilizer products containing amide-N) (IFA, 2010). This underlines the need to manage urea as efficiently as possible.

Urea is not an 'optimal fertilizer' in terms of plant N nutrition when compared to calcium ammonium nitrate (CAN), ammonium nitrate (AN)[8] and others such as ammonium sulphate nitrate (ASN)). However, it has a number of advantages in cost, handling and application. The leading position of urea in the world N fertilizer market is mainly due to its low production cost and because of its high N content (46% N), the costs associated with its transport and storage are relatively small also. Furthermore, there is no fire and explosion hazard. Its solubility, however, results in a degree of hygroscopicity. It is suitable for the production of compound fertilizers and also for application in the form of prills, granules, in solution or coated.

The main disadvantage of urea as a N fertilizer is the large losses in the form of ammonia (NH_3). Expressed in percentage of the N applied, these losses can range from 20% (Bundy, 2001), 21% (Basten *et al.*, 2005), up to 47% (Watson, 2005), or between 15 and 60% (Cantarella *et al.*, 2005). On grassland such losses can be as large as 50% and more of the quantity of ammonia applied (Amberger, 1996). Losses of ammonia occur at pH above 7.0. When urea (or excreta/urine on grassland) is applied, hydrolysis produces alkaline conditions when the fertilizer (or manure) gets in contact with soil. Therefore, such losses from applied urea will occur when urea-containing fertilizers are

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[8] *A 50/50 combination of nitrate and ammonium generally represents the optimum in plant N nutrition.*

surface-applied and not incorporated immediately after application. Bundy (2001) lists the factors responsible for these losses:

- no rainfall or irrigation after applications,
- crop residue on the soil surface,
- high temperatures,
- high soil pH,
- little clay and organic matter in the soil (low cation exchange capacity),
- application of urea to initially moist soil followed by drying conditions.

If urea or UAN solution is not incorporated into the soil, by rainfall or tillage within 72 hours of application (especially with no-till, high residue conservation tillage and minimum tillage), significant losses can be expected. If there is no rainfall within five days of urea application, significant losses can be expected. When at least some rainfall – particularly in spring – occurs after application, losses of ammonia will be considerably reduced. Ammonia losses from applied urea will also occur when urea is used on flooded rice (Watson, 2000). Ammonia losses from urea application are not only a substantial economic loss for farmers, but ammonia lost to the atmosphere will be deposited by rain to land and water, causing acidification and eutrophication.

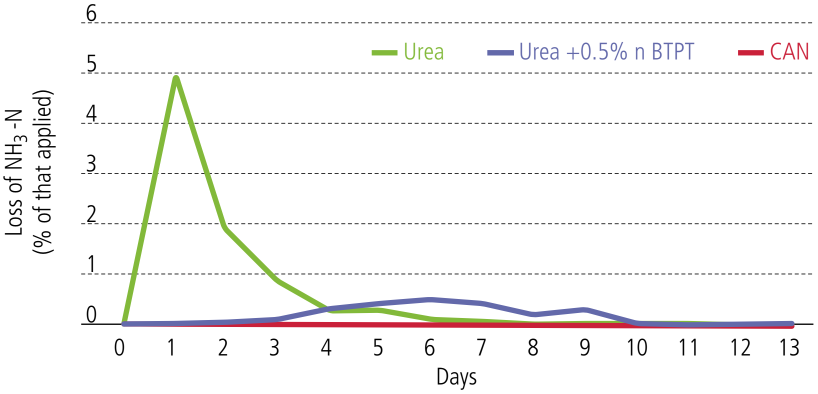


Figure 12. Daily loss of ammonia-N (Adapted from Watson, 2005).

Though plants can take up and assimilate urea directly (Watson and Miller, 1996) shortly after application, the major part dissolves in soil water and is subsequently hydrolyzed. When amide-N, as in urea, UAN or in some NPK fertilizers, is applied to the soil, it is transformed relatively rapidly (within a few days) through the activity of the ubiquitous soil bacterial enzyme urease to ammonia, CO_2 and H_2O (Amberger, 1996, 2006). In the first step, urea is transformed into the unstable ammonium carbamate, and then to ammonia.

$$\underset{\textit{urea}}{NH_2 - CO - NH_2 + H_2O} \xrightarrow{\textit{urease}} 2\,NH_3 + CO_2$$

The full equation is:

$$CO(NH_2)_2 + H_2O \longrightarrow \underset{\textit{(ammonium carbamate)}}{NH_2COONH_4} \longrightarrow 2NH_3 + CO_2$$

Urease activity increases as temperature increases, thus hydrolysis is normally completed within ten days at a temperature of 5°C and within two days at a temperature of 30^{O}C (Vilsmeier and Amberger, 1980). Hydrolysis is also highly correlated with the organic matter, total N and cation exchange capacity (CEC) of the soil; increasing as these factors increase.

This transformation has two major drawbacks:

- It leads to – sometimes very high – volatilization losses of ammonia if urea is surface-applied – 'surface-phenomenon' (Amberger, 1996; Grant *et al.,* 1996b; Watson *et al.,* 1994a). Such ammonia losses will occur particularly on soils poor in sorption capacity, without plant cover and with a high pH. Long droughts at high temperatures also favour ammonia losses.
- It can cause severe germination and seedling damage due to ammonia and nitrite (NO_2^-) (Watson and Miller, 1996) when the amount placed near the seed is too large (Grant *et al.,* 1996a). The protonization of ammonia to ammonium leads to a slight rise in pH value ($NH_3 + H_2O \rightarrow NH_4^+ + OH$) (Amberger, 2008b).

Applying a urease inhibitor with urea/urea-containing fertilizer will prevent or delay for 7 to 14 days the transformation of amide-N to ammonium-N. It is particularly beneficial on soils where ammonia losses from applied urea are large, on soils where incorporation of urea into the soil is difficult or impossible, where urea is not washed into the soil due to drought and where cultivation of the soil is minimal or nil (no-till), and where, in consequence, organic matter has accumulated (Watson, 2005).

An important and relatively new field of application for urease inhibitors is on cattle or dairy farms, where cattle excreta is a main source of ammonia emissions (Leinker *et al.,* 2005; Varel *et al.,* 1999). Feedlot cattle normally retain less than 20% of their dietary N intake. Normally, 60 to 80% of the excreted N is lost either through nitrate leaching or ammonia volatilization. Ammonia volatilization from cattle and pig excreta contributes to odour, adverse environmental impact and loss of valuable nutrients (Amberger, 1996; Watson, 2005). Urease inhibitors (NBPT and others) have been shown to delay the hydrolysis of urea in slurry, urine or cattle excreta, to reduce ammonia emissions from livestock facilities and to improve the N: P ratio in the organic manure for plant growth (Varel *et al.,* 1999).

The use of urease inhibitors added to urea or to UAN solutions increases their efficiency and reduces ammonia volatilization when surface applied on arable land, grassland and on flooded rice (Byrnes *et al.,* 1995) and decreases the toxicity of seed-placed urea (Kincheloe and Sutton, 1996). For the farmer, urease inhibitors offer greater flexibility in managing the application of urea/UAN to minimise volatilization losses. They also offer more options for the timing of N applications and for conservation tillage programmes. Up to now, there is no urease inhibitor that is as easy to handle as a granular fertilizer (Weber *et al.,* 2004b). Currently, the only marketed urease inhibitor, Agrotain, is available in either a liquid or dry form.

3.3.2. Types of urease inhibitors available for application

3.3.2.1. NBPT - N-(n-butyl) thiophosphoric triamide – Agrotain®

NBPT is the normal butyl derivative of thiophosphoric triamides. Besides hydroquinone in China and very limited regional use of neem extracts in India, NBPT is at present the only urease inhibitor of commercial and practical importance in agriculture. Sold under the trade name Agrotain®, NBPT was first marketed by IMC-Agrico in the United States in 1996. In 2000, the Lange-Stegmann Company purchased the Agrotain-related assets and licenses and a separate company, Agrotain International, was created to manage the worldwide development and marketing of Agrotain. Agrotain has been registered in several countries, Canada, United States, Brazil, Australia, United Kingdom, and the European Union and it is available in more than 70 countries where Agrotain International has a license or has sold Agrotain Technology. Licensed partners include Fertipar Fertilizantes do Paraná. in Brazil, Incitec Pivot in Australia, Summit-Quinphos in New Zealand, Philom Bios in Canada and Yara International in Europe.

Agrotain, is a non-aqueous, liquid formulation of NBPT. It can be injected into molten urea before granulation, applied to the surface of granules or prills in batch- or continuous-processes, or added to a UAN solution. Specific, updated information about rates, mixing instructions and uses are described in the Product Information Guidebook or on the Agrotain International website.

NBPT is a non-toxic compound with an oral LD_{50} of 1,000 to 4,000 mg/kg. The Ames Tests (*in vitro* mammalian cell gene mutation and *in vitro* mammalian chromosome damage) were both negative (Wilkinson, 1996). The product has received EPA approval. It is registered as a TSCA (Toxic Substances Control Act) substance. It is also registrered as an 'EC fertilizer' under the fertilizer legislation of the European Union and has registration in several other countries. NBPT can – like urea – also be taken up directly by the plants (Watson and Miller, 1996).

The use of NBPT has not been shown to have environmental or personal safety risks. No special precautions or warnings are required for NBPT for end-users although basic safety procedures for fertilizer handling and use should always be followed. NBPT targets an enzyme that exists independent of soil organisms and it does not produce toxic or static effects on microorganisms (Agrotain International internal registration documents).

NBPT degrades into its constituent elements: N, P, S, C and H. (Byrnes *et al.,* 1989b), and there is no evidence of any long-term adverse effect on grass production with repeated applications of NBPT-treated urea, nor is there any indication that its efficacy declined when used repeatedly on the same soil (Watson *et al.,* 1998).

NBPT has consistently demonstrated its ability to inhibit the activity of the enzyme urease (Gardner, 1995; Marking, 1995). Its urease inhibiting activity in the soil is associated with the activity of its derivative, the oxygen analogue, *N*-(*n*-butyl) phosphoric triamide (Phongpan *et al.*, 1995). It prevents N losses by temporarily inhibiting urease activity (Gardner, 1995; Marking, 1995). Slowing the urease-catalyzed transformation of urea to ammonium minimises ammonia losses and allows time for absorption or dissipation of the N forms into the soil. Reductions in ammonia volatilization from urease can range from 55 to over 99% (Watson *et al.,* 1994a), with a typical volatilization reduction of 75 to 80% in the field environment. NBPT provides the greatest agronomic benefit when urea-based fertilizers are surface-applied because ammonia losses are significantly reduced and there are opportunities to reduce time- or resource-consuming operations. For example, tillage or irrigation operations necessary to incorporate straight urea can be avoided, which could save time and fuel. NBPT can be applied pre-emergence, pre-plant, side-dress, top-dress or other post-planting applications. The amount of Agrotain applied is in the range 400 to 1,100 ppm NBPT; the actual amount is adjusted to the cultural practices for the crop being grown and the local conditions. Urea treated with NBPT at the recommended rate inhibits the activity of the enzyme urease, regardless of the amount of urea applied. In dry bulk blends, the urea should be pretreated prior to the introduction of other fertilizer materials. The Product Information Guidebook available from Agrotain International provides details and recommendations for treating urea or UAN solutions.

According to Watson *et al.* (2008), the half-life of NBPT is about six months for surface-treated urea and more than one year if NBPT is injected into the melted urea before granulation. Others have found shorter half-lives (Kincheloe, 1997b), depending on conditions, in particular temperature. In current practice, Agrotain is mostly applied as a surface treatment (of urea granules or prills) shortly before application of urea; therefore, the half-life of NBPT does not affect commercial applications.

When large amounts of urea are incorporated into the soil, seed-placed urea may adversely effect germination and cause leaf-tip burn because of excessive ammonia concentrations. This can be avoided by using a urease inhibitor (Malhi *et al.,* 2003; Wang *et al.,* 1995). Watson and Miller (1996) found that although NBPT-amended urea affected plant urease activity and caused some leaf-tip scorch, the effects were transient and short-lived.

For solid urea, NBPT can be added before or after granulation. Urea liquor can be directly injected with Agrotain just before granulation/prilling to give a homogeneous distribution throughout the solid urea granule. Alternatively, solid urea can be treated before or during a batch or continuous mixing operation. The rubbing of urea granules during the mixing operation is sufficient to evenly distribute NBPT across all granules/prills. This 'self-distribution' of NBPT in the mixing process avoids the need to treat each granule/prill individually. The liquid formulation of Agrotain does not contain water, so the handling and storage properties of urea are not degraded by the treatment. There is no difference in the performance of NBPT when dispersed inside or applied on the surface of urea granules.

For liquid urea formulations like UAN, NBPT is simply added to the UAN solution just before application. Storing the treated UAN solution for several days is not recommended because the product could begin to degrade if stored in the presence of water.

NBPT-stabilized urea can be applied as a straight N fertilizer in solid or liquid form. Incorporation is unnecessary even on alkaline soils; and it can also be used for second and third dressings in cereal crops on light sandy soils and on grassland later in the growing season. In a soil incubation study, using a wide range of soil types, the effectiveness of NBPT in lowering ammonia volatilization was greatest in soils with a high pH and low buffering capacity (NBPT decomposes faster in acid soils) (Watson *et al.,* 1994b). Because there are larger ammonia losses from non-amended urea on alkaline soils, NBPT clearly has considerable potential to improve the efficiency of urea for temperate grassland. Furthermore, there is no evidence of any long-term adverse effect on grass production with repeated applications of NBPT-amended urea over a three-year period, and no indication that its efficacy to reduce ammonia losses from urea-treated swards declined when used repeatedly on the same soil (Watson *et al.,* 1998).

Products from Agrotain International for use in agriculture include:

- Agrotain – liquid, non-aqueous,
- Agrotain Dry – dry concentrate,
- Agrotain Plus – dry concentrate,
- Super U – granulated urea with incorporated Agrotain Plus.

Agrotain Plus is a dry concentrate containing the urease inhibitor NBPT plus the nitrification inhibitor DCD. It is easily mixed into UAN solution and is compatible with most herbicides and surfactants. It reduces volatilization losses of ammonia as well as N losses from denitrification and leaching. It offers improved environmental performance through reduced nitrous oxide (N_2O) emissions and less nitrate leaching to ground water. It is formulated as a dry stabilized N concentrate for use with UAN fertilizer (28, 30 or 32%).

Super U is granulated urea containing the urease inhibitor NBPT plus the nitrification inhibitor DCD. Super U is officially classified as a stabilized nitrogen fertilizer.

Picture 3. Spreading of urea granules treated with Agrotain. Inhibitors are not affected by mechanical abrasion which is advantageous with high-throughput applications (Photo: Agrotain International, Wade, 2008).

Results from 50 field experiments from 2002 to 2004 in France, Germany, Italy, Spain and the United Kingdom on winter wheat and maize testing NBPT confirmed enhanced N-use efficiency. The optimium concentrations of NBPT for maximum efficacy for the majority of growing conditions on different soils and crops in Europe is between 0.04% and 0.1% NBPT (Basten *et al.*, 2005). On average, in 21 field trials commissioned by Yara in Germany during 2003 and 2004, N was applied at 190 kg/ha to winter wheat, split over two or three applications, the better availability of N in urea + NBPT increased grain yield by 2% and the protein content. Overall, N use efficiency of urea + NBPT was 7% higher compared to urea without inhibitor (Basten *et al.*, 2005).

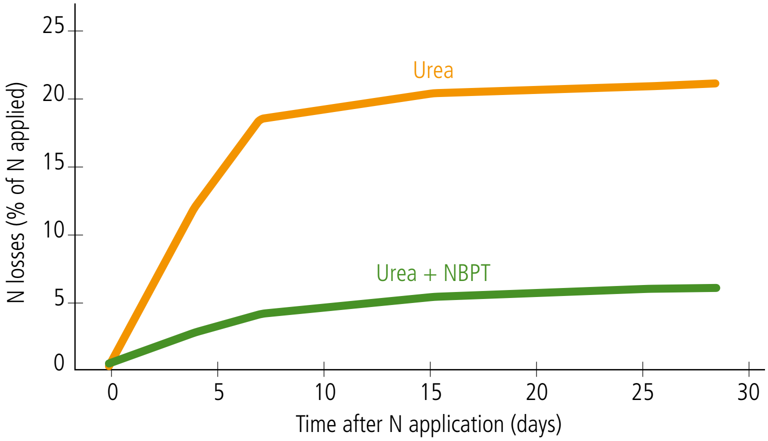


Figure 13. Reduction of N-volatilization (Adapted from Basten *et al.*, 2005).

Decreased nitrogen losses and reduced toxicity from free ammonia resulted in larger yields and better crop quality when urea + inhibitor was compared to urea without inhibitor. In Brazil, yield of tropical grassland was increased by 15%. Cantarella *et al.* (2005) measured a reduction in ammonia volatilization of 30 to 90% through the addition of NBPT to urea in Brazil.

Table 13. shows that grain yields obtained with urea were significantly lower than those given by urea treated with NBPT or AN. The average yield for all sites was 7.3 t/ha, the addition of NBPT to urea increased grain yield by 0.35 t/ha as compared to the urea alone treatment; the corresponding yield increase obtained with ammonium nitrate was 0.47 t/ha. This study shows that NBPT may be an option to reduce ammonia losses and increase grain yield when urea is used for maize production in subtropical areas of Brazil.

Table 11. Ammonia loss due to volatilization following surface application of urea and percentage reduction in loss due to the addition of NBPT. Summary of eight field experiments on soils covered with plant residues (Adapted from Cantarella, 2005).

Crop/Location	Ammonia volatilization (Percentage reduction compared to urea)	
	Urea	Urea + NBPT
	% of applied N	
Maize Mococa	45	24 (47)
Maize Rib. Preto	37	5 (85)
Maize Mococa	64	22 (65)
Maize Pindorama	48	34 (29)
Pasture 1	18	6 (69)
Pasture 2	51	22 (56)
Pasture 3	18	3 (83)
Pasture 4	18	2 (89)
Average	37	15 (60)

Table 12. Ammonia loss due to volatilization following surface application of urea and percentage reduction in loss due to addition of NBPT. Summary of field experiments on soils covered with plant residues (Cantarella, 2008).

Location	Month	Prevalent weather condition	NH_3 losses from			% reduction by NBPT
			AN or AS	Urea	Urea-NBPT	
			% of applied N			
Rib. Preto	Jun	dry	0.3	15.2	11.2	26
Araras II	Aug	dry	0.4	16.4	13.4	18
Iracemapolis	Sep	dry	0.2	25.4	15.2	40
Araraquara	Oct	dry	0.2	25.1	21.3	15
Araras	Nov	rainy	0.1	11.2	7.2	36
Jaboticabal	Nov	very rainy	0.1	1.1	0.8	-
Pirassununga	Dec	rainy	0.1	7.2	1.6	78
Average 6 locations			0.2	16.8	11.7	30

Other results from Cantarella *et al.* (2009) show yield response from addition of Agrotain to urea in comparison to urea alone or ammonium nitrate as a non-volatile standard.

Table 13. Maize grain yield at seven sites responsive to nitrogen in Brazil. Fertilizers were side-dressed surface-applied to no-till maize (Cantarella *et al.*, 2009).

N source	Yield[1]	Yield increase
	kg/ha	
Urea	7054 a	-
Urea+NBPT	7405 b	351
Ammonium nitrate	7526 b	472

[1] Means followed by the same letter do not differ (Tukey, $p \leq 0.05$)

Improving the performance of urea is important in relation to new agricultural production techniques. Burning sugar cane fields can simplify harvest and tillage operations, but is increasingly banned in large areas of Brazil. Large amounts of surface residue (9 to 15 t/ha dry matter) often impedes tillage and favours surface application of fertilizers like urea, while also promoting potential volatilization losses. Cantarella *et al.* (2009) showed that urea treated with NBPT could reduce volatilization losses by an average of 30% over six field sites. Further research with NBPT rates and fertilizer timing may be useful to further reduce volatilization of ammonia and improve yields with this production practice.

The recommendations for use of urea fertilizers containing NBPT should be based on the nitrogen recommendations for the crop and fertilizer best management practices (FBMPs). Where farmers currently over-apply urea to compensate for volatilization losses, NBPT could enable lower application rates.

3.3.2.2. N-phenylphosphoric triamides (2-NPT)

The urease inhibitor 2-NPT is under registration procedures in the European Union, after submission by SKW Piesteritz, following registration in Germany. Schuster *et al.* (2007) carried out 25 field trials using 2-NPT in winter cereals in 2005 and 2006 in different locations with different soil types and growing conditions. Urea amended with 2-NPT was compared with urea alone and calcium ammonium nitrate (CAN). Effects on N uptake, N recovery efficiency, N use efficiency, crude protein content and yield were measured. A statistically significant increase in N uptake by cereals from urea amended with 2-NPT compared to urea alone was obtained in 10 of the 13 (2005) and 11 of the 12 (2006) trials. Although the crude protein content was increased by 0.5-2.3% in 21 of the 25 trials, yield was increased in only three trials in 2005 and four in 2006. The results indicate a high biological efficiency of 2-NPT when applied at low concentrations: 0.05-0.10% on a N basis and, 0.023-0.046% on a product (urea) basis and a possible indirect indication of reduced ammonia losses.

3.3.2.3. Hydroquinone (HQ)

Hydroquinone (1,4 dihydroxybenzol) has been known as a urease inhibitor since 1933 (Quastel, 1933) and this was confirmed by Conrad (1940).

A disadvantage of hydroquinone is its apparent toxicity, with LD_{50} of 300 to 1,300 mg/kg body weight, and its classification as a mutagenic and carcinogenic substance. Another disadvantage is its negative effect on germination. Early studies on the urease inhibiting effect of hydroquinone by Bremner and Douglas (1971, 1973) were followed by those of Bremner and Krogmeier (1990) who tested hydroquinone at rates of 2.5 mg/g soil on a range of soils and showed that it had a significant negative effect on germination of maize and wheat seeds. Kiss and Simihaian (2002) comprehensively reviewed studies with hydroquinone as a urease inhibitor. They pointed out that large amounts of hydroquinone are used in China where it is recommended to apply it in combination with DCD (Xu *et al.*, 2000). Xu *et al.* (2005b) concluded from rhizobox studies that urea amended with DCD or DCD + HQ can improve crop growth and reduce N losses as nitrous oxide in rice cultivation. Khanif and Husin (1992) did not find significant effects of hydroquinone in direct seeded and transplanted rice compared to urea + DCD. Urea amended with hydroquinone did not have any significant effect on yield, N uptake and N-use efficiency. Hydroquinone is photosensitive and this has to be taken into account when urea is treated with hydroquinone.

3.3.2.4. Phenyl phosphorodiamidate (PPD/PPDA)

Limited research has been made with PPD and there is no product available for practical application.

4. Advantages and disadvantages of slow- and controlled-release fertilizers and nitrification and urease inhibitors

4.1. Advantages

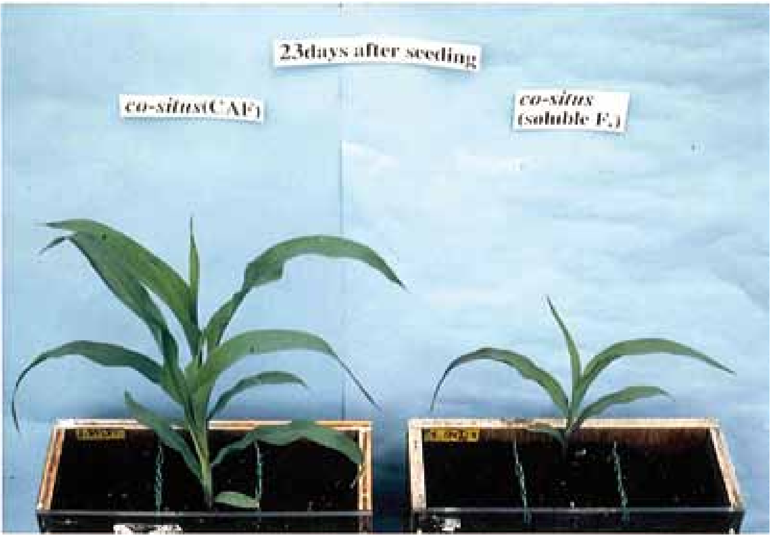
4.1.1. Slow- and controlled-release fertilizers

The use of controlled-release fertilizers decreases nutrient losses and enhances nutrient use efficiency (NUE). A decrease of 20 to 30% (or more) of the recommended application rate of a conventional fertilizer is possible when applying controlled-release fertilizers while maintaining the same yield. In 1999, the Japanese Ministry of Agriculture, Forestry and Fishery (MAFF) recommended the replacement of conventional fertilizers with smaller amounts of controlled-release fertilizers (Tachibana, 2007).

The application of controlled-release fertilizers may reduce toxicity, particularly to seedlings, that can result from the application of soluble conventional fertilizers through high ion concentrations inducing osmotic stress and specific damage to plants at different growth stages. They may also reduce lodging and injury from ammonium ions. Thus, controlled-release fertilizers, especially those that release nutrients in a sigmoidal pattern, contribute to improved agronomic safety, permitting co-situs application (Aglukon, 1992, 1993; Grace Sierra, 1993, 1994; Shaviv, 2005; Shaviv and Mikkelsen, 1993a; Shoji, 2005; Sierra, 1991a, 1991b; Tachibana, 2007). The application of coated fertilizers, particularly sulphur-coated types, may increase the acidity of the soil. However, acidification may favour the uptake of phosphorus and iron (Fe).

Controlled-release fertilizers make it possible to meet the full nutrient requirements of crops grown under plastic covers, and multiple cropping by making a single fertilizer application. The possible reduction in toxicity and the salt content of substrates, could allow substantially larger amounts of fertilizer to be applied ('depot fertilization'), reducing the frequency of application. This results in greater convenience in fertilizer use and significant savings in labour, time and energy. These factors constitute the greatest advantage for the majority of present consumers of slow- and controlled-release fertilizers, such as the large proportion of 'side-business' and aged farmers in Japan. In addition, they are recommended especially in no-till farming, with crops such as rice and maize.

Controlled-release fertilizers improve the uptake of nutrients by plants through synchronized (preferably sigmoidal) nutrient release, and significantly reduce possible losses of nutrients, particularly of nitrate-N by leaching and volatilization losses of ammonia. This substantially decreases the risk of environmental pollution (Koshino, 1993; Ma *et al.,* 2007; Mikkelsen *et al.,* 1994; Rietze and Seidel, 1994; Shaviv, 1996, 2005; Shoji, 2005; Wang, 1996; Zhang, 2007; Zhang *et al.,* 2001). Their use also contributes to



Picture 4. Growth of maize plants fertilized with polyolefine-coated controlled-release N fertilizer (left) and with a conventional N fertilizer (right). The maize plant fertilized with the conventional N fertilizer shows serious salt injury (Photo: Konno, 1999).

a reduction in N_2O emissions (Chu *et al.,* 2004; Shaviv and Mikkelsen, 1993b; Shoji and Kanno, 1993, 1994; Shoji *et al.*, 2001).

A reasonably good prediction of nutrient release is possible with controlled-release fertilizers coated with hydrophobic materials, particularly polymer-coated fertilizers because they are less sensitive to soil and climatic conditions (Shaviv, 1996, 2005; Shoji, 1999, 2005). Their linear or sigmoidal temporal nutrient release synchronizes advantageously within certain limits with the plant's nutrient requirements. Therefore, they can contribute to advanced fertilizer management programmes and to innovative, high technology farming systems such as no-till farming with single *co-situ* fertilizer application (Fujita, 1996a; Shoji, 2005; Tachibana, 2007).

The reasonable good prediction of long-term nutrient release from some types of controlled-release fertilizers makes it possible to develop software progammes for their use on different crops and for various soil and growing conditions. Such software programmes can be very reliable for polymer-coated fertilizers, because, there is a reasonable good correlation between temperature, release of nutrients and plant growth (Shoji, 2005).

In intensive vegetable production, slow- or controlled-release fertilizers offer one-time application of the fertilizer with multiple cropping, e.g. multi-cropping of spinach, lettuce, Chinese cabbage, broad beans, broccoli, etc. in Japan (Tachibana, 2007). They also give the possibility to enhance the quality and safety of vegetables and farm produce: e.g. low protein in rice, high protein in wheat, high sugar and ascorbic acid with low nitrate and oxalic acid in leafy vegetables (Shoji, 2005; Tachibana, 2007).

4.1.2. Nitrification inhibitors

Nitrification inhibitors delay the nitrification (and indirectly denitrification) of ammonium from soil organic matter and mineral fertilizers. This is of great economic importance for agricultural farm management and crop production, as well as protection of the environment.

The use of N fertilizers amended with a nitrification inhibitor improves N-use efficiency. It makes it possible to either reduce the amount of applied N without loss of yield, or to maintain the amount of applied N with a corresponding increase in yield. Farmers may be able to reduce loss of nitrate-N by improved management practices. For example, by monitoring the plant-available nitrogen content in the soil and adapting fertilizer N applications accordingly and choosing the most appropriate type of N fertilizer. They may use GPS and special equipment for different forms of fertilizer application from side-dressing to 'spoon feeding', injection of liquid fertilizer, and foliar application (Nielsen, 2006).

Depending on the weather conditions, the optimum N fertilizer rate varies from season to season, making it very difficult to predict each year the optimum amount of N fertilizer to apply.

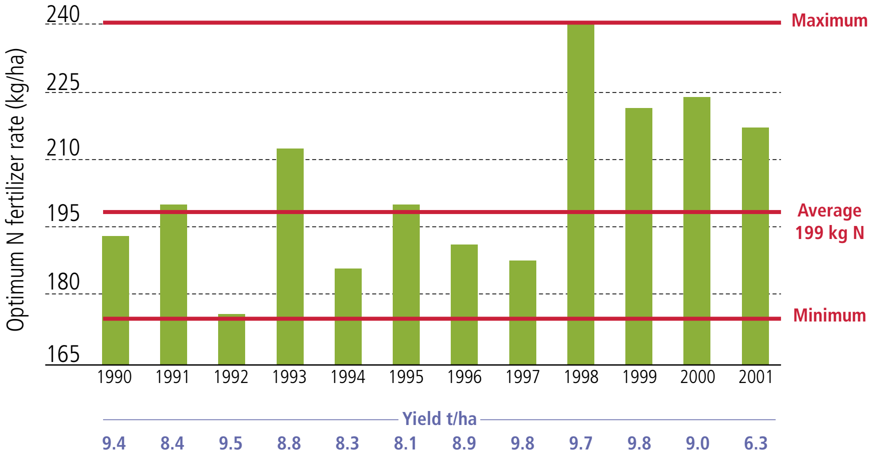


Figure 14. Yearly optimum N fertilizer rates on winter wheat. Long-term trial at Rothamsted, UK (Adapted from Lammel, 2005).

The use of N fertilizers amended with a nitrification inhibitor, means that the number of applications can be decreased, resulting in a saving of labour, without increasing N losses. Grant (2005) lists the following advantages: (i) substitute for capital investment (stabilized fertilizers can be used with current or simplified equipment), (ii) reduce on-farm labour (replace extra applications), (iii) increase flexibility of application timings, and (iv) avoid potential to miss the 'window of application'. By delaying nitrification, the nitrate content of plants is reduced, and the nutritional quality of vegetables and fodder plants is improved (Hähndel and Wehrmann, 1986; Montemurro *et al.*, 1998).

Nitrification inhibitors favour the partial ammonium nutrition of plants because plants need less energy to incorporate ammonium into amino acids; if nitrate has to be reduced first to ammonium this requires energy (Amberger, 2008b). The possible direct incorporation of ammonium into protein has a positive effect on the synthesis of polyamines, cytokinins and gibberellins (Pasda *et al.*, 2001b). Sattelmacher and Gerendás (1999) and Gerendás and Sattelmacher (1995) discuss the influence of ammonium on phytohormones in plants and on the formation of polamines.

Advantages of ammonium and nitrate nutrition (Wissemeier, 2008)

Advantages of ammonium nutrition:

- Low energy consumption for nutrient uptake, increased N uptake even at low root-zone temperature;
- Low energy consumption for N assimilation in the plant, because ammonium is already reduced;
- Increased synthesis of the phytohormones like cytokinin, and larger content of polyamines.

Advantages of nitrate nutrition:

- It is a low energy containing, less reactive form of N storage in plants;
- It functions as an osmoticum in cells;
- It has advantages for the electrical balance in the cells; NO_3^- acts as a cation (+) carrier.

Plant productivity is, however, better with a mixed nutrition of nitrate and ammonium:

- Mixed nutrition means use of synergies;
- Because both nitrate and ammonium have their specific advantages and disadvantages.

The addition of a nitrification inhibitor with a N fertilizer can improve the mobilization and the uptake of phosphate and micronutrients in the rhizosphere, because it delays ammonium oxidation (Amberger, 1991b; Rahmatullah *et al.*, 2006; Sarker and Jones, 1982).

The inhibition of ammonium nitrification significantly reduces losses of nitrate by leaching to surface and ground water bodies, while maintaining N availability to crops (Grant *et al.*, 1996b; Gutser, 2006; Watson *et al.*, 1994a). By avoiding or reducing N losses, nitrification inhibitors protect the environment and significantly improve the use efficiency of applied N fertilizers. During the processes of nitrification of ammonium and denitrification of nitrate by soil microbes, dinitrogen (N_2), nitrogen oxides (NO_X) and nitrous oxide (N_2O) are formed (Amberger, 1996, 2006). By using nitrification inhibitors the emission of these gases can be decreased (Bronson and Mosier, 1993, 1994; Bronson *et al.*, 1992; Bundesrat 1996; Delgado and Mosier, 1996; Kumar *et al.*, 2000). Nitrogen oxides can be deposited from the air to the ground and water bodies in the form of dilute acids. Nitrous oxide is an important greenhouse gas having a role in climate change through the absorption of light rays in the atmosphere, and the formation of acid deposition. In the stratosphere, it reacts with ozone (O_3), thus contributing to the depletion of the protective ozone-layer (Amberger, 1996). A reduction of up to 60%

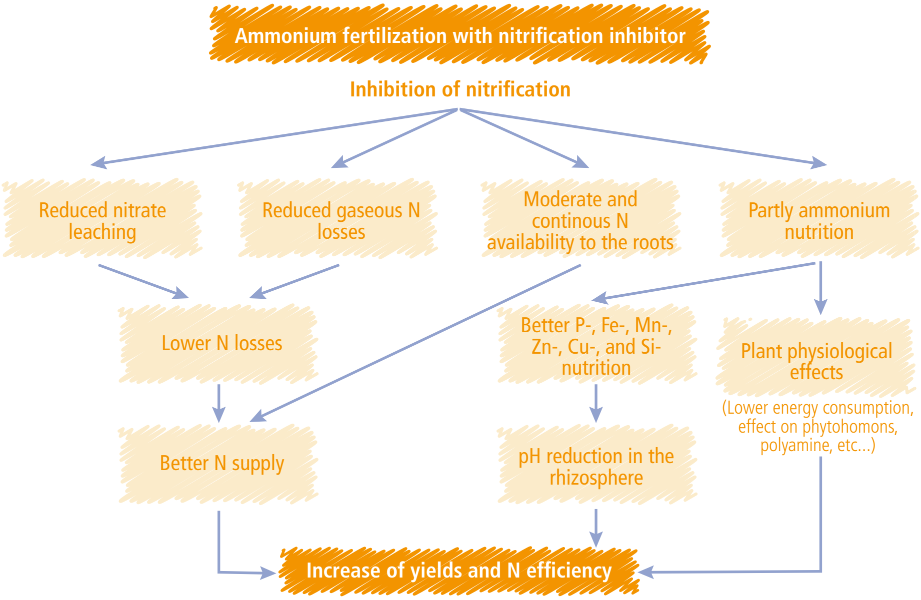


Figure 15. Ammonium nutrition with nitrification inhibitor (Adapted from Wissemeier, 2008).

of nitrous oxide lost to the atmosphere was determined by Kumar *et al.* (2000) in a laboratory experiment using urea + DCD in comparison to urea alone. The effect of soil moisture, fertilizer type and temperature on losses of nitrous oxide and nitrogen oxides from grasslands were investigated by Del Prado *et al.* (2006)

Nitrification inhibitors (DMPP) apparently depress the release of methane (CH_4), a greenhouse gas, from the soil. It is produced through microbial fermentation of cellulose under anaerobic conditions. Mitigation of its release is another positive contribution of nitrification inhibitors (Amberger, 2008b; Bronson and Mosier, 1994; Ottow *et al.*, 1999; Weiske *et al.*, 2001a, 2001b, 2001c).

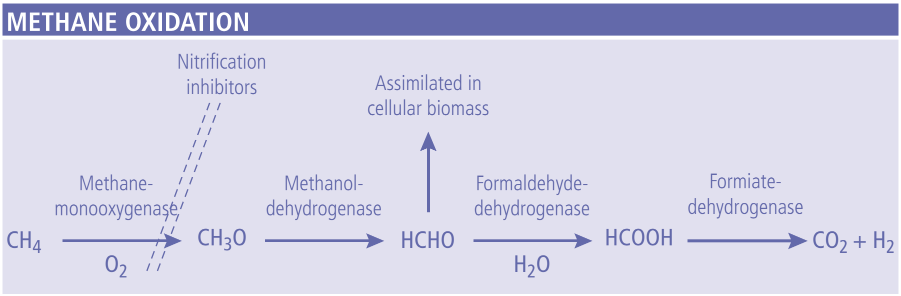


Figure 16. Methane oxidation pathway and possible blocking due to nitrification inhibitors (Adapted from Weiske *et al.*, 2001a).

On grasslands, especially grazed pastures, farmers have practically no management practice that will decrease N losses originating from the soil or from animal urine and manure, particularly where animals congregate at watering or milking places, or generally from urine/manure patches. The regular application of a nitrification inhibitor is the most promising method to limit losses of N by leaching and emission to the atmosphere.

4.1.3. Urease Inhibitors

Urease inhibitors reduce ammonia losses to the atmosphere from broadcast, top-dressed applications of urea (Watson, 2005) especially where reduced tillage is practised (Bayrakli and Gezgin, 1996; Wang *et al.,* 1991a, 1991b, 1994). Ammonia lost to the atmosphere may be deposited on land or water causing eutrophication and acidification. As with nitrification inhibitors, urease inhibitors – by delaying ammonia formation and subsequent nitrification – can reduce the nitrate content in plants and improve the nutritional quality of vegetables and fodder plants.

When urea is applied to the soil, it is usually hydrolized quite rapidly. However, plants can take up urea through the roots as a neutral molecule. In this case, the hydrolysis takes place within the root (soybean) or within the shoot (maize) (Hartel, 1977). With the use of urease inhibitors increasing the availability of urea over a longer period, the direct uptake of urea may become important because it can lead to increased ammonia within the plant. This may result in the formation of more basic amino acids, preferably arginin, a precursor of polyamines, the so-called 'secondary messengers' (Amberger, 2008b). According to Sattelmacher and Gerendás (1999), it is assumed that phytohormones as well as polyamines play a special role in ammonium-induced growth stimulation. According to Marschner (1986), ammonium nutrition activates the arginine-mediated pathway with a greater increase of polyamines.

Besides ammonia losses from the application of urea to crops and grass, cattles are a substantial source of ammonia emissions. Ledgard (2001) found large N losses from urine patches on pastures due to ammonia volatilization. Urease inhibitors can control ammonia losses from urine and excreta patches and dairy shed effluents, which is most important in countries with large areas of grazed pastures. Leinker *et al.* (2005) tested the effect of applying nitrification inhibitors on the floor of dairy houses to reduce ammonia losses.

Because the accumulation of ammonia increases soil pH, urea may damage seedlings/crop emergence, inhibit germination (Watson, 2005) and cause severe leaf-tip burn (Edmeades 2004; Watson and Miller, 1996). Urease inhibitors reduce such damage when seed-placed levels of urea/urea-containing fertilizers are too large (Grant *et al.,* 1996a; Malhi *et al.,* 2003; Xiaobin *et al.,* 1994). Watson and Miller (1996) found that NBPT may cause some leaf-tip scorch. These effects were, however, transient and short-lived.

4.2. Disadvantages

4.2.1. Slow- and controlled-release fertilizers

As yet there are no standardized methods for reliably determining of the nutrient release pattern from such fertilizers. There appears to be a lack of correlation between the data from laboratory testing – which are made available to the consumer – and the actual functioning of the nutrient release pattern in field conditions (Shaviv, 2005). Furthermore, when reporting the advantages of slow- and controlled-release fertilizers, in comparison to conventional mineral fertilizers, controlled-release fertilizers have not always been compared to the best existing fertilizer management practices (Hall, 1996; Kloth, 1996; Lammel, 2005; Raban, 1995).

When testing the nutrient release pattern of (mainly) polymer-coated/encapsulated fertilizers, several manufacturers determine the duration of the release of 80% of the nutrient at 25°C (Shoji and Gandeza, 1992). However, tests for 75% or 80% release indicate that the user can reasonably expect that about three-quarters of the nutrients will be released during the growth period. It ignores the possible existence of a 'burst' (Shaviv, 1996). This might have severe agronomic and environmental implications, when slow-release fertilizers with a large initial 'burst' (such as SCU or UF), or polymer-coated fertilizers, having a large proportion of damaged granules, are compared to controlled-release fertilizers that perform well (Shaviv, 2003b, 2005). With some chemical reaction products, such as UF fertilizers, it appears that a proportion of the N may be released in plant available forms extremely slowly (or not at all). The release of nutrients can be too slow if they are too thickly coated. Sulphur-coated fertilizers, with a parabolic nutrient release pattern (with or without 'burst'), may initially release nutrients too quickly, causing damage to the crop, and the final release of N too slow for it to be available to the plant (Shaviv, 2005). The cost of a sulphur-coated fertilizer with a rapid initial nutrient release, even if it does not cause damage to the developing plant, is more expensive than the equivalent amount of conventional soluble fertilizer.

Application of a coated fertilizer may increase the acidity of the soil. This can be the case if large amounts of sulphur-coated urea are applied, because both sulphur and urea contribute to increase soil acidity. This may, posibly, improve the uptake of phosphorus and iron.

Polymer-coated or encapsulated controlled-release fertilizers may leave undesired residues of synthetic material in the soil. Some types of polymers used in the coating of conventional fertilizers used currently decompose extremely slowly or not at all in soil. Their use may lead to an undesirable accumulation of plastic residues, up to 50 kg/ha/yr (Hähndel, 1997). According to Shaviv (2005), polyolefin coatings have lower degradation rates than alkyd resins and polyurethane-like resins, the three main types used in practice.

Though within ten years, a 500 kg/ha maximum accumulation would be only 200 ppm of dry soil, research should be intensified to develop degradable polymeric coating materials. It is, however, obvious that coating substances that regulate the release of nutrients for several months or even longer, will not decompose immediately afterwards, but will need a relatively long time for total decomposition; fragments smaller than sand particle size, may become part of the soil.

In modern intensive agriculture application of the optimum amount of mineral fertilizer N follows continuous monitoring of growing conditions and farmers prefer to adapt the N dressings to crop development and yield objectives. This is incompatible with the practice of early basal/depot fertilization with coated or encapsulated N fertilizers applied in one single dressing which, if applied in excess, cannot be corrected later.

The manufacturing cost of most coated or encapsulated controlled-release fertilizers is still considerably greater than that of conventional mineral fertilizers. This has prevented their wide use in mainstream agriculture (Detrick, 1995; Fujita, 1996a; Goertz, 1993, 1995; Gordonov, 1995; Hähndel, 1997; Hall, 1996; Kloth, 1996; Van Peer, 1996). This cost differential appears to be changing with the development of Agrium's large-scale production of ESN (Environmentally Smart Nitrogen), launched in 2000, which is available for a moderate premium.

The higher production costs are generally due to:

- Some fertilizers have to go through complicated production processes;
- In trying to achieve a perfect coating, producers usually employ size separation of raw granular materials, this also makes the product more expensive;
- The coating material is several times greater in price than the fertilizer material;
- The usually relatively small capacities of manufacturing plants, with the exception of Kingenta's capacity in China for slow- and controlled-release fertilizers, which reached about 850,000 tonnes at the end of 2007 and which will be further increased, of Agrium's ESN® production capacity in Canada of some 150,000 tonnes, and of Hanfeng's capacity in China at 150,000 tonnes;
- Coated/encapsulated controlled-release fertilizers require improved marketing through specialized advisory services and sales expertise compared to conventional fertilizers, except where manufacturers or extension services have developed software for the exact application of slow- or controlled-release fertilizers, and this has considerably promoted their use.

4.2.2. Nitrification inhibitors

Ammonia-containing fertilizers amended with a nitrification inhibitor can favour an increase in ammonia volatilization, if they are not incorporated into the soil immediately or soon after application. However, Linzmeier *et al.* (1999) found that ASN plus DMPP did not cause increased ammonia volatilization, and this was confirmed in laboratory investigations (Wissemeier and Weigelt, 1999).

Depending on the type of nitrification inhibitor, the activity of soil bacteria may be interrupted for a certain period of time, and some soil bacteria may actually be killed by bactericidal action. This could be considered an undesirable interference in natural soil – even if localized to the area where the nitrification inhibitor is applied.

DCD has been tested extensively in field experiments on agricultural and horticultural crops in the United States. Frye *et al.* (1989) and Frye (2005) concluded that a yield response to DCD only occurs if N is prone to losses by leaching or denitrification and then only if those losses result in N deficiency sufficient to reduce crop yields. If nitrification inhibitors are used with N application rates only slightly above optimum, yield increases are rarely observed. However, nitrification inhibition may have environmental benefits in crop production even when there is no increase in yield.

Ammonium ions stabilized with inhibitors and not taken up by the plants may be stored in the soil and be available to the following crops, thus decreasing the amount of N required (Gutser, 1999a).

If nitrification and urease inhibitors were available in different formulations, e.g. in liquid, suspension and granular forms, particularly for grassland/pastures and dairy farming, it might stimulate farmers to use them.

4.2.3. Urease inhibitors

The increase in yield is small when urea combined with a urease inhibitor is applied to soils that are very rich in N (Edmeades, 2004). There is also some evidence that this combination may have phytotoxic effects, e.g. leaf-tip scorch (Bremner and Krogmeier, 1990; Watson, 2005; Watson and Miller, 1996). It is not clear, whether this is a direct or indirect effect of urea; whether it is transitory, and whether it only occurs in situations where large amounts of urea and inhibitor are used. However, the benefits of NBPT – reducing ammonia volatilization and increasing yield – would appear to far outweigh any observed short-term leaf-tip necrosis (Watson and Miller, 1996).

5. Options for the application of slow- and controlled-release fertilizers and nitrification and urease inhibitors

5.1. Slow- and controlled-release fertilizers

The relatively higher prices of slow- and controlled-release fertilizers compared to conventional mineral fertilizers explain why there has been limited use on many agricultural crops. Initially these products established niches in highly specialized market sectors (Kafkafi, 1996). Only since the end of the 1990s have they been used for a wider range of commodity or conventional agricultural crops, such as maize, rice, winter wheat, potatoes, fruit trees (apple, citrus), vegetables (tomato) and forage crops. This change was made possible through large-scale production and excellent promotion and advisory work (e.g by Agrium/Hanfeng and Kingenta).

It is only in the last decade that field experiments with slow- and controlled-release fertilizers in agricultural crops have been carried out in the United States, Canada, China and Japan. In Western Europe, however, with the exception of some results for fruit trees and citrus, no data is available for these types of fertilizer. Field experiments in Western Europe, have focused mainly on testing nitrification inhibitors on commodity crops.

In the United States, crops on which controlled-release fertilizers have been used in the past are mainly strawberries, citrus and other fruits, nuts and vegetables. There is no doubt that it is cost-effective to apply encapsulated controlled-release fertilizers in high-value crops (Hauck, 1993). In the case of strawberries, the expenditure on fertilizer per unit area is relatively small when compared to the large annual investment cost in plastic mulch and planting material even when expensive polymer-coated controlled-release products are used. Furthermore, when plastic mulch is used, the most practical and responsible way of applying plant nutrients is to use a polymer-coated fertilizer with a longevity of six to nine months, before laying the plastic mulch and setting the plants.

On permanent crops, particularly when they are grown on soils liable to leaching, where the total fertilizer nitrogen requirement may be given in 15 applications per season, for example in Florida, the use of slow-release fertilizer significantly reduces labour cost. Reducing the number of applications and the amount of nutrients applied may compensate, in part, for the much higher cost of polymer-coated fertilizers.

On commodity crops such as maize and wheat, the use of controlled-release fertilizers improved economic yield and quality with the same or with only half the amount of N compared to conventional fertilizers (Ma *et al.,* 2006). Yang *et al.* (2005) showed that a combined application of urea and CRU at the normal rate or 30% less, increased winter wheat grain yield significantly, raised or maintained the protein content, and markedly reduced nitrate accumulation due to improved N-use efficiency.

On young Valencia orange trees the use of controlled-release fertilizers showed that their application frequency could be reduced from 15 to 6 with no adverse effects on the trees' growth. This suggests that combining soluble and controlled-release fertilizers in a plant nutrition programme for citrus is an economical and effective strategy (Zekri, 1991a, b).

For various crops in Japan, Tachibana (2008) gives the percentage reduction in the recommended N rate when controlled-release fertilizers replace conventional fertilizers. This saves labour and energy costs, and greater N-use efficiency will minimize possible nitrate leaching losses. Shao *et al.* (2007) confirmed similar beneficial results with the application of controlled-release fertilizers on apple trees; controlled-release fertilizers promoted tree growth and increased yield and quality.

Table 14. Comparative effect of Meister® and organic fertilizer applications on Japanese pear 'Hosui' (Tachibana, 2007).

	Organic pellet fertilizer	Meister application
Fertilizer		
Total-N	230 kg N/ha	161 kg N/ha
Application time	4 times	1 time
Results		
Yields	60 kg/tree	70 kg/tree
Fruits weight	410 g/n	512 g/n
Sugar content	12.2 brix	12.8 brix
Partially high water	0.75	0.55

Average data of three years (2000-2002)
Agricultural Research Center of Kumamoto Prefecture, October 2003

Although nutrient release from controlled-release fertilizers is much faster, and the longevity of release much shorter at soil temperatures up to 30°C, opportunities for applying controlled-release fertilizers on field crops should be greater in tropical countries than in temperate regions. This applies especially to regions with light-textured soils with excess rainfall or irrigation. Under these conditions losses of N from conventional N fertilizers, particularly urea, can be large.

Following the introduction of sulphur-coated urea (SCU) in the 1960s, experiments, mainly on wetland rice and mostly in Asia, have compared the recovery of N from polymer-coated urea or NPK fertilizers with that from other sources of N. In general, N recovery was greater from controlled-release fertilizers than from conventional N fertilizers, such as urea or ammonium sulphate. In a field experiment with wetland rice, Raju *et al.* (1989) compared a number of different types of N fertilizer; SCU and urea supergranules gave the largest grain yields. However, the wider use of SCU has

Table 15. Examples of reduction of the nutrient application rates in different horticultural crops with utilization of Meister, Nutricote and CDU (Tachibana, 2008).

Crops	Fertilizer	Application method	Reduction (%)
Cabbage	Meister	Single basal app.	20
	Nutricote	Single basal app.	40
	Nutricote	Single app.	40-70
Spinach	Nutricote	Single app.	30
Onion	Nutricote	Single basal app.	20
Welish onion	Meister	Single app.	20-70
	Nutricote	Single app.	20-50
Celery	Meister	Single app.	20-60
	Nutricote	Single app.	50
Chinese cabbage	Nutricote	Single app.	35-60
	Meister	Single app.	30
Lettuce	Meister	Single app.	20
Radish	Meister	Single basal app.	30
	Nutricote	Single basal app.	25
Carrot	CDU	Single app.	50
Burdock	Nutricote	Single app.	40-50
Taro	Meister	Single app.	30
	Nutricote	Single app.	20-30
Potato	Meister	Single basal app.	20
Japanese yam	Meister	Single basal app.	30
Ginger	Nutricote	Single basal app.	30-50
Lotus	Meister	Single basal app.	30
Tomato	Nutricote	Single basal app.	20-30
Green pepper	Nutricote	Single basal app.	25-30
Eggplant	Nutricote	Single basal app.	30
	Meister	Single basal app.	30

not become general practice for rice (or for other agricultural field crops) despite the fact that (i) the price ratio between SCU and conventional urea is generally less than 2 to 1, (ii) when applied as a basal treatment, SCU has proved superior to urea in the majority of field experiments, and (iii) sulphur is a necessary plant nutrient. This is still the case in spite of the fact that, in other countries, special types of polymer-coated urea granules have been developed which do not float, but sink immediately on application (Polyon® PCU by Agrium/Pursell; AF/Anti-Float, marketed in Japan by Sumitomo; Haifa Chemicals resin-coated anti-floating urea Multicote®).

Japan has a unique agricultural structure and a protectionist agricultural policy. It was the first country where a large proportion of the total fertilizer used in rice were of slow- and controlled-release types with large amounts being blended with conventional fertilizers. These special fertilizers included UF and CDU-based N fertilizers, but were primarily polymer-coated NPKs and urea. In addition to rice, they are used on vegetables and in professional horticulture.

Use of controlled-release fertilizers in rice

Use of controlled-release fertilizers for rice can be recommended based on cultural methods (direct seeding or transplanting), method of fertilization, soil supply of nutrients, length of plant growth, amount and pattern of plant nutrient uptake, climate (mean air or soil temperature), etc. (Shoji, 2005). The average growing period in the field is about 130 days for transplanted rice and 150 days for direct seeded rice, from May through October.

Two examples of Meister use recommendations for rice are:

- **For direct seeded rice (no-till):**
  Site: Central Japan (Aichi Prefecture)
  Length of growing season: 150 days (May to October)
  Natural N supply: small (N from fertilizer is required at all growth stages)
  Recommended fertilizer: blend of LP-140 and LP-SS100 (4:6)
  Nitrogen release pattern of the blend is shown in Fig.4.5 on page 73 of Meister Controlled-Release Fertilizer (1999)
  LP-140 can supply N to rice at all growth stages, but LP-SS100 only in the middle growth stage
  Fertilization and sowing: single basal co-situs application with rice seeds.
- **For transplanted rice:**
  Site: Northeast Japan (Miyagi Prefecture)
  Length of growing season: 35 days in the nursery and 130 days in the field
  Natural N supply: large
  Recommended fertilizer: LP-S80
  Nitrogen release pattern of Meister is shown in Figure 17. Because the available N supply is large, only LP-S80 is recommended. This fertilizer can supply N mainly in the middle growth stage when rice needs more N
  Fertilization and sowing single basal co-situs application in nursery boxes: Largest N-use efficiency of Meister is about 80% when applied as a single basal co-situs application, this is several times higher than that of a conventional N fertilizer.

In rice, the soil-fertilizer regime is completely different from that of other crops, particularly for applied fertilizer N (Allen, 1984; Bouldin, 1986; Garcia *et al.*, 1982). Under flooded soil conditions, losses through denitrification may be high when nitrate-containing fertilizers are applied or if ammonium-N nitrifies prior to flooding. Ammonia-N may also be lost to the atmosphere (Fillery and Vlek, 1986) when floodwater becomes alkaline during daylight hours, as algae consume all available carbonate (IFA, 1992). For this reason, ammonium- or amide-containing fertilizers have been given preference in the fertilization of paddy rice because losses may be reduced when these types of fertilizer are applied in floodwater. However, losses are significantly higher where flooding and drying alternate because of lack of irrigation water or cultivation under rainfed conditions.

Where farmers broadcast urea into standing floodwater (De Datta, 1986), urease activity at the flooded soil surface leads to rapid hydrolysis of the urea, high ammonium-N concentrations in the floodwater, and potentially large volatilization losses when weather conditions facilitate the removal of ammonia from the water-air interface (Byrnes *et al.,* 1989a). Under such conditions slow- and controlled-release fertilizers will be more efficient, in particular polymer-coated fertilizers.

In Japan the fertilizer industry has met the demand for special fertilizers for rice growers while, at the same time, supporting the official objectives of reducing fertilizer application rates. Thus, especially for application in rice, Chissoasahi has developed a special fertilizer ('Naebako-makase' Meister®) with a sigmoidal nutrient release. With this special controlled-release fertilizer, a co-situs placement for rice in seedling boxes is possible, providing the entire N requirement for the whole of the growing period, i.e. it is not necessary to apply N in the rice field (Shoji and Takahashi, 1999). The accurate nutrient release in combination with placement of the fertilizer enhances N-use efficiency (Ueno, 1994). On average, Japanese farmers have a relatively small farm, they are aged and are involved in other businesses. As far as possible, they prefer cultural practices that reduce both the amount of fertilizer and their labour and the latter is one of the great advantages of controlled-release N fertilizers for them (Wakimoto, 2004; Ando *et al.*, 2000).

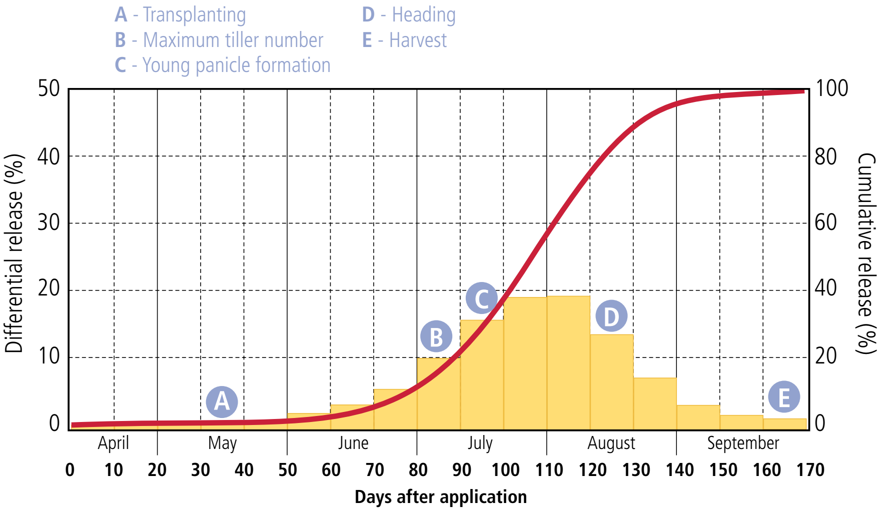


Figure 17. Nitrogen release of Meister®-S12 (LP-S80) for rice nursery application in Sendai, NE Japan (Adapted from Fujita and Shoji, 1999).

The development of sigmoidal controlled-release N fertilizers such as Meister® has enabled farmers to use a single basal nursery application and a single basal field application. Both applications can meet the whole plant N demand throughout the growing season without any topdressing. A further advantage is that the large amount of sigmoidal-release fertilizer can be applied to rice seedling boxes without fertilizer salt injury to the seedlings; the same is the case when applied by co-situs placement (Shoji and Takahashi, 1999). This is also the reason why Japanese rice growers prefer coated fertilizers vs. nitrification or urease inhibtitors. In contrast, in Western Europe, with larger and highly mechanized farm units, farmers prefer split N application strategies, sometimes based on crop N analysis or canopy measurements, or the use of nitrification inhibitors.

Table 16. Comparison of NUE using Meister® and a conventional N fertilizer on wetland rice in NE Japan (Tachibana, 2007).

Culture method	Nitrogen use efficiency		Research institute
	Meister	Conventional fertilizers	
Transplanted	83%	33%	Akita Agri. Res. Center
Direct seeding	80%	30%	Yamagata University
Direct seeding	83%	41%	Aichi Agri. Res. Center

1. Fertilizer application: Single basal co-situs application for Meister, 2 to 3 times band or broadcasting for conventional fertilizers
2. Determination of NUE: by the tracer method using ^{15}N labeled fertilizers

Table 17. Comparative studies on N uptake and yields of cultivar Koshihikari grown with conventional and innovative N fertilization in no-till direct seeded rice in 1996-1998 (Ikeda *et al.*, 1998).

Treatment	N rate	N uptake	N use efficiency[1]	Brown rice yield
	kg/ha	kg/ha	%	t/ha
Conventional[2]	117	101	41	4.45
Innovative[3]	80	119	83	6.35

All the data were expressed as the means of the results obtained for three years.

[1] Determined by the difference methods

[2] Split application of ammonium sulphate by broadcast

[3] Single basal application of Meister blend (LP-70: LP-100: LP-SS100-3:2:6) by co-situs placement

In summary, rice growing in Japan is extremely labour-intensive so that the labour-saving aspect of controlled-release fertilizers is the main reason for their use. In addition to the possibility of reducing the N rate, other advantages in using polyolefin-coated fertilizers are:

- Their use permits innovative fertilizer applications, e.g. *co-situs* placement, one single basal application and simplification of planting;
- They simplify multiple-cropping with a single fertilizer application, leading to labour saving from no-till culture;
- No or reduced lodging due to the more gradual release of N from resin-coated fertilizers (Tanaka, 1990);
- Enhancing quality and safety of farm products such as decreasing nitrate and oxalic acid and increasing sugars and ascorbic acid (Shoji, 2005).

Though polyolefin-coated urea (POCU or Meister®) is more expensive than conventional N or NPK fertilizers, it can contribute to innovative fertilizer applications and farming systems, whereby total production costs can be reduced by 30 to 50% (Kitamura and Imai, 1995). For example, rice production with no-till transplanted rice using seedlings with a single basal fertilizer application and no additional fertilizer in the paddy field or no-till direct seeded rice with a single basal *co-situs* fertilizer application.

Nitrogen absorption was 79% greater from coated urea than from a conventional fertilizer when both were applied as a single applictaion to rice and this resulted in larger grain numbers and yield at harvest (Kaneta, 1995; Kaneta *et al.,* 1994). Shoji and Kanno (1994), discussing experiments by Kaneta *et al.* (1994), reported a decrease in farming cost of 65% with no-till transplanted rice with a single basal fertilization compared to conventional rice cultivation. This suggests that controlled-release fertilizers such as POCU may be used for low-value crops. In addition, because of agro-environmental

Picture 5. Layered co-situs application of Meister® – S15 (LP-S100) in a nursery box for no-till transplanted rice culture (single basal application) (Photo: Kaneta, 1995).

issues, some local authorities recommend the use of controlled-release fertilizers to control pollution and this may stimulate their use in new innovative farming systems.

The possibility to predict quite reliably nutrient release patterns from various types of controlled-release fertilizers, has led to precise fertilizer recommendations for various cropping systems. The Japanese fertilizer industry and various official institutes and research centres use special software to give farmers very detailed fertilizer recommendations. As a result approximately 70% of the total polyolefin-coated fertilizers produced and used in Japan are applied to paddy rice. Polymer-coated urea is mostly blended with conventional fertilizers at ratios of 10:90 to 30:70 to reduce total fertilizer costs. There is no doubt that rice is one of the most interesting agricultural crops on which to use encapsulated controlled-release fertilizers. However, further developments are required for their practical application, for example, their characteristics for blending, and making granules which do not float but sink immediately on application to paddy rice. Lower costs could certainly contribute to controlled-release fertilizers being used for rice in countries other than Japan.

In India in a field trial on rice, neem cake (as a slow-release agent) coated urea (NCU) produced substantially larger yields than prilled urea (Singh and Singh, 1994). Similar results were reported by Budhar *et al.* (1991). De *et al.* (1992) concluded that for rice 30 kg/ha less N is required when applied as neem-extract (nimin) coated urea (NICU) compared to prilled urea. Geethadevi *et al.* (1991) obtained larger rice yields in field experiments with NCU than with prilled urea, but urea supergranules gave the largest yield. Jena *et al.* (1993) and Kumar and Thakur (1993) also obtained larger yields of rice with NCU but Pandey and Tripathi (1994) did not obtain improved yields with NICU.

In field experiments in China, Song *et al.* (2005) increased rice yield by 10-40% with controlled-release fertilizers compared to those with urea. Even when a third less N was used, controlled-release fertilizers increased rice yield by 15%.

It is, however, essential to carry out further extensive experiments under field conditions to compare controlled-release fertilizers with the most advanced conventional fertilizer management systems and calculate the value/cost ratio of the different options.

Approximately 30% of the total polyolefin-coated fertilizers in Japan consist of polyolefin-coated compound fertilizers (Nutricote®) that have both linear and sigmoidal release patterns with a wide range of nutrient release duration. They also contain nitrate and ammonium in an equal ratio, offer (for many horticultural crops) efficient use when employing innovative fertilization methods, and permit a reduction of the application rates by 20-60% (Tachibana, 2007).

Muraro and Holcomb (1992) cited by Raigon *et al.* (1996) studied the use of slow-release and resin-coated controlled-release N and NPK fertilizers for citrus. They concluded that the use of slow-release N fertilizer is economically more feasible when hand labour is used to fertilize the grove, because this application method is twice as expensive as mechanical fertilization. 'These results and personal experience allow us to conclude that slow-release fertilizers permit better utilization of soil applied nutrients.' Even small amounts of slow-release N fertilizers gradually provide sufficient N for the whole of the growing season and eliminate local and excessive inputs of traditional fertilizers. The amount of N and P at risk of leaching to both underground and surface water is generally less where slow-release fertilizers are used. In Japan, Canada and the United States, the predictability of the nutrient release pattern of controlled-release fertilizers, particularly under different temperature and humidity conditions, has enabled extension services, universities, research institutes and industry to develop software for more precise fertilizer recommendations under different cultivation, soil and weather conditions. For example, for maize growers in the United States, Agrium, in collaboration with universities and extension services, can give very exact and detailed recommendations on a field basis for the timing and rate of application of ESN on commodity crops. In China, Kingenta has developed in collaboration with Chinese and American universities a very detailed fertilizer recommendation for the application of their coated fertilizers Syncote® (PCU, PCF, SCU, SCF and PSCU) in agricultural crops (e.g. rice, potatoes, tomatoes).

5.2. Nitrification inhibitors

Fertilizers containing nitrification or urease inhibitors are exclusively used on agricultural crops, on some long-growing season vegetables and, in orchards and vineyards. According to Hall (1995), the economics of using nitrification inhibitors should be more attractive compared to those of slow- and controlled-release fertilizers.

5.2.1. DCD

In the United States, it is assumed that N fertilizers amended with DCD are applied more or less to the same crops as those receiving fertilizers with Nitrapyrin. In Western Europe, stabilizing the ammoniacal-N in fertilizers with only DCD has been replaced by the combination of DCD + Triazole (10:1, w/w). Fertilizers amended with this combination of nitrification inhibitors, as well as N solutions with Triazole + 3-MP, are recommended for most of agricultural crops fertilized with ammonium-containing fertilizers. For incorporation into slurries, a mixture of Triazole + 3-MP is available in liquid form.

The combination of DCD + Triazole has been widely tested in field and laboratory studies in China from 1998 to 2000 (Wozniak *et al.*, 2001). In 25 field trials, compared to urea alone, DCD + Triazole significantly increased crop yields; maize by 12%; rice by 9%; wheat by 12%; potatoes by 22% and beet by 13% under a range of soil and climatic conditions. The N-use efficiency in rice and maize was increased by 15%. In addition, there was a significant reduction in nitrous oxide emissions.

Recommendations for N fertilizers with DCD are best when crops are grown on light textured soils or with heavy rainfall within the 6-8 weeks following application (Amberger, 1989, 1993b, 1995, 2006; Sturm *et al.*, 1994). These recommendations were for maize, potatoes, sugar beet and malting barley, crops with relatively slow growth early in the growing season (Amberger, 1995; Amberger and Gutser, 1986; Zerulla and Knittel, 1991a, 1991b). In addition to a saving of one fertilizer application at a cost of approximately € 10/ha, there has been a good response to nitrification inhibitors through improved yields (Zerulla, 1996). However, it is necessary to clearly define the soil and growing conditions under which such positive results can be expected. This is of particular importance where nitrification inhibitor-containing N fertilizers are used on cereals such as winter wheat and winter barley (Mokry, 1986; Brenner and Solansky, 1990; Mokry and Amberger, 1992). NPK fertilizers formerly containing DCD were also used in orchards and vineyards (Kannenberg, 1993) and vegetables with a long growing season.

Amberger (1991a) emphasized that with DCD-containing N fertilizers only one or two applications were necessary with a considerable saving in application costs compared to several dressings with calcium ammonium nitrate (CAN). Spielhaus (1991) confirmed that the same yield could be obtained from only one or two applications of stabilized fertilizers. Brenner (1991) found in extensive field experiments from 1977 to 1990 that the nutrient use efficiency from stabilized N fertilizers is 20 to 30% greater than that of conventional N fertilizers suggesting that the amount applied can be reduced by 20 to 30% without risking loss of yield.

In Japan, tea growers have used extremely large amounts of ammonium sulphate (AS) because there is a double advantage, namely tea plants prefer to take up ammonium, which improves the quality of the leaves (Shoji and Higashi, 1999) and soil pH is decreased and tea plants prefer acid soils. However, using AS has led to large N losses from the soil of the tea fields with adverse environmental effects. In 2005, the Japanese Ministry of Agriculture, Forestry and Fishery (MAFF) launched a project aimed at reducing N fertilization rates to agricultural crops by using N fertilizers in combination with a nitrification inhibitor ('Dd-Meister') and slow- and controlled-release fertilizers. Dd-Meister is a combination of urea and DCD, where urea is first coated with DCD, and then covered with a polyolefine to control N release. Results from 2003 to 2005 in five major tea plantation research centers indicate that using Dd-Meister allowed a substantial reduction in the amount of N fertilizer applied, while obtaining high-quality leaves, equal yields, and reducing adverse environmental effects (Tachibana, 2007). In leafy vegetables, particularly spinach, the use of Dd-Meister has considerably reduced the nitrate-N content of leaves.

When using DCD-stabilized fertilizers the amount of N applied to maize, potatoes and sugar beet and rapeseed could be reduced by 20 to 30 kg N/ha, without reducing yields (Sturm *et al.,* 1994). In field experiments carried out over several years by Hege and Munzert (1991), DCD-stabilized fertilizers gave different degrees of efficiency with different crops. The increase in yield, as well as the economic benefit, was significant for wide-row crops, like maize and maize for silage, where the fertilizer was band applied, and crops with a longer growing season and those with a 'preference' for ammonium-N, like potatoes, were grown. However, with winter cereals, winter rapeseed and sugar beet, there was no increase or insufficient increase in yield to justify using DCD-stabilized N fertilizer.

More recently, outside Europe, a new field of application has been developed for grazing systems where using DCD has improved pasture yield and quality (Moir *et al.,* 2007). It can be applied to slurry or on grassland where there are excreta or urine patches. Its use has led to significant decreases in nitrate leaching (Di and Cameron, 2007). DCD, formulated as a fine particle suspension, is applied as a spray, using traditional applicators, at 10kg DCD/ha applied in 100–150 litres of water twice per year in late autumn and early spring (Di and Cameron, 2002, 2004). An example is Eco-N^{TM} of Ravensdown Fertilizer in New Zealand.

For promoting the use of DCD-containing fertilizers, the leading distributors in Western Europe have used a strategy similar to that of the manufacturer of Nitrapyrin/N-Serve® by Dow AgroSciences in the United States. In Germany and neighbouring countries, BASF has for many years carried out a large number of field experiments with its own research and advisory staff to clearly define the conditions for an efficient use of N fertilizers amended with DCD. In these experiments, the relation between soil type, rainfall, temperature, N rate applied and the crop have been investigated (BASF, 1991, 1993). Further comprehensive data have been obtained from research in cooperation with official institutes and universities. Such research work has also been carried out by SKW Trostberg (now AlzChem Trostberg), primarily in close cooperation with the Technical University of Munich, Institute of Plant Nutrition, Freising, as well as by SKW Piesteritz (Amberger, 1986,1989; Amberger and Gutser, 1986; SKW Trostberg, 1993; Wozniak, 1997).

5.2.2. DMPP

The agricultural and environmental benefits from using DMPP have been shown in a large number of pot, lysimeter and field experiments. Up to 2004, there had been more than 700 field trials on agricultural and horticultural crops, on fruit trees, vines and grassland mainly in Western Europe, to demonstrate the advantages of DMPP, and also show some limitations of this new nitrification inhibitor (Hähndel and Zerulla, 2004). Between 1997 and 1999, 136 field trials were carried out under various soil-climatic conditions on a large number of agricultural and horticultural crops (Pasda *et al.,* 2001a, b). DMPP can increase yield and/or improve crop quality, e.g. by reducing the nitrate concentration in leafy vegetables. For some crops, the same yield as obtained with the control (fertilizer without DMPP) was achieved with one less N application or with a reduced amount of N.

In more than 200 field trials in France, Spain and Italy between 1997 and 1999, a larger yield was achieved with N fertilizer + DMPP than with N alone on both less fertile and very fertile soils. In five field trials with rice in Spain and Italy, a yield increase of 600 kg/ha was obtained using ASN + DMPP, the yield of winter wheat was also increased (Pasda *et al.,* 1999, 2001b). The effect of DMPP-amended N fertilizers on intensively-cultivated tomatoes in the region of Valencia in Spain showed that DMPP preserves a larger amount of ammonium in the soil, resulting in less loss of N by leaching (Bañuls *et al.,* 2000a). Furthermore, DMPP improved both yield and size of the tomato fruit. In a greenhouse experiment in Valencia with citrus plants grown in 14-litre pots, Bañuls *et al.* (2000b, 2001), showed that N fertilizer amended with DMPP improved N fertilizer use efficiency and reduced nitrate leaching losses, retaining the applied N in the ammoniacal form. The larger amounts of ammonium caused no damage to the plants. On the contrary, a large ammonium concentration in the soil possibly favours the uptake of N by citrus plants because they are capable of absorbing ammonium faster

Table 18. Average yield increases with DMPP (Hähndel, 2005).

		Marketable yield (t/ha)						
			N fertilization level suboptimal			N fertilization level optimal		
Crop	No. of trials	Without fertilizer	Without DMPP	With DMPP	% difference to without DMPP	Without DMPP	With DMPP	% difference to without DMPP
Broccili	3	2.2 a	14.3b	12.9 b	-10	12.6 b	13.7 b	+9
Brussels sprouts	1	14.2 a	25.3 b	30.4 bc	+20	33.0 c	31.8 c	-4
Carrots	6	65.7 a	82.5 b	86.3 b	+5	84.4 b	84.5 b	0
Cauliflower	9	19.3 a	34.5 b	36.1[1] bcd	+5	38.1 cd	39.4[1] cd	+3
Celeriac	6	11.3 a	69.8 bc	71.7 cd	+3	70.8 bcd	75.7 e	+7
Chinese cabbage	6	13.8 a	77.0 b	81.9[1] c	+6	87.9 bc	95.2[1] d	+8
Head cabbage	4	53.5 a	99.8 b	96.6[1] bc	-3	95.1 bc	99.7[1] cd	+5
Kohlrabi	5	10.9 a	42.7 b	47.6 c	+13	51.3 c	51.3 c	0
Lambs lettuce	16	1.2 a	5.4 b	8.4 d	+55	6.0 c	9.0 d	+50
Leek	8	36.4 a	44.6 b	45.4 b	+2	44.8 b	47.9 c	+7
Lettuce	24	11.9 a	37.1 b	39.1 c	+6	42.3 c	42.5 c	0
Onions	8	19.4 a	64.8 b	64.5 c	0	65.4 b	68.0 c	+4
Radish	3	11.4 a	25.6 b	30.2 c	+18	29.9 c	32.1 c	+7
Weighted mean					+12			+11

[1] Only one fertilizer application

Between 1998 and 2002 a total of 95 field trials with vegetables were conducted in Central Europe with ASN/NPK in comparison to ASN/NPK + DMPP (ENTEC) at an optimal N level with 75% of the optimal N level.

Values in a row followed by the same letter do not differ significantly (Duncan's test, 5% level).

than nitrate (Serna *et al.*, 1992, 2000). Plants fertilized with N fertilizer + DMPP had darker green leaves. In an experiment on Clementine trees using a low frequency drip irrigation system, Bañuls *et al.* (2002) demonstrated that the use of N fertilizer + DMPP improved the N-use efficiency in citrus-growing systems.

Experiments with winter wheat (Knittel and Große-Kleimann, 2002; Knittel and Mannheim, 2004; Knittel *et al.*, 2007) studied the interactions between fertilizing systems, climatic conditions and soils, and the adaptation of N supply to N demand for wheat. Where normally, three N applications are necessary to obtain the best possible N-use efficiency, with N fertilizer + DMPP only two applications were needed, resulting in substantial labour saving. Moreover, the use efficiency of the applied N was higher with N fertilizer + DMPP, leaving less residual N in the soil and, thus, reducing the risk of nitrate leaching. In 24 winter wheat trials with ASN + DMPP yields were increased by more than 7% (Hüther *et al.,* 2000). This increase was achieved with only two N applications instead of three, the standard N fertilization strategy in Western Europe. They also showed that, with only one application of ASN + DMPP, larger yields could be achieved than with ASN alone. For winter rapeseed, the conventional two N applications can be replaced by only one when using an N fertilizer + DMPP very early in the spring. In Western Europe, it is important, however, that whatever N fertilizer is applied, it should be supplemented with sulphur (S) (Knittel and Zirm, 2002).

Tests conducted in various European countries on field-grown vegetables and fruit trees during the late 1990s showed that DMPP-containing N fertilizers reduced N leaching losses and increased yields, even with reduced N fertilizer applications. Furthermore, plants receiving N fertilizers amended with DMPP had darker green leaves with lower nitrate-N content (Hähndel and Zerulla 1999, 2000, 2001).

Xu *et al.* (2004) measured the effect of ASN + DMPP on yield, nitrate accumulation and quality of cabbage under various soil-climate conditions in two regions in China. Yield was increased by 2.0 t/ha in Jinhua and 5.5 t/ha in Xinch and the nitrate content of the cabbage was decreased by 9.4 and 7.3%, respectively. The nutritional quality of the cabbage was improved significantly by increasing the content of vitamin C, soluble sugars, K, Fe and Zn. In the trial in 2005, yield increases could not be repeated. However, the reduction of the nitrate-N concentration in the cabbage and the soil on which they were grown was significant. There was also a decrease in nitrate in the cabbage during the early stage of storage (Xu *et al.*, 2005a).

Guillaumes and Villar (2004) studied the influence of DMPP when added to pig slurry on the growth and chemical composition of ryegrass. The application of pig slurry + DMPP significantly increased the production of above-ground dry matter and reduced N leaching.

Chaves *et al.* (2006) investigated the effect of DCD and DMPP on the accumulation of ammonium-N and nitrate-N after incorporating cauliflower residues into soil. Results showed that DMPP inhibited nitrification from crop residues for 95 days.

5.2.3. Nitrapyrin (N-Serve®)

In the United States, N-Serve® is labelled for use on maize, sorghum, wheat, cotton and strawberries (restricted). However, of the total use, more than 90% is on maize, the rest on wheat, and some on grain sorghum (Huffman, 1996; Christensen and Huffman, 1992, Dow Agrosciences, 2007).

Because Nitrapyrin must be injected or immediately incorporated into the soil due to its volatility, its use is limited in the regions where N is not normally injected. Consequently, N-Serve® is commercially available only in the United States, though there are research programmes that have documented its benefits in several other parts of the world.

Nitrapyrin is very stable in cool soils, providing excellent activity from fall or winter applications and this meets the interest of American farmers in terms of time management. Farmers prefer to apply fall N plus a nitrification inhibitor rather than spring N, and spring N plus nitrification inhibitor instead of side-dressed N.

Picture 6. N fertilization of corn with and without the addition of a nitrification inhibitor. The light coloured strip of corn in the center of the photo received fall-applied nitrogen; corn to the left received the same amount of fall-applied N plus N-Serve; corn to the right received spring applied nitrogen. Yields were: 227 bu/ac for fall N+N-Serve, 194 bu/ac for fall N and 217 bu/ac for spring-applied N. This pattern of similar yields with fall N plus a nitrification inhibitor and spring-applied N with both being superior to fall-applied N is found widely (Photo: J. Huffman, DowElanco).

In cooperation with Iowa State University and the Cooperative Extension Service, DowElanco has developed a special computer programme to estimate N losses: "Fate of anhydrous ammonia in Iowa soils" (Killorn and Taylor, 1994). The programme requires state and county soil temperatures, rainfall amounts, and established risk of leaching and denitrification. This computer programme can be used as a tool to help make N management decisions.

In most years, the greatest loss of N occurs before the maize plant can take up N. Thus, it is to the advantage of both the farmer and the environment to retain the maximum amount of ammoniacal N in the soil until the period of maximum N loss is over. N-Serve® results in delayed nitrification and, accordingly, may reduce the risk of N loss by leaching and by denitrification (Killorn and Taylor, 1994). Christensen and Huffman (1992) demonstrated experimentally with maize that the N rate could be reduced without losing yield when N fertilizers were amended with Nitrapyrin.

Emphasis in research is shifting to the precise application of N-Serve®, targeting applications to soils where N losses are large, such as on poorly drained and sandy soils. According to Huffman (1997) this will:

- lower the cost of N fertilizer by allowing growers to use less N without riski of yield loss;

Picture 7. Photograph of a spring-applied nitrogen rate/nitrification trial at Iowa State University, Ames, Iowa, USA, 1996. In this wet season, nitrogen deficiencies were obvious in the zero N check and in the low N rate plots. Also corn size varied in response to N rate and to nitrification inhibitor. Yield response to the nitrification inhibitor, N-Serve, averaged 10% (160 vs 145 bu/ac). This result is typical of the response seen on poorly drained soils in a wet year (Photo: J. Huffman, DowElanco).

- lower the cost of N-Serve® by applying it only where it offers a good potential return; and
- reduce the risk of nitrate-N moving into water bodies due to less applied N and decreased nitrate leaching.

5.3. Urease inhibitors

The principal advantages of urease inhibitors are:

- a significant reduction in volatilization losses of ammonia resulting in an increase in plant-available soil N;
- an improvement of N-use efficiency from amide-N;
- a reduction of seedling damage, and
- a decrease in the emission of nitrogen oxides and nitrous oxide.

Grant *et al.* (1996a) listed the circumstances under which NBPT would increase yield through reduced volatilization losses from surface-applied urea/urea-containing fertilizers. These are when

- N fertility limits crop yield when NBPT is not applied and,
- volatilization losses from the applied N are sufficient to impact crop yield.

Grant *et al.* (1996a) concluded that “Maximum benefits of NBPT use can, therefore, be expected where crop yield potential is high, soil N levels are low and soil and environmental conditions promote extensive volatilization losses. Since we cannot effectively predict far in advance when environmental conditions that will lead either to volatilization losses or seedling damage, the use of NBPT can help to reduce the risk of damage, if weather conditions become detrimental. This will help to improve the long-term economics of crop production.”

Results from field trials on maize in various US states are summarized in Table 19.

Table 19. Effect of surface-applied urea fertilizer, with and without the addition of NBPT, on maize yield (t/ha) in trials in Kansas (Lamond *et al.*, 1993, 1994, unpublished data).

N rate	Irrigated 1993		Osage Co 1993		N Farm 1994		Sandyland 1994	
	Urea	Urea+ NBPT	Urea	Urea+ NBPT	Urea	Urea+ NBPT	Urea	Urea+ NBPT
0	5.08	5.08	1.25	1.25	3.07	3.07	8.97	8.97
67	5.39	6.96	2.76		4.26	4.64	10.91	11.97
135	7.52	8.65	2.76		5.27	6.65	11.91	12.04
202	8.03	8.90	3.89	4.45	6.21		12.29	12.41
Mean	6.96		3.14		5.52		11.66	12.10
LSD (0.05) Means	0.69		0.56		0.75		NS	

Watson *et al.* (1994b) and Watson and Miller (1996) have evaluated a range of NBPT concentrations (0.01, 0.05, 0.1, 0.25 and 0.5% NBPT w/w) to determine the optimum incorporation rate for temperate grassland under a range of environmental conditions. Increasing the inhibitor concentration lowered ammonia volatilization according to the law of diminishing return.

NBPT was very effective at low concentrations in controlled-environment chambers (Figure 19.), resulting in approximately 50% inhibition at a concentration of 0.01% (Watson, 2005). Larger amounts of inhibitor are useful in the more demanding field conditions and when extended inhibition of urease activity is desired. Only at high temperatures is NBPT less effective (Carmona *et al.*, 1990).

In Italy, Palazzo *et al.* (1995) studied the effect of NBPT over a three-year period in field experiments on maize. They found that the addition of NBPT resulted in significant decreases in ammonia volatilization.

NBPT appears to be effective in reducing damage from seed-placed fertilizer where conditions are such that damage will occur (Xiaobin *et al.*, 1994). Damage to seed germination and seedling growth occurs because of the large concentrations of ammonia-N and nitrite-N (NO_2^--N) following the immediate hydrolysis of urea (Grant and Bailey, 1999; Wang *et al.*, 1995).

Total N consumption in 2007/08 in Western and Central Europe reached 11.6 Mt N, mainly in the form of CAN, AN, ASN, AS and NP/NPK fertilizers (IFA, 2010). Of this

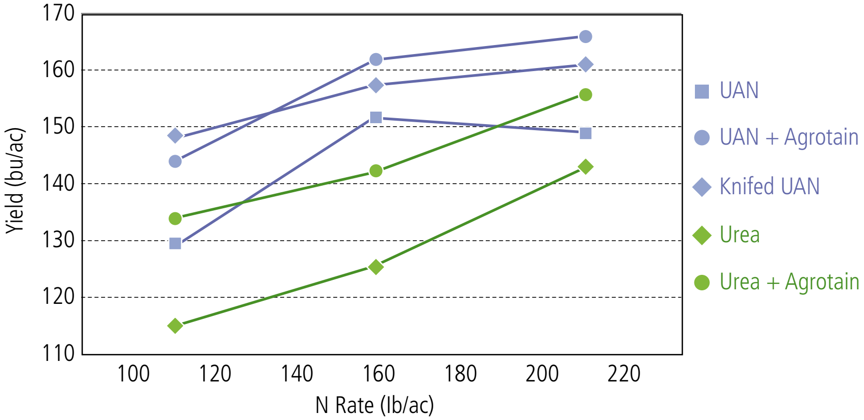


Figure 18. Effect of Agrotain on maize grain yields (Adapted from IMC-Agrico, 1996). Agrotain increased corn grain yields by an avarage of 10 bu/ac when applied with UAN and by an average of 15 bu/ac when applied across all rates of urea. Results reflect trials where rainfall did not occur within 72 hours.
Two-year study SEPAC, Purdue University, Ind.

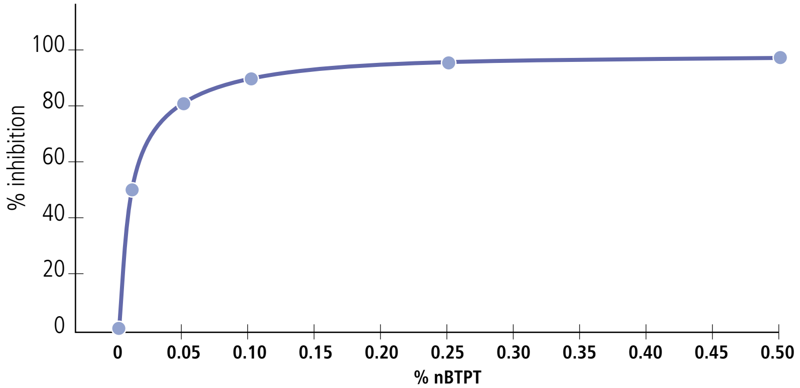


Figure 19. Effect of different levels of nBTPT (also NBPT) on the % inhibition of NH_3-N volatilization (Adapted from Watson, 2005).

total, almost 2 Mt was urea and 1.2 Mt N was UAN solutions, containing about 0.6 Mt of amide-N (i.e. about 2.6 Mt amide-N = 22% of total N). If there was a large increase in the use of N fertilizers containing amide-N then there would be both potential and need in Western Europe for urease inhibitors. A possible new additional use of NBPT would be in animal husbandry with grasslands and grazed pastures. However, a formulation of NBPT separate from any urea or UAN would be necessary.

5.4. Nitrification and urease inhibitors in tropical crops

At high temperatures nitrification, denitrification and ammonification of amide-N to ammonium occur faster, but the efficiency of nitrification and urease inhibitors decreases with increasing temperatures. Consequently, the conditions and factors under which these N stabilizing compounds may be effective have to be defined more strictly, i.e. the effect of nitrification and urease inhibitors have to be tested under conditions of high temperature. Based on field trials on the growth and yield of maize in Egypt in 1991-92 to assess the efficiency of N applied at 15 to 105 kg N/feddan (25 to 175 kg N/ha) with and without Nitrapyrin, Hammam (1995) concluded that the use of Nitrapyrin could save 40 kg N/feddan (67 kg N/ha). Serna *et al.* (1993, 1994) tested ASN in several experiments on citrus in Valencia without and with DCD. DCD reduced nitrate losses and improved N-use efficiency, minimizing the economic and environmental risks that are inherent in irrigated citrus production. Bañuls *et al.* (2001) concluded from a greenhouse experiment with citrus plants in 14-litre-pots, that DMPP improved N-use efficiency and reduced nitrate leaching losses by retaining the applied N in the ammoniacal form.

Yadav *et al.* (1990) compared urea supergranules, neem cake-coated urea (NCU) and DCD-coated urea for sugarcane. There was no significant difference in yield between the three treatments. Joseph and Prasad (1993) also compared urea coated with neem cake and with DCD for wheat, DCD-coated urea was the most effective treatment. Vyas *et al.* (1991) obtained similar yields of rice with 70 kg N/ha in the form of NCU as with 100 kg N/ha applied as unamended urea. Vimala and Subramanian (1994) produced larger yields with NCU or nimin-coated urea (NICU) than with prilled urea in field trials on rice. Though Gour *et al.* (1990) obtained better yields of rice with NCU than with prilled urea, the largest yields in their trials were from urea super granules. Tomar and Verma (1990) produced nearly equal yields with 80 kg N/ha with urea plus nitrification inhibitor as with 120 kg N/ha with prilled urea without inhibitor. Ketkar (1974), in a rice trial, investigated how far NCU was able to increase N-use efficiency compared to urea alone. He found that on acid soils, NCU at 50 kg N/ha significantly increased paddy yield compared to unamended urea. With larger N rates, there was no benefit from using NCU. On neutral soils the results were the opposite, NCU at the larger rate of 100 kg N/ha significantly increased the yield of paddy, whereas the increase in yield was not significant at lower N application rates.

Khanif and Husin (1992) obtained the largest grain yield, N uptake and fertilizer N recovery in flooded rice from ASN plus DCD (2%). However, Tracy (1991) concluded from field trials that the application of DCD is not cost-effective for use on short season cotton in Missouri because it did not improve yield or N uptake. The influence of temperature on the rate of ammonia mineralization with DCD and ATS was investigated by Guiraud and Marol (1992). Sachdev and Sachdev (1995) concluded from a laboratory experiment with DCD that it is effective only at relatively low temperatures because at 35°C it has no influence on the nitrifying bacteria in soil. Hence, in India, DCD is more useful during the winter rabi season than during the monsoon kharif season.

According to Byrnes *et al.* (1995), research in tropical rice systems indicates that urease inhibitors such as NBPT and cyclohexylphosphoric triamide (CNPT) can play an important role in increasing the efficient use of urea. In flooded rice, the soil-fertilizer regime is completely different from that of upland crops (De Datta, 1995). The active biology and warm conditions of tropical rice paddies cause urea hydrolysis to be complete in 2-4 days, though, in some studies, it has taken up to 10 days. When farmers simply broadcast urea into standing water (De Datta, 1986) large ammonia volatilization losses have to be expected due to the rapid hydrolysis of urea, and this causes a high ammonia concentration in the flooded water (Amberger, 2006; Byrnes and Amberger, 1989; Byrnes *et al.*, 1989a, 1989b). The high pH and algal growth, sustain ammonia volatilization. Byrnes *et al.* (1989a) compared phenyl phosphorodiamidate (PPDA) with NBPT as urease inhibitors for use in flooded rice soils. Although PPDA is a powerful urease inhibitor, under the high pH conditions in floodwater, the inhibition effect of PPDA ended abruptly while that of NBPT continued for a long period of time. With a loss of 49.9% of the N from unamended urea, Byrnes and Amberger (1989) assumed that this loss was principally from ammonia volatilization but the loss of 7.8 to 9.6% of the N from urea with NBPT was probably through denitrification, because there was essentially no ammonia in the floodwater to volatilize. This finding does not support the idea that N not lost by ammonia volatilization would be largely lost by denitrification because Byrnes and Amberger (1989) also showed that the ammonia was retained in the soil.

In a greenhouse experiment with transplanted rice, Byrnes *et al.* (1989a) found that losses from the split application of urea were less than 10% when NBPT was added. In two other experiments on flooded and puddled soils, Byrnes and Amberger (1989) demonstrated the inhibition of urea hydrolysis with NBPT because no ammoniacal N was found in the floodwater.

Recent studies by the Cuu Long Delta Institute confirm the benefits of Agrotain in improving urea efficiency and crop yield in flooded rice (Chu and Le, 2007). When a range of amounts of Agrotain-treated and normal urea were compared on different soils in different seasons, the amended urea gave sizeable increases in yield and N-use efficiency. Net economic benefits of Agrotain addition were calculated (not shown) to identify the best nitrogen rate. Table 20. summarizes the key indicators at the nitrogen rate that produced the best economic return in each trial. Averaged across all trials, Agrotain improved N-use efficiency by approximately 32% and rice yields by some 6%.

In experiments in which the urease inhibition was only partially successful, the addition of an algicide, to reduce ammonia losses, and of nitrification inhibitors, to reduce losses by denitrification, improved the efficiency of the urease inhibitor. These results are supported by those of Chaiwanakupt *et al.* (1996) and Freney *et al.* (1995) in experiments on flooded rice in Thailand.

Further research on tropical soils in different environmental conditions with urease inhibitors is required to prove their efficiency in reducing N losses and increasing yields under upland, but particularly under flooded soil conditions. This research is urgently needed. There is enormous potential for the use of urease inhibitors because more than

Table 20. Effect of Agrotain on nitrogen rate, N-use efficiency and rice yield that produced the best economic return in Vietnam (Chu and Le, 2007).

Time	Product	N rate kg N/ha	Efficiency kg rice/kg N	Yield t/ha
Mekong Delta Institute, Can Tho				
Summer	Urea	80	11.4	2.77
	Urea+Agrotain	60	16.7	2.89
	Net effect	-25%	+46.5%	+4.3%
Winter	Urea	75	20.1	6.18
	Urea+Agrotain	75	24.1	6.48
	Net effect	–	+19.9%	+4.9%
Hoa An Farm, Phung Hiep, Hau Giang				
Summer	Urea	40	5.0	1.76
	Urea+Agrotain	40	7.3	1.87
	Net effect	–	+46.0%	+6.3%
Long Phu, Soc Trang				
Summer	Urea	80	19	4.51
	Urea+Agrotain	80	34	4.80
	Net effect	–	+26.0%	+6.4%
Winter	Urea	100	21.3	4.71
	Urea+Agrotain	100	25.4	5.02
	Net effect	–	+19.2%	+7.6%

half of all the N fertilizers used in agriculture is as urea, and that a large proportion of this urea is still surface-applied or used on flooded rice. However, the combined use of nitrification inhibitors, urease inhibitors and algicides is, in practice, not economical.

6. Environmental aspects of slow- and controlled-release fertilizers and nitrification and urease inhibitors

6.1. Slow-and controlled-release fertilizers

The environmental impact of fertilizer use is lessened by all those measures that improve nutrient use efficiency (NUE), specifically that of nitrogen, i.e. increasing the uptake of nutrients by plants and thus leaving less in the soil at risk to loss to the environment. The environmental aspects of controlled-release fertilizers have been investigated by Shaviv and Mikkelsen (1993b). Comparing several types of polymer-coated urea, Shaviv (1995) found that increasing N-use efficiency and lowering their impact on the environment can be critically affected by the release characteristics of the amended urea in relation to the pattern of demand for N by the crop.

With slow- and controlled-release fertilizers, the best agronomic and environmental results are obtained with products that do not have the so-called ‘burst effect’ and ‘tailing effect’ (Shaviv, 1995, 2005). Large yields and, at the same time, minimal adverse effects on the environment can be expected when the release pattern of nutrients from slow- and controlled-release fertilizers are synchronized to the crop’s nutrient uptake pattern. Consequently, for good N fertilizer management, much detailed information is required about the release pattern in water and in the soil. In addition to the adverse ‘burst effect’ on excess nutrient release, any ‘tailing effect’ after harvest of the fertilized crop must be studied to assess the positive effects of controlled-release fertilizers on the environment.

According to Shaviv (2005) an effective assessment must include:

- nutrient release characteristics and mechanisms,
- the effects of environmental factors (temperature, moisture, aeration, bio-activity, root exudates, soil type, etc.) on the release and the nutrient use efficiency, and
- the plant’s demand for nutrients under a range of agricultural conditions.

This information is important, because encapsulated controlled-release fertilizers are products designed to solve a number of specific technical and environmental problems in agriculture and horticulture, landscape management and gardening. Users who prefer coated fertilizers because of the savings in labour, should also be aware of the environmental benefits through their nutrient release properties.

Dou and Alva (1998) studied the effect of several controlled-release fertilizers compared to urea on citrus rootstock seedlings in a sandy soil. They demonstrated that, for a given N application rate, the total N uptake by the seedlings was greater for controlled-release fertilizers than for urea and they concluded that N losses would therefore be less when using controlled-release fertilizers as an N source compared to a soluble N fertilizer.

With intensive agriculture in Japan, N fertilizer commonly makes the greatest contribution to crop production while it has the highest potential for environmental degradation (Shoji and Kanno (1993) and Shoji (1999, 2005). Shoji and Mae (1984) considered that to minimize nitrate pollution but optimise yield in a given farming system, it is necessary to maximize N-use efficiency as shown in Table 21. Maximizing NUE requires programmed fertilization using controlled-release fertilizers (e.g. such as Meister®), best fertilizer placement, and soil conditions favourable to plant growth. Innovative farming systems as well as using controlled-release fertilizers contribute to the improvement of the agro-environment (Shoji, 1995, 2005). For example, appropriate controlled-release fertilizers in no-till rice culture can effectively improve the water, atmospheric and biological environments of rice fields.

Table 21. Minimizing nutrient pollution by maximizing nitrogen use efficiency: Case study in a rice field in North-east Japan on NUE (Shoji, 2005).

Case	NUE %	N rate kg N/ha	N rate reduction %	N uptake by rice kg N/ha	Max. potential fert. pollution kg N/ha
1	30	100	0	30	70
2	80	40	60	32	8

Notes:
30% NUE: average data of conventional fertilizer basal application
80% NUE: highest data of Meister application

Masuda *et al.* (2003) studied the decrease in nitrate leaching when polymer-coated N fertilizers were applied to sugarcane and showed that N fertilizer use could be decreased by about 40% without causing a reduction in sugar yield. Nitrogen absorption was estimated at 57.7% and 90.9% with conventional and controlled-release fertilizers, respectively.

Zhang (2007) reported the results from experiments, demonstrations and advisory work on more than twenty crops over several years at the Shandong Agricultural University. Crop yields were larger when using a controlled-release fertilizer, than when using conventional fertilizers although the amount of nutrient applied was a third or a half less with the controlled-release fertilizer. The quality of the crops and food products was also improved. In addition to the increase in N-use efficiency, N volatilization and leaching losses were considerably reduced through the application of controlled-release fertilizers. Zhang (2007) concluded that, in regions where there was excess application of conventional fertilizers, the increase in severe non-point pollution could be reduced considerably by using controlled-release fertilizers. Ma *et al.* (2007) found in experiments on the main soil types in Shandong Province, that ammonia volatilization is influenced by soil type and that N losses from conventional fertilizers are greater than those from controlled-release fertilizers. Zhang *et al.* (2001) found in N leaching experiments with various fertilizers in soil columns that, in addition to other positive aspects, controlled-release fertilizers had less influence on changes of the soil pH than conventional fertilizers. Figure 20. is the result of investigations with ESN showing the reduction in nitrate leaching losses.

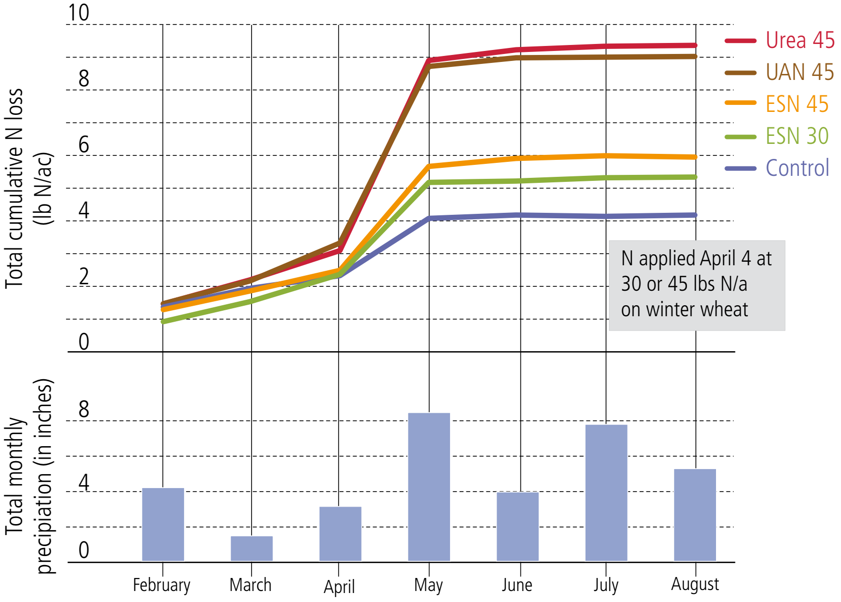


Figure 20. Measurement of ESN effect on N leaching losses in Piketon (Ohio) in 2003 (Adapted from Agrium, 2005).
Inorganic N in leachate from 100- x 30-foot lysimeters. Calculated from total water volume and N concentration (Islam, Ohio State University).

The following graph (Figure 21) shows how the polymer-coated urea ESN reduces ammonia volatilization.

The reduction of nitrate leaching and ammonia volatilization through the use of ESN is also reported by Blaylock (2010). Halvorson and Del Grosso (2010) have found that using ESN also results in reduced N_2O fluxes. However, significant results have only been obtained in no-till crop rotations with maize (reduction of 49%); whereas results with conventional tillage maize have been negligible.

Various agricultural research centers in Japan have demonstrated that for rice, maize, sugarcane, potatoes, tea and numerous vegetables nutrient application rates could significantly be reduced (by 20 to 60%) when slow- or controlled-release fertilizers are applied, without sacrificing yield. In addition, only one single basal application is necessary (Tachibana, 2007). Shoji *et al.* (2001) compared a polyolefin-coated urea with nitrification inhibitor and unamended urea on flood irrigated barley, center-

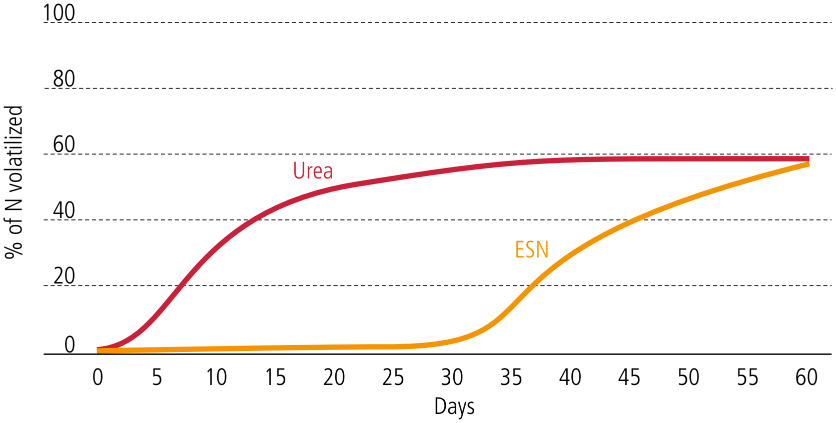


Figure 21. Measured ammonia losses from surface applied urea and ESN (Adapted from Agrium, 2005).

pivot irrigated potato and maize grown in a large-scale lysimeter, all on different soils. Nitrous oxide emissions from the controlled-release fertilizer plots were almost one third of those with urea, and N recovery was almost twice that achieved with urea. The authors concluded that the contribution of controlled-release fertilizers and nitrification inhibitors to air and water quality conservation is basically due to greater NUE and reduced N fertilization rates.

Alva and Tucker (1993) and Alva *et al.* (1993) concluded from experiments in a citrus orchard in Florida that there is no adverse affect on the growth of young citrus trees when the frequency and rate of N application is reduced by using polyolefin-coated controlled-release fertilizers and that nitrate leaching can be minimized also.

6.2. Nitrification inhibitors

While N is essential for crop production there are environmental issues related to its use (Zerulla *et al.,* 2001a). From their initial development, research on nitrification inhibitors has shown that they can significantly delay nitrification, and consequently the risk of nitrate leaching to groundwater. Furthermore, they can reduce losses of nitrogen oxides (NO_X) and nitrous oxide (N_2O) to the atmosphere (Weber *et al.*, 2004b). At the IFA International Workshop on Enhanced-Efficiency Fertilizers, Grant (2005) said: “One of the most important challenges facing humanity today is that of increasing food production while avoiding environmental degradation. As the world’s population grows, the crop yield on land currently under production must be increased to maintain food security without converting marginal land or natural ecosystems to agriculture. This increase in production will require an adequate supply of plant-available N to support both crop yield potential and nutritional quality. Therefore, N fertilization will play a critical role in improving crop yields and ensuring food security (Mosier *et al.*, 2004). Inorganic fertilizer is the single largest input into the global N cycle (Smil, 1999).

Currently, it is estimated that cereal crops recover only about 30 to 50% of applied fertilizer N. Without major improvement in N use efficiency, increasing N inputs may lead to negative environmental impacts as the organic N moves from the soil-plant system to the air or water (Cassman *et al.,* 2002).

Farmers adopting fertilizer best management practices (FBMPs) are already using several methods to adapt the amount of N fertilizers and other plant nutrients applied to meet the needs of plants to avoid N losses, to maintain safe and clean groundwater, and to reduce emissions of ammonia and other environmentally relevant gases to the atmosphere. Such methods begin with testing the soil to avoid any over- or undersupply of N, dividing the total N requirement into smaller applications to match the plant's N demand pattern, timing the application according to rainfall, side-dressing the fertilizer, injecting or incorporating it into the soil, etc. It will not always be possible – mainly depending on weather and soil conditions, but also on the availability of labour – to choose the optimum amount and the best timing for N fertilizer application. Nitrification and urease inhibitors can contribute to better NUE and to reducing N losses through denitrification, leaching and volatilization (Prasad and Power, 1995). Nitrification and urease inhibitors should, therefore, be part of FBMPs.

Minimizing N losses implies an enhanced N-use efficiency. Even in cases where the use of nitrification inhibitors does not lead to an increase in crop yield, there are still environmental benefits (Frye, 2005). The majority of studies, tests and investigations have clearly proved the reduction of nitrate leaching, when N fertilizers have been amended with nitrification inhibitors. There are only very few cases where a reduction in nitrate leaching has not been shown. This has special importance within the EU because of the 'Nitrate Directive' (Jonkers and Smeulders, 2005). The latest developments and actual status are given in the following box.

The EU Nitrate Directive

The Nitrate Directive (1991) aims at reducing pollution of surface waters by nitrates from agricultural sources. It sets a maximum threshold of 50 mg NO_3^-/l. Another EU directive, recently revised, specifically addresses groundwater. Consistency between both directives is ensured by the Water Framework Directive (2000), which defines the principal pollutants, standards and monitoring obligations.

A directive is an obligation of result, i.e. the Nitrate Directive mandates achieving maximum 50 mg NO_3^-/l in surface waters. The directive has to be enforced at the national level, where actions and measures are defined. For the Nitrate Directive, national action plans have to be revised every four years.

Enforcement of a directive may be different from one country to another, and derogations are possible. For instance, The Netherlands, with reference to their grassland farms with N surpluses in the form of animal manure, reached an agreement with the European Commission, laid down in the Third Action Programme (2004). This programme introduces a system of application standards, both for animal manure, total manure and phosphate from 2006 onwards. For animal manure, the maximum application level is of 170 kg N/ha. The application standards for total N is aimed at reaching 50 mg NO_3^-/l or less in surface water in 2009. Farms with at least 70% of grassland may request a specific derogation for animal manure application: 250 kg N/ha instead of the 170 kg N/ha.

In the United States, a seven year study at the University of Minnesota showed that the use of nitrapyrin reduced leaching of nitrate-N by about 15% annually (when averaged across seven years), with fall applied anhydrous ammonia compared to fall application of ammonia without nitrapyrin (Huffman, 1997). Yields were increased by 6% for the fall comparison. Fall applied ammonia plus nitrapyrin produced similar yields and similar levels of nitrate-N leaching as the same rate of N applied in the spring. In 2003, Arise Research conducted a trial at Martinsville (Illinois, USA), in which nitrapyrin with spring-applied urea reduced nitrate leaching by 30% (Dow AgroSciences, 2003).

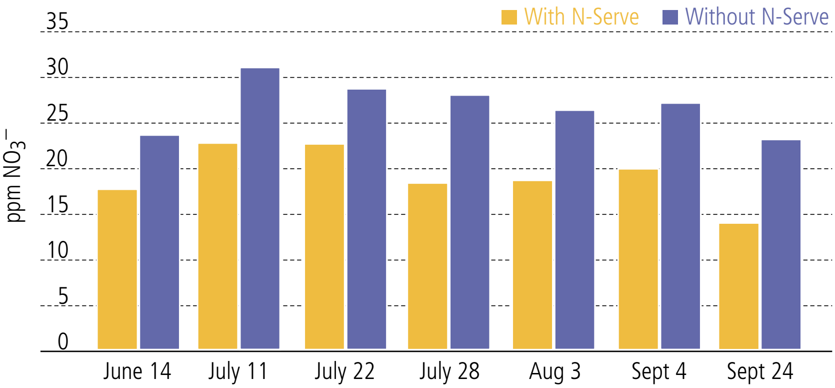


Figure 22. Nitrate leaching in spring-applied urea (Adapted from Dow AgroSciences, 2003).

In Germany, nitrate leaching was decreased by 27% with DCD-stabilized fertilizers compared to calcium ammonium nitrate on a podsol-gley soil and by 40% on a loamy soil over a seven-year period (Scheffer, 1991). Furthermore, in various studies it was also emphasized that nitrate leaching can be decreased significantly during humid springs and under crops like maize or sugar beet (Amberger 1991a, 1993a; Amberger and Germann-Bauer, 1990; Gutser, 1991, 1999a).

The use of DMPP with urea reduced nitrate leaching when maize was irrigated with an overhead mobile-line sprinkler system (Diez-López *et al.*, 2008).

Serna *et al.* (2000), applied ammonium sulphate nitrate with and without DMPP to six-year-old citrus plants grown individually outdoors in containers in Spain with consecutive flood irrigation. The experiment ended after 120 days and the results indicated that DMPP improved N-use efficiency and reduced nitrate leaching by retaining N in the ammoniacal form. An additional effect was the increased ammonium nutrition of the plants, which are able to absorb larger amounts of ammonium compared to nitrate (Serna *et al.*, 1992). Similarly, in 1993 and 1994, Serna *et al.* studied ammonium sulphate nitrate on citrus with and without DCD. DCD reduced nitrate losses, improved N-use efficiency and minimized environmental risks associated with the irrigated production of citrus.

Picture 8. Lysimeter citrus trial (Photo: IVIA/Spain; Serna *et al.*, 2000).

Carrasco and Villar (2001) studied the use of manufactured and organic fertilizers with and without DMPP on irrigated maize and wheat in the Northeast of Spain. They concluded that using DMPP could reduce nitrate losses in 'Nitrate Vulnerable Zones'. Reduced nitrate leaching was found also by Bañuls *et al.* (2001). Chaves *et al.* (2006) incubated cauliflower leaves with DCD and DMPP. Under favourable conditions, DCD inhibited nitrification of the crop residues for 50 days and DMPP for at least 95 days indicating their potential, especially of DMPP, to reduce nitrate leaching after incorporation of crop residues.

The requirement to reduce leaching of nitrate in water catchment areas with restrictions on N fertilizer use may provide an opportunity to increase the use of nitrification inhibitors. In recent years, there has been increasing attention to nitrate leaching from intensively managed grassland grazed by cattle, mainly due to the application of organic manures with the largest proportion being produced from animal urine (McKervey *et al.,* 2005). The urine patch is the primary source of N losses, not fertilizer N (Edmeades, 2004). New Zealand has a lead position in investigating nitrate leaching from grazed grassland (Suter *et al.,* 2006) and there it has been shown that the application of DCD reduces nitrate leaching from grassland by 61% on average (Clough *et al.,* 2007). McKervey *et al.* (2005) concluded however, that nitrification inhibitors alone will probably not provide a complete solution to the problem of nitrate leaching from pastures, but they could be a useful tool in conjunction with the adoption of good management practices.

According to Gutser (2006) and Ebertseder and Gutser (2006), N losses from slurry, when applied to arable crops, could be largely avoided by choosing the right time of application. Nevertheless, the incorporation of a nitrification inhibitor into the slurry would stabilize the ammonium and reduce the risk of nitrate losses through leaching.

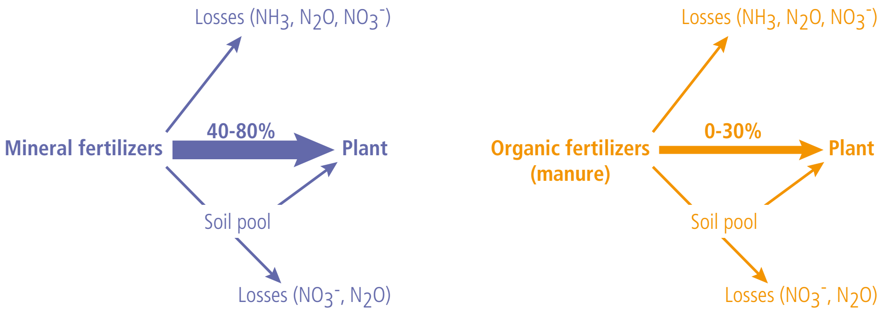


Figure 23. Long-lasting evaluation of mineral and organic fertilizers under BMP fertilization strategy (Adapted from Gutser, 2006).

In addition to the reduction of nitrate leaching, amending N fertilizers with a nitrification inhibitor will also improve the quality of crops grown, particularly of green leafy vegetables. N fertilizers with and without a nitrification inhibitor have been tested for various horticultural crops (Pasda *et al.*, 2001b). Nitrate concentrations in leeks (*Allium ampeloprasum* L. *var. porrum*) and celery (*Apium graveolens* L. *var. dulce*) tended to be lower with the addition of DMPP, while the general appearance of these vegetables was noticeably better than with the reference treatments. Comparatively, large nitrate concentrations were found in spinach (*Spinacia oleracea* L.). To develop practical approaches to control nitrate accumulation in vegetables in China, Xu *et al.* (2005) used ammonium sulphate nitrate plus DMPP. They concluded that the nitrification inhibitor decreased nitrate accumulation in leafy green vegetables and at the soil surface, and that its use was beneficial for the protection of the environment and positive for human health. Egea and Alargón (2004) found similar results with melon. Nearly all studies have shown that nitrification inhibitors not only reduce the risk of nitrate leaching to groundwater and improve the quality of crops, but they also considerably reduce emissions of nitrogen oxides and nitrous oxide.

Whereas nitrogen oxides contribute to acid deposition to soil and surface water, nitrous oxide is an important greenhouse gas (Amberger, 1996). In a laboratory experiment comparing urea plus DCD with urea alone, Kumar *et al.* (2000) achieved a reduction of up to 60% of nitrous oxide emissions. Weiske *et al.* (2001a, b) compared the effect of CLMP (4-chloro-3-methylpyrazole), DCD and DMPP on emissions of nitrous oxide, carbon dioxide and methane from soil under field conditions. DCD lowered the release of carbon dioxide by 7% on average over three years, CLMP by 6% and DMPP by 28%. DMPP also stimulated methane oxidation throughout the three growing seasons by 28% compared to the control. The results were site and experiment specific, but in total the global warming potential (GWP) was reduced by 7% by DCD and CLMP and by 30% by DMPP.

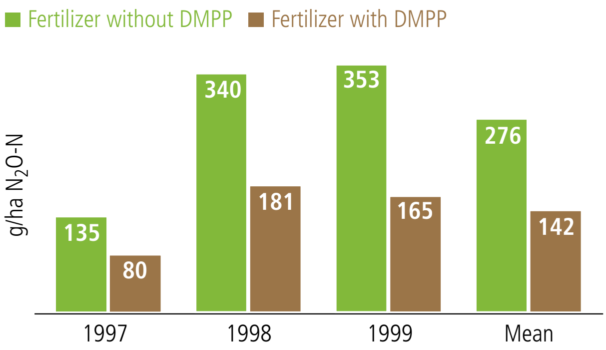


Figure 24. Effect of DMPP on N_2O emissions in a field trial (Adapted from Weiske *et al*., 2001a).

Weber *et al.* (2004a) found in laboratory and field experiments that DCD and TZ reduced nitrous oxide emissions by about 20% with urea-ammonium sulphate and by some 40% with urea. Reduced nitrous oxide emissions when using DCD+TZ was found also by Schuster *et al.* (2005) and Wissemeier *et al.* (2001) also showed that DCD and DMPP reduced nitrous oxide emissions, and that there was no ammonia volatilization from ammonium-containing fertilizers stabilized with DMPP. On average, nitrous oxide emissions have been reduced by 72% in New Zealand when DCD was applied to grassland to minimize nitrate leaching (Clough *et al.*, 2007; Di and Cameron, 2003, 2006; Di *et al.*, 2007). Nitrification inhibitors are not the only solution to reduce nitrate leaching and nitrous oxide losses from pastoral systems in New Zealand. After reviewing a range of inhibitors, including nitrapyrin, DCD, DMPP, etridiazole, acetylene, 2-EP and neem, the Research Consortium PGg in New Zealand concluded that DCD and DMPP appeared most suited for use in pastoral systems but DMPP would be preferred because it did not produce any phytotoxic effect (Suter *et al.*, 2006).

In Spain, Menéndez *et al.* (2006) tested DMPP on grassland after slurry application and concluded that DMPP is an efficient nitrification inhibitor that reduces nitrous oxide and nitrogen oxide emissions from grasslands. Merino *et al.* (2005) applied DMPP twice after cattle slurry application on grassland in autumn and in spring, and reduced nitrous oxide losses by 69 and 48%, respectively. In Devon, England, Dittert *et al.* (2001) showed that DMPP was very efficient in reducing nitrous oxide emissions from injected dairy slurry.

Nitrous oxide emissions were decreased significantly when urea and ammonium nitrate amended with DCD and nitrapyrin were applied to grassland over two growing seasons (McTaggart *et al.*, 1993). Bronson and Mosier (1993) showed that emissions of methane and nitrous oxide following the application of urea plus nitrapyrin and encapsulated calcium carbide (ECC) to irrigated maize were reduced by 41 and 71-74%, respectively.

The report of the German 'Scientific Advisory Committee on Fertilizers' (*Wissenschaftlicher Beirat für Düngungsfragen*)[9] 'Experience with the use of nitrification inhibitors with reference to their possible influence on the vitality of soil organisms and the formation of climatic relevant trace gases like N_2O', discussed the positive environmental benefits of using nitrification inhibitors. This report, published by the German Federal Government as Drucksache 239/96 (Bundesrat, 1996), concludes that "Various investigations on the influence of nitrification inhibitors on N_2O, primarily using DCD, acetylene (in pot experiments) and nitrapyrin, clearly demonstrate that the emissions of climate-relevant gases can be reduced by up to 50% for N_2O, and up to 35% for methane, through the use of nitrification inhibitors."

6.3. Urease inhibitors

Ammonia volatilization is the greatest environmental problem where urea or amide-containing fertilizers are used and also from urine patches in grazed grassland. One of the most promising ways to reduce ammonia losses to the atmosphere and to increase the efficient use of urea is to use urease inhibitors, delaying the transformation of urea to ammonium ions. All urease inhibitors of practical relevance will diminish ammonium losses from urea and urea-containing fertilizers and NBPT (Agrotain), currently the market leader, is very effective at low concentrations. Adding NBPT to urea can reduce ammonia losses by up to 70% compared to untreated urea (Watson, 2005). Though the majority of field experiments with NBPT in the United States focused on yield increases, ammonia losses from urea or urea-containing fertilizers have ranged from 5 to 25%. Other studies have shown losses of 12 to 15% and some up to 30% of the amount of N applied. Amendment with NBPT reduced losses by 50 to 90%, with an average of 70%. Although a reduction in ammonia volatilization does not always translate into an increase in yield, certainly not on very N rich, fertile soils (Hendrickson, 1992; Watson *et al.,* 1998), the environmental benefit remains. Therefore, urease inhibitors are potentially useful tools for controlling or reducing nitrate leaching losses and gaseous losses of N from arable soils and grassland/pastures (Singh *et al.,* 2004). Halvorson and Del Grosso (2010) also reported a significant (51%) reduction of N_2O fluxes using Super U (urea with incorporated Agrotain Plus) in no- till maize crops.

Global budgets for atmospheric ammonia emissions have been calculated by Schlesinger and Hartley (1992). With regard to emissions from fertilizer applications, a compilation of recent studies suggests that at least 20% of urea-N and 10% of ammonium sulphate-N are lost in a short period after application to upland soils. A 'Three-dimensional Model of the Global Ammonia Cycle' has been used by Dentener and Crutzen (1994) to determine the global distribution of ammonia and ammonium, calculating a volatilization fraction of 15% for the nitrogen applied as urea, of 2% for ammonium nitrate, 8% for ammonium sulphate and 3% for the other nitrogen fertilizers. For developing countries, long-term scenarios with regard to emissions of

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[9] *Translation by the author*

ammonia, nitrous oxide and methane into the atmosphere from animal waste products and fertilizer use have been compiled by Bouwman (1995).

The costs of using fertilizers with a built-in enhanced efficiency are borne by the agricultural sector. For farmers, the value of such fertilizers is primarily based on the increase in yield and/or reduced production costs (Grant, 2005). However, increased crop production and environmental protection benefit both agriculture and society at large. In many communities, the environmental benefits to society are not ascribed an economic value but if they are substantial, some costs should perhaps be borne by society, possibly through incentives for development and advisory work on slow- and controlled-release and stabilized fertilizers, and for encouraging their wider adoption by farmers (Grant, 2005).

Environmental and societal value (Grant, 2005)

Environmental benefits to society are not always given economic value

- Life-cycle analysis could more clearly define value;
- Define the costs and benefits throughout the system;
  - Including manufacturing, emissions on and off farm, transport, off-site impacts.

Clarification of value to society

- Current costs are borne by the agricultural industry;
- Benefits are to both agriculture and society in general;
  - Environmental benefits, security of food supply, reduced food prices, improved food quality, maintenance of natural ecosystems, strong rural economy;
- If benefit to society is substantial, should some costs be shifted to society?
  - Subsidies or incentives for adoption;
  - Support for development and adaptive research.

7. Consumption and economics of slow- and controlled-release and nitrification and urease inhibitors

The following data are based on information from companies marketing the products concerned, and on notes in fertilizer magazines, reports and official publications.

7.1. Consumption

7.1.1. Slow- and controlled-release fertilizers

World consumption of synthetic slow- and controlled-release fertilizers in 2004/05 was estimated at 786,000 metric tonnes (t), a 45% increase compared to 1995/96 (Table 22.).

Table 22. World consumption of manufactured slow- and controlled-release fertilizers (metric tonnes of fertilizer product).

Region	1983	1995/96	2004/05	2006/07 Estimate
United States	202,000	357,000	569,000	590,000
Western Europe	76,000	87,000	120,000	125,000
Japan	47,000	96,000	97,000	110,000
China				1,350,000[1]
Canada				150,000[1]
Total	325,000	540,000	786,000	2,275,000

[1] Only capacities, consumption unknown.

Key data on the global market for slow- and controlled-release fertilizers, as well as first estimates for 2009 are given by Landels (2010b).

Since 2005, the observed dramatic increase in consumption is due to additional production capacity for sulphur-coated urea (SCU) in China and to a new generation of polymer-coated urea (PCU) fertilizers developed by Agrium (ESN). In 2002, Agrium started to introduce their ESN® for agricultural crops in the USA, primarily for maize and wheat. The company announced that they would enlarge the ESN production capacity to 150,000 t in 2006/2007. This is not yet included in the estimated consumption for 2006/07.

In China, Shandong Kingenta increased production capacity for slow- and controlled-release fertilizers from 350,000 to 500,000 t in 2007. This company produces

SCU, sulphur-coated fertilizers (SCF), PCU and polymer-coated fertilizers (PCF). Hanfeng Evergreen, another Chinese company, increased its capacity to 150,000 t for the production of SCU and polymer-coated/sulphur-coated fertilizers (PSCF), in addition to 500 t urea-formaldehyde (UF) condensation products. Shikefeng Chemical Industry started with 200,000 t production of SCU in 2006, and enlarged the capacity by a further 500,000 t in 2007.

In the mid-1990s, UF-formulations had the largest market share among the slow- and controlled-release fertilizers. However, since 2000, SCU, polymer-coated/sulphur-coated urea (PSCU) and PCFs have become the largest group of products sold. Now, however, PSCU is increasingly replacing SCU.

Table 23. World consumption of slow- and controlled-release fertilizers by product type (metric tonnes of fertilizer material).

Region	Urea reaction products	SCU/PSCU	PCF	Others	Total
			1995/96		
USA	205,000	100,000	45,000	7,000	357,000
W. Europe	65,000	2,000	20,000	_	87,000
Japan	36,000	60,000			96,000
					540,000
			2004/2005		
USA	223,000	226,000	120,000	_	569,000
W. Europe	80,000	5,000	35,000	_	120,000
Japan	5,000		92,000	_	97,000
					786,000

Compared to UF-based products and PCFs, the production of SCU/PSCU is more economical and these types of slow- and controlled-release fertilizers (e.g. ESN in the USA and Canada) are thus becoming attractive for use on field agricultural crops. In contrast, in Western Europe, UF-based slow-release fertilizers are still the dominant group although their use on field crops remains negligible.

In Japan, the authorities started a campaign aimed at reducing the very large fertilizer application rates, especially of N fertilizers. Consequently, mineral fertilizer consumption has declined by about 30% over the past thirty years. The Japanese Ministry for Agriculture, Forestry and Fishery (MAFF) then launched a programme to replace conventional N fertilizers by slow- and controlled-release fertilizers, mainly coated fertilizers, and consumption of these special types of fertilizers has grown steadily. Polymer-coated fertilizers (mainly urea) have become the most important. The main crops to which slow- and controlled-release fertilizers are applied are rice and high-value vegetables.

Estimates for China, suggest that of the total production capacity of 1 million metric tonnes (Mt) of slow- and controlled-release fertilizers, 500,000 t are SCU and PSCU and the other 500,000 t are PCFs and PCU. Ninety percent of the production is intended for the local market for all crops, and 10% for export.

According to IFA estimates (IFA, 2010), world fertilizer consumption reached 155.6 Mt nutrients in 2004/05, corresponding to approximately 420 Mt of fertilizer product. Consequently, the estimated consumption of slow- and controlled-release fertilizers in 2004/05 (786,000 t without the Chinese capacity of 1.350 Mt) still amounts to no more than 0.20% of total world fertilizer consumption. If the total output of all the new production capacities is included the share of slow- and controlled-release fertilizers would still only reach 0.47% of world mineral fertilizer consumption.

Although the market for speciality fertilizers is negligible it is, however, a fast-growing one, as demonstrated by the large increase in production capacity in China and by Agrium. The potential for increased use in agriculture is tremendous considering the advantages in terms of labour saving, increased nutrient recovery (N-use efficiency/efficiency design), reduced fertilizer application rates, improved yields and reduced negative environmental impact. Increased energy costs, but also increased income through higher prices for agricultural produce, would further favour the application of slow- and controlled-release fertilizers in agricultural crops. In addition, programmes such as that of MAFF in Japan to reduce fertilizer application rates by replacing conventional fertilizers by slow- and controlled-release fertilizers would further promote their use.

7.1.2. Nitrification inhibitors

There are no reliable, publicly-available statistics on the use of nitrification inhibitors and of fertilizers containing these products due, in part, to the limited number of producers, e.g. there is only one manufacturer of nitrapyrin in the United States. The same is true for the consumption of DCD in the United States, Canada, East Asia and Western Europe.

The importance of nitrapyrin and DCD as nitrification inhibitors in agriculture can only be demonstrated from estimates of the cropland area on which N, NP and NPK fertilizers containing nitrification inhibitors are applied. For the United States, the total area on which treated fertilizers were applied in 1994/95 was estimated at 1.820 million hectares (Mha). Of this area, approximately 1.620 Mha had N fertilizers with nitrapyrin and 200,000 ha with DCD-containing N fertilizers. Favoured by wet weather and environmental considerations in 1995/96, this total area had increased to approximately 1.860 Mha but this was still only 1.16% of the total cropped area of 160 Mha in 1995/96. No similar estimates can be made for Western Europe.

7.1.3. Urease inhibitors

There is only one main producer (and several licensees in various parts of the world) of urease inhibitors and there are no data on the total worldwide consumption.

7.2. Costs and benefits of slow- and controlled-release fertilizers and nitrification and urease inhibitors

Prices for controlled-release and stabilized fertilizers vary locally and seasonally. No exact costs are given in any publication, or only model calculations based on several assumptions. In general, the prices for slow- and controlled-release fertilizers are substantially greater than those for standard fertilizers but as raw material prices rise, the cost gap becomes smaller while the benefits from efficiency increase. Lammel (2005), at the IFA International Workshop on Enhanced-Efficiency Fertilizers presented the following figure on the price relationship of the different product groups.

Figure 25. shows that the cost of adding nitrification (and urease) inhibitors to N fertilizers is still in a range that is attractive for their use in agriculture. Slow- and controlled-release fertilizers, however, are economical in agriculture only under exceptional conditions, e.g. if their use allows a large decrease in amounts applied and/or labour costs. The situation may change with the large-scale production of coated urea (ESN from Agrium and Syncote from Shandong Kingenta). In general, the current trends towards increasing energy costs, increased cost of fertilizer N, and scarcity of agricultural labour will make slow- and controlled-release fertilizers more attractive (Grant, 2005).

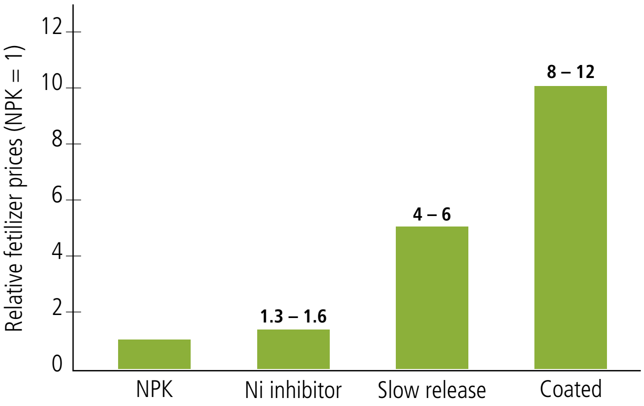


Figure 25. Price comparisons of slow- and controlled-release fertilizers with standard fertilizers (Adapted from Lammel, 2005).

7.2.1. Slow- and controlled-release fertilizers

The main obstacle to the wider use of slow- and controlled-release fertilizers, particularly in agriculture, is their cost compared to conventional fertilizers. Farmers who grow high-value crops can more easily afford to pay for slow- and controlled-release fertilizers.

Table 24. Comparative return on investment of farmers growing high-value crops agains low-value crops (Lammel, 2005).

	High-value crop (melons) US$/ha	Low-value crop (Wheat[1]) US$/ha
Production cost	12100	750
Yield value	13750	780
Profit	1650	30
Value of 5% yield increase	687	39

[1] Yield: 6 t/ha, no subsidies considered

The price difference is:

- least with SCU and PSCU (generally less than 2 to 1),
- greater with UF products, 3-5 times higher per unit N compared to conventional fertilizers, and
- greatest with polymer-coated controlled-release fertilizers, ranging between 4 to 8 times that of corresponding conventional fertilizers.

There are several important reasons for these differences:

- Cost of the materials used for encapsulated/coated products, particularly the price of the coating materials;
- The organic polymer coating materials, which consist primarily of single polymers, polymer mixtures or co-polymers may cost 10 to 30 times that of the fertilizer itself.

To put this in perspective, the following example is given for a fertilizer with a cost index of 100 and a coating polymer with a cost index of 3000. A coated fertilizer, comprising 12% (by weight) of polymer coating and 88% of fertilizer encapsulated by the coating, would have a materials cost as follows:

Table 25. Cost comparison of urea vs. conventional polymer-coated urea (Detrick, 1996).

Component	Cost index	Weight %	Materials cost index
Urea 46-0-0	100	88	88
Polymer coating	3000	12	360
PCU 40-0-0		100	448

Note that PCU contains only 40%, since the 12% coating result in only 88% urea in the PCU (88% x 46% N = 40% N)

This model calculation can serve for actual calculations. It demonstrates that the material cost of the coated fertilizer is four times that of the basic fertilizer and in addition, the cost of production adds to this cost (Detrick, 1995). Further improvement of polymer coating of sulphur-coated fertilizers ('hybrid-coating') will permit the production of products in a price range becoming economically interesting for use in conventional agriculture.

Larger production capacities since 2006/07 contribute to a reduction in production costs, but the majority of manufacturers still have only a small or limited production capacity. This results in relatively high costs of slow- and controlled-release fertilizers. Furthermore, some producers manufacture their products in special batches (1,000 to 5,000 kg). To achieve perfect coating quality, producers usually use size separation of raw granular materials, which adds further to the cost of encapsulated/coated fertilizers.

There are also higher marketing and sales expenses associated with slow- and controlled-release fertilizers because their use has to be explained much more carefully to the user than with conventional fertilizers in order to ensure their correct application.

An economic indicator for the farmer to determine the profitability of using fertilizer products is the value/cost ratio (VCR). Unfortunately, there is practically no data from reliable field experiments with slow- and controlled-release fertilizers to allow this to be calculated. Such field experiments are urgently needed worldwide. The minimum profitability is fixed normally at a VCR of 2. However, under more risky conditions, e.g. under tropical and sub-tropical farming conditions, the VCR should be at least of 3 (Trenkel, 1993). Detrick (1996) calculated VCR (Table 26 and Table 27) using controlled-release fertilizers on low-cash value (LCV) crops and high-cash value (HCV) crops, which should serve as model for calculations with actual data.

Table 26. Low-cash value crop with 50% controlled-release urea-N. Standard fertilization practice vs. experimental fertilization practice (Detrick, 1996).

Standard fertilization practice	US$/ac
150 lb N/ac x US$ 0.30/lb N (urea-N)	45
Application costs, basic- and side-dressing	20
Total costs	65
Crop yield value	300
Experimental fertilization practice, 50% CR urea-N	US$/ac
75 lb N/ac x US$ 0.60/lb N – CR urea-N	45
75 lb N/ac x US$ 0.30/lb N – urea-N	23
150 lb N/ac – total N	68
Application costs, basic-dressing	10
Total costs	78
Crop yield value (with 10% yield increase)	330
Value – incremental increase	30
Cost – incremental increase	18
Value/cost ratio (VCR)	1.7

This calculation clearly shows that the application of only 50% of total N in the form of controlled-release urea would not give a satisfactory value/cost ratio. In addition, in this example the cost of controlled-release urea is only twice that of urea. Such a small difference is not found generally for conventionally encapsulated products.

The situation is different with high-cash value (HCV) crops:

Table 27. High-cash value crop with 44% controlled-release urea-N Standard fertilization practice vs. experimental fertilization practice (Detrick, 1996).

Standard fertilization practice	US$/ac
300 lb N/ac x US$ 0.30/lb N (urea-N)	90
Application costs, basic- and 2 side-dressing	30
Total costs	120
Crop yield value	3000
Experimental fertilization practice, CR urea 44% of total N	US$/ac
133 lb N/ac x US$ 0.90 lb N – CR urea 44% of total N	120
167 lb N/ac x US$ 0.30/lb N – urea-N	50
300 lb N/ac - total N	170
Application costs, basic- & 1 side-dressing	20
Total costs	190
Crop yield value (with 10% yield increase)	3300
Value – incremental increase	300
Cost – incremental increase	70
Value/cost ratio (VCR)	4

With high-cash value crops, using a controlled-release urea fertilizer at a cost three-times that of urea, the value/cost ratio is 4. In this case, it is profitable to apply at least part of the urea as a controlled-release fertilizer. The use of controlled-release fertilizers is to be recommended more for high cash value crops where production is pushed to the maximum through an oversupply of fertilizers, increasing the potential for greater nutrient losses.

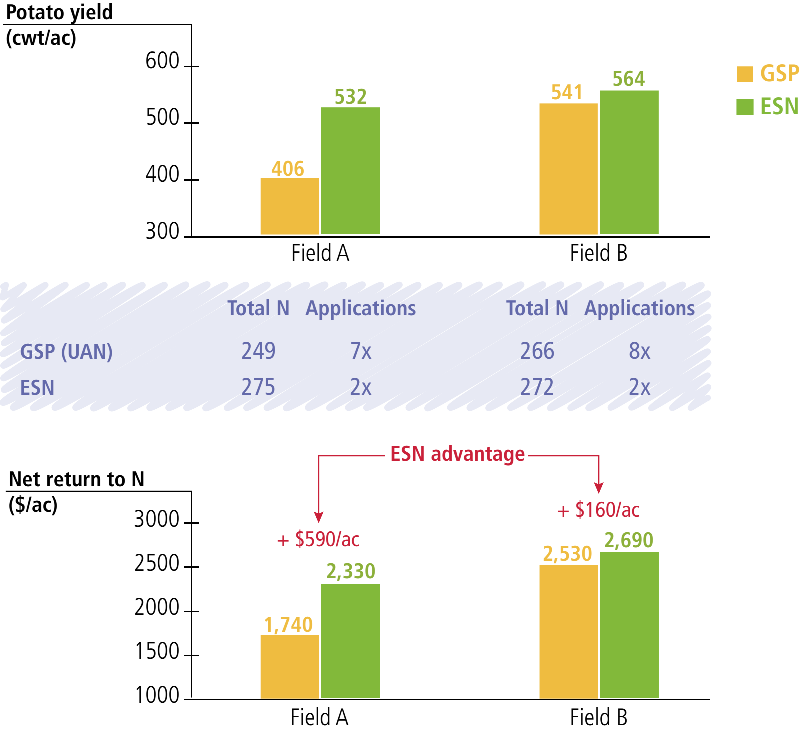
For polymer-coated urea, Agrium gives the following calculations based on a premium of ESN to granulated urea of about US$ 60-100 per tonne (Hasinoff, 2005):

Table 28. Three-year maize yield average at TSM Research, Illinois: Return on investment with N rates of 100 lb/ac (Agrium, 2005).

	Yield (bu/ac)	N (US$/ac)	Gross profit less N cost	ESN advantage (US$/ac)
ESN	166	47.72	292.58	
Urea	143	38.04	255.11	37.47
UAN side dressing	154	44.39[1]	271.31	21.27

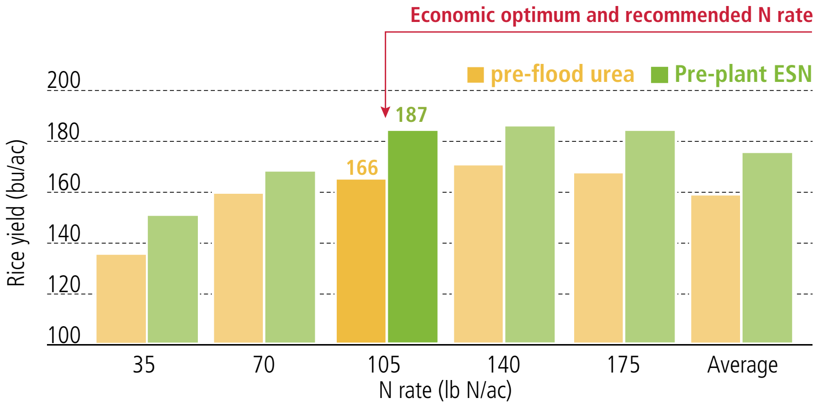
Retail cost per t/lb N per t of product = cents per lb of N
ESN @ US$ 420.00/t: 47.72 cents/lb N
Urea @ US$ 350.00/t: 38.04 cents/lb N
[1] UAN @ US$ 215/t: 38.39 cent/lb N, plus US$ 6.00/ac application cost
Corn @ US$ 2.05/bu

Another example is for the application of ESN to potatoes (Figure 26) in Minnesota and to rice in Arkansas, 2004 (Figure 27).



	Total N	Applications	Total N	Applications
GSP (UAN)	249	7x	266	8x
ESN	275	2x	272	2x

Figure 26. Measurement of ESN effect on potato production in field trials in Minnesota in 2004 (Adapted from Agrium, 2005).



N source	Pre-flood urea	Pre-plant ESN
Rice yield (at 105 lbs N/ac)	166	187
Application cost (US$/ac)	11.41	0*
Fertilizer cost (US$/t)	290	410
Total N cost (US$/ac 105 lbs N/ac)	49	56
Crop value (US$3.50/bu)	581	655
Net return (US$/ac)	532	599
Net benefit (US$/ac)		67
Value of urea application savings (US$/t ESN, assuming equal yield)		96

*ESN applied pre-plant with broadcast P&K

Figure 27. Measurement of ESN effect on rice production in field trials in Arkansas in 2004 (Adapted from Agrium, 2005).

These results clearly demonstrate that the use of polymer-coated urea (ESN), though more expensive than conventional urea, is also profitable in field crops like maize, rice, wheat and potatoes.

7.2.2. Nitrification inhibitors

With the increasing cost of energy, prices for mineral fertilizers are expected to increase, particularly for N fertilizers. This will improve the economics in favour of stabilized fertilizers. Also, the increased value of agricultural products should favour a wider use in agriculture of fertilizers stabilized with nitrification and urease inhibitors. In addition, higher energy and fertilizer prices should provide incentives for farmers and growers to use nitrification inhibitors to increase crop yields through improving N-use efficiency and apply less N decreasing losses by leaching and gaseous emissions. Such environmental incentives have yet to be calculated.

Economic analyses of using slow- and controlled-release fertilizers are rarely published because their prices are only given on request. Dow AgroSciences gives a calculation from experiments carried out in Iowa. For maize with fall-applied N, 160 lb/acre, as conventional anhydrous ammonia was compared with 145 lb N/acre as anhydrous ammonia stabilized with N-Serve®. Where N-Serve® was used the yield was 15.2 bushels higher. With a 15-bushel/acre increase in yield, maize growers would have made a net profit of US$ 25.50 per acre based on:

- US$ 30.00 per acre larger income (15 bushels at US$ 2.00 per bushel of maize).
- US$ 3.45 saved per acre through using 15 lb less N (at approximately USc 23 per lb).
- US$ 8.00 less per acre for the approximate cost of N-Serve®.

Frye (2005) has estimated the cost per hectare at around US$ 15.00.

For Germany, Gutser (2006) has made the following calculation. Amending fertilizers with a nitrification inhibitor increases the fertilizer cost by 8 to 20%, which for an N application of 160 kg N/ha equates to between € 8.00 and 20.00/ha. Total savings are due to one fertilizer application less = € 8.00 to 12.00/ha (average € 10.00/ha), and 5 to 15 kg N/ha less, corresponding to € 3.00 to 9.00/ha. Total savings = € 13.00 to 21.00/ha depending on the local situation. The extra value of any increase in yield is not included. Fertilizer systems using nitrification inhibitors have no financial disadvantages. In this very careful calculation, the environmental benefit of using a nitrification inhibitor has not been calculated.

In Western Europe, the most widely used nitrogen fertilizer is still calcium ammonium nitrate (CAN). If ammonium sulphate nitrate (ASN) with a nitrification inhibitor (DMPP) is compared with that of CAN (with the exception of sulphur deficient soils or crops), the labour saving and greater labour flexibility, and reduced N application rates will compensate for a higher price compared to CAN. A similar calculation can be made where the same amount of N fertilizer is used without and with a nitrification inhibitor, the latter producing a larger yield. Farmers or extension services should make an actual calculation, showing that, in general, a very moderate increase in yield can compensate for the larger cost of an N fertilizer with a nitrification inhibitor.

The greater flexibility in the use of labour should also be taken into account. Ebertseder and Kurpjuweit (1999) made an impressive labour saving calculation for a 600 ha farm using N fertilizers stabilized with DMPP. Casar *et al.* (2007b) gave an economic analysis for the use of DMPP in a four-year experiment with pomaceous fruits (Table 29). The treatments were: T 1 – without fertilizers, T 2 – conventional fertilizer, T 3 – conventional fertilizer + DMPP.

Casar *et al.* (2007b) concluded that the best results were obtained with fertilizer plus DMPP applied at high frequency, which increased average yield by 45%. An economic analysis showed that T3 increased the accumulated profitability of the pear orchard by 30% (conventional fertilizer, € 210/t; DMPP + fertilizer, € 280/t; and pear price at € 0.5/kg).

Though farmers may be able to obtain a better N-use efficiency through specific fertilization strategies, use of slow-and controlled-release and stabilized fertilizers should become an integrated part of fertilizer best management practices (FBMPs).

Table 29. Average and accumulated yield of pears for each treatment in a four-year trial (Casar *et al.*, 2007b).

	Yield for the 4 years (t/ha)[1]				Average yield (t/ha)	Accumulated yield (t/ha)	Economic yield for the 4 years (€)[1]
Treatment	Year 1	Year 2	Year 3	Year 4			
T1 control	20.1 a	11.2 a	9.4 a	13.2 a	13.1 b	67.4 a	26,946 a
T2 N conventional	19 a	12.1 a	13.2 a	12.4 a	14.9 b	74.6 a	27,960 a
T3 N conventional + dMPP	28.3 a	19.2 a	22.8 a	17.8 a	21.7 a	108.5 a	43,363 a

Different letters indicate significant differences at $p<0.05$

[1] Only considered the fertilizer cost. Average prices for pear ‘Conference’ (Mercolleida) : year 1 = 0.40 €/kg, year 2 = 0.62 €/kg, year 3 = 0.43 €/kg, year 4 = 0.60 €/kg

Average prices of fertilizers. Ammonium nitrosulphate = 0.210 €/kg, ammonium nitrosulphate + DMPP = 0.280 €/kg.

Improved NUE, whether with mineral fertilizers, nutrients from leguminous crops or farm manure, will become even more essential because of environmental issues, calling for voluntary and regulatory compliance (*Subbarao et al.*, 2006).

At the IFA International Workshop on Enhanced-Efficiency Fertilizers, Frye (2005) concluded his contribution about ‘nitrification inhibition’ as follows: “Inhibiting nitrification is an effective means of ameliorating the economic effects and ecological consequences of N losses from the soil. The combined effects of using a nitrification inhibitor together with an effective urease inhibitor can enhance the appeal and practicality of both chemicals. Increasing N fertilizer prices, heightened concerns for pollution from N and its ecological effects, and a promising new nitrification inhibitor (DMPP) on the horizon most likely will renew interest in using nitrification inhibitors as a management tool, making their future the brightest ever”.

7.2.3. Urease inhibitors

Similar to economic calculations for nitrification inhibitors, calculating the return on investment from a urease inhibitor requires some key data (for a multi-factor equation). Such key data include the rate of urea or UAN applied, the response of the crop to nitrogen, the value of the crop (e.g. maize vs. wheat vs. rice), the selling price of the crop, and the cost of the urease inhibitor.

Results from field trials with maize and wheat to measure the increased yield attributable to the urease inhibitor NBPT (Agrotain) are summarized in Table 30.

Table 30. Maize and wheat yield increases due to Agrotain treatment of urea or UAN (Agrotain, 2010).

		Maize response		Wheat response	
		Urea + Agrotain	UAN + Agrotain	Urea + Agrotain	UAN + Agrotain
N-responsive sites		408	167	64	19
Average nitrogen rate	kg N/ha	133	133	81	84
Yield increase vs urea/UAN	kg/ha	842	554	242	330
Average nitrogen rate	lb N/ac	119	119	75	75
Yield increase vs urea/UAN	bu/ac	13.4	8.8	3.6	4.9

Though the economic returns can be calculated, specific examples like that above are only applicable for the particular inputs used because these are changing constantly. Figure 28. shows a more universal illustration of the economic returns for grains in general. The illustration assumes a urea rate of 133 kg N/ha, Agrotain cost of 53.00 US$/t urea, and it illustrates three different yield increases of 200 to 1000 kg/ha due to using Agrotain.

To give some perspective, the example of the financial return from maize marked with a dot in Figure 28 is based on the market price of maize on the Chicago Board of Trade on 1 January 2010 (167 US$/t) and the yield increase from Agrotain (842 kg/ha) in Table 30 along with the other data above. The net return under that scenario was 134 US$/ha from the use of Agrotain. Although even small yield gains of 200 kg/ha provide

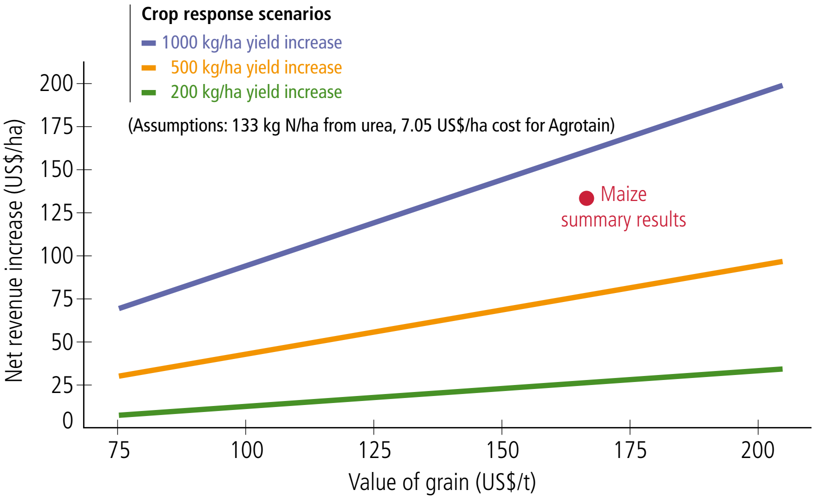


Figure 28. Economics of Agrotain-treated urea with grains (Adapted from Wade, 2010).

a positive return, substantial returns can be achieved with larger increases in yield from the Agrotain-treated urea and/or higher prices for the grain.

Where farmers still apply an extra of 13.5 to 18 kg N/ha (15 to 20 lbs N/acre) for no-till or minimum-tillage cropping systems to compensate for possible ammonia losses, this practice should be discontinued (it is environmentally negative) and instead a urease inhibitor should be used. The above calculation can be used as a model for a calculation with actual prices to calculate the possible net profit resulting from the use of urea/UAN with NBPT/Agrotain.

8. Legislation and registration

8.1. Slow- and controlled-release fertilizers

In the United States, Canada, China, Japan, Europe and Israel, a wide range of slow- and controlled-release fertilizers are produced and distributed for specific applications in agriculture and horticulture. However, no universally accepted legislation exists yet to protect the consumer in the United States, Western Europe or Israel. The method used traditionally to test slow- and controlled-release properties of fertilizers is to determine the time taken for 80% of the nutrients in the fertilizer to be released under constant conditions at 25°C in water. The official testing method used in Japan and the new method for the Chinese speciality fertilizer industry are given as examples in Annexes I and II. Additional new and improved methods for determining nutrient release characteristics have been recently presented by Medina (2010).

It is obvious that appropriate legislation and regulations are becoming more urgent if more slow- and controlled-release fertilizers are used in agriculture and horticulture in the future (AAPFCO, 1995; Cramer, 2005, 2007; Kluge and Embert, 1992).

In the United States, 50 states regulate their own agricultural policies, including fertilizers (Crawford, 1995; Crawford and Dubberly, 1995; Hall, 1996; Pigg, 1995; Yelverton, 1995). There are some guidelines and Federal Environment Protection Agency (EPA) regulations, which can be imposed on individual states if their policies and laws do not meet or exceed the federal regulations. This is predominantly the case concerning registration of pesticides under EPA's Resource Conservation and Recovery Act (RECRA). However, fertilizers are excluded. Therefore, AAPFCO (1995) has formulated definitions for controlled-release fertilizers (Official Publication No. 48).

Definitions for controlled-release fertilizers (AAPFCO, 1995)
Slowly released or controlled plant nutrients

a) No fertilizer label shall bear a statement that connotes or implies that certain plant nutrients contained in a fertilizer are released slowly over a period of time, unless the slow-release components are identified and guaranteed at a level of at least 15% of the total guarantee for that nutrient(s) (Official 1991).

b) The different types of fertilizers with slow nutrient release characteristics are listed.

c) Until more appropriate methods are developed, AOAC international method 970.04 (15th edition) is to be used to confirm the coated slow-release and occluded slow-release nutrients and others whose slow-release characteristics depend on particle size. AOAC international method 945.01 (15th edition) shall be used to determine the water insoluble nitrogen of organic materials (Official 1994).

Example of AAPFCO label statements which imply slow-release properties: Coated Slow-Release or Occluded Slow-Release Nutrients

When nutrients in a fertilizer are coated or occluded to obtain slow-release properties, then the guarantees for those components may be shown as footnotes rather than as a component following each nutrient. For example, a fertilizer with one coated material:

Fertkote 10-15-20

Guaranteed analysis:

- Total nitrogen (N) 10%
- 2.5% ammoniacal-N
- 2.5% nitrate-N
- 5.0% urea-N[1]
- Available phosphate (P_2O_5) 15%
- Soluble potash (K_2O) 20%
- Sulfur (S) 14%

[1] __% Slowly available urea-N from ___

In its latest Policy Statement on Slow-Release and Stabilized Fertilizers, AAPFCO affirms that one of the goals of its model legislation is to provide for consumer protection while encouraging free commerce. Pursuant to this goal, AAPFCO endorses and recommends that the term 'Efficiency Design (ED)' be adopted to describe fertilizer products with characteristics that minimize the potential of nutrient losses to the environment, as compared to a 'reference soluble' product. (AAPFCO, 1997).

AAPFCO further declares that through its body of model legislation, it develops and promotes simple and effective regulatory procedures for ED products. These include:

- identification of methodology for determining 'release rate' or 'longevity of response' that is straight-forward and universally accepted;
- development of definitions and labelling requirements that confirm with this policy statement, and that are readily understood and supported by industry;
- development of guidelines for consistent and effective enforcement of regulations for ED products; and
- flexibility to include future product concepts and technology that may be developed and brought to market.

To meet present and future needs for regulation and methodology, a task force has been formed jointly by AAPFCO and The Fertilizer Institute (TFI) in the United States. Members of the Controlled-Release Task Force come from the Department of Agriculture, manufacturers, AAPFCO and TFI. It has the following five-subcommittees: (i) methodology, (ii) labelling, (iii) enforcement, (iv) new products/concepts and (v) policy.

A new method for extraction and analysis of fertilizer ED would have to meet the following requirements:

1. It must be able to categorize the material's tree structure with logic for computer base.
2. The status of current materials will not change significantly.

3. It can be run in an analytical laboratory.
4. It can be run in seven days, preferably less.
5. It can be performed by technicians using available equipment, thus gaining wide acceptance.
6. It would be applicable to a wide variety of blended material.
7. It can be correlated to agronomic data.
8. It may be used for extraction of multiple nutrients (N, P, K, secondary and micronutrients).

One of the most important points is item No. 7, i.e. the development of laboratory tests, the application of which should match field data.

In Western Europe, there are no EU Commission regulations for slow- and controlled-release fertilizers; they are non-regulated fertilizers. To date, there are no coated controlled-release fertilizers within the EU-type fertilizer list.

As in the United States, a task force has been formed. The CEN TC260/WG4/Task Force on slow-release fertilizers (CEN TFsrf) has the challenge of presenting proposals to the official authorities/legislators on the classification of these fertilizers.

The aim has been to define the conditions under which a type of fertilizer, which is already included in the list of EU fertilizer types, may be newly categorized as a slow- or controlled-release fertilizer.

The CEN TFsrf started with the development of an adapted analytical method to evaluate encapsulated, water-soluble fertilizers. In 1995, such an adapted analytical method was tested by 14 European and one US laboratories. The results from this test have been analyzed and represent the basis for the formulation of a 'CEN-Norm'.

Furthermore, the CEN TFsrf has proposed that manufacturers have the responsibility for the biological testing of their products. Also, the manufacturers will be asked to prepare a comparative study between official CEN-standard-long-time cold water leaching (in preparation) – and an accelerated short-time control measurement (in preparation), which has to be declared on the label, combined with the longevity of the said nutrients (information: www.nal.din.de).

CEN/TC290, 1998 focused on a method for the identification and determination of slow-release properties of nutrients from coated fertilizers. Shaviv (2005), who presented a conceptual model of nutrient release from coated fertilizers, considered this as a basis for new official standards and for legislation related to labelling and definition of slow- and controlled-release fertilizers. This may avoid the generation of a number of individual new slow- and controlled-release fertilizer types.

Within European Regulation No. 2003/2003, neither slow-release nor coated fertilizers have been defined. Currently (2010), a new fertilizer legislation is in preparation ('New Approach'). The new directive has as a working title 'mutual recognition' with this aim: Any fertilizer registered in any EU country may be sold in all member countries of the EU. This new legislation will, apparently, be valid for conventional as well as for special fertilizers (including slow- and controlled-release fertilizers).

In Germany, if a fertilizer is coated, 'coated or with coated nutrient' (at least 90% is coated) or 'partly coated or with partly coated nutrient' (at least 25% is coated) this must be stated. Furthermore, the percentage of the coated fertilizer in relation to the total fertilizer, or the coated nutrient in relation to the total nutrient content, has to be indicated in whole figures (Cramer, 2007).

Within other national fertilizer legislations, there are categories such as coated NPK, partly coated NPK, coated urea, etc., with a specified minimum amount of coated product, e.g. 50% or 70% – the coated part of partly coated fertilizer has to be stated.

The coating must be certified to be harmless. According to the 2007 Fertilizer Regulation in Germany, coating materials would have to be classified under 'application aids' (Anwendungshilfsmittel). Permission to use non degradable (non degradable synthetic polymers) for the coating process would end in 2013, to be replaced by biodegradable (or photodegradable) coatings (Cramer, 2005; Ministry, 2007; Kolybaba *et al.*, 2003)[10].

In Germany, CDU, IBDU and UF are classified as individual nitrogen fertilizers. In addition, the fertilizer legislation covers the group of N fertilizers (N, NPK, NP and NK fertilizers) containing CDU, IBDU or UF.

To analyse, for example, the slow-release N content in UF-based slow-release fertilizers, AOAC adapted methods that are used in most EU Member States. For IBDU- and CDU-based fertilizers, as well as for coated and encapsulated slow- and controlled-release fertilizers, national or manufacturers' methods are used. France and The Netherlands prescribe special procedures.

At present, the following methods are generally used to test the slow-release pattern of slow- and controlled-release fertilizers:

- Plant tests: ornamentals, vegetables, lettuce, grass.
- Different leaching procedures: e.g. percolation, substrate storage, cold water, tempered water, cumulative, incremental.
- Chemical analysis: e.g. amount of coating/product.

In Israel the following recommendation for the registration of slow- and controlled-release fertilizers was made in 1995. Authorities and users should be interested in proper registration of controlled-release products, because fertilizers that are declared as controlled-release fertilizers but do not have real controlled-release properties, will not bear any agronomic or environmental benefits. Compilation of systematic registration instructions regarding slow- and controlled-release fertilizers is essential

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[10] *Though the German government has substantially supported research for degradable polymers in the past, this regulation announced in 2007 is no longer valid, because within the final text that become law in Germany on 16 December 2008, the following exception has been included (8.2.9. Synthetische Polymere' – 'symthetic polymers): 'Ab dem 31.12.2013 Verwendung nur, soweit sämtliche Bestandteile und das Endprodukt sich vollständig abbauen, ausgenommen sind...' (From 31 December 2013, use is only allowed when all constituents and the final product are completely degradable, exemptions are...): 1. solche Bestandteile, die als Hüllsubstanz für Düngemittel der Steuerung der Wirkung der Düngemittel dienen... Für Düngemitteln als Hüllsubstanz zur Steuerung der Nährstoffverfügbarkeit (exemptions are... such substances regulating the efficiency of the fertilizers... coating substances regulating the nutrient availability) (Ministry, 2008).*

The author does not know for which other purposes than regulating their nutrient release, fertilizers are coated with synthetic polymers.

for proper introduction of these fertilizers into routine use. Complete formal definition of controlled-release products has to refer to the identification of the mechanism that controls the release, the expected release curve, and the factors that might affect the release. In addition, strict instructions have to be given regarding product labelling. Apart from the basic information that describes nutrient content, labels should describe the release characteristics of the product (Raban, 1995; Gordonov, 1995).

Raban (1994) prepared a conceptual model describing the nutrient release from coated granules. Other models of controlled-release of nutrients from coated fertilizers have been developed and investigated by Zaidel (1996). Raban and Shaviv (1995) have defined the mechanism controlling the release of nutrients from coated fertilizers as either coating failure or as diffusion. In an investigation, they tried to give a systematic assessment of the release mechanism of four different types of coated urea. An evaluation of the solute diffusion coefficient of a controlled-release fertilizer using wetting and dissolution characteristics in a gel-based controlled-release fertilizer was made by Shaviv *et al.*, (1995).

In Japan, all fertilizer products should be registered prior to production, sale, importation and exportation. Each slow- and controlled-release fertilizer has its individual registration standard with reference to the composition. UF has the upper limit of the water-soluble segments. Registration instructions require a release and/or a mineralization test. The test methods are: in the laboratory, release in water; and release or mineralization in soil and in the field (Fujita, 1996a; Tachibana, 2007).

Although data on the nutrient release or mineralization rate of slow- and controlled-release fertilizers is not necessary for registration, it is sometimes attached as additional information.

8.2. Nitrification inhibitors

In the United States, fertilizers, but not additives to fertilizers, are excluded from the EPA 'RECRA' regulations. Therefore nitrapyrin, the leading nitrification inhibitor is classified as a pesticide under EPA regulations. In 1996, it was decided that, in the United States, all nitrification inhibitors would have to be registered by the EPA (Huffman, 1997).

Officials claim that manufacturers or distributors of DCD and DCD-containing fertilizers should also have to apply for registration under 'RECRA'. Experts disagree, however, they believe that nitrification inhibitors such as DCD and ammonium thiosulphate (although showing certain herbicidal potential) are not pesticides, and that the EPA regulations for registration of these types of inhibitors would, therefore, have to be amended. In consequence, in spite of the new regulation, DCD does not require registration as a pesticide.

In the European Union, there has been no uniform regulation for nitrification inhibitors. For the EC Regulation No. 2003/2003, the inclusion of DCD is recommended, 'one of a number of substances known as nitrification inhibitors'; minimum content of 1.5% and maximum content of 3% in proportion to the total amount of nitrogen present as ammonium plus nitrification inhibitor N.

As in the case of slow- and controlled-release fertilizers, several EU Member States have established national classifications and legislation. In several countries, DCD is designated in fertilizer legislation as a nitrification inhibitor and classified under several N fertilizer types amended with DCD as a nitrification inhibitor (for instance in Germany 'DCD-containing ammonium sulphate nitrate') (Bundesminister, 1995; Cramer, 2005. 2007; Kluge and Embert, 1992; Zerulla, 1996). The addition of DCD is, however, only permitted to ammonium sulphate (AS) and ammonium sulphate nitrate (ASN).

For organo-mineral fertilizers and fertilizers based on organic manure and sewage sludge, a nitrification inhibitor may be added if these products contain at least 55% of ammonium-N, carbamide-N or cyanamide-N in relation to the total N content, and if they have not yet been designated as 'EC Fertilizers' (Cramer, 2005, 2007).

A registration, not only according to the Fertilizer Law but also to the Chemical Act (See also DMPP, 3.2.2.2.), permits the marketing and use of the product concerned in all EU countries. DMPP has been declared under the Chemical Act and it has been registered internationally according to the Fertilizer Law.

Table 31. Nitrification inhibitors registered in Germany (DüMV, 2008).

Substance	Minimum content (in %) relative to the total ammonium-, carbamide-and cyanamide-N	Other regulations
Dicyandiamide	10.0	
Mixture of dicyandiamide and ammonium thiosulphate	dicyandiamide 7.7 ammonium thiosulphate 4.8	
Mixture of dicyandiamide and 3-methyl-pyrazol	2.0	Relation 15 : 1 Max. content of methylpyrazol 0.5%
Mixture of dicyandiamide and 1H-1,2,4 Triazol	2.0	Relation 10 : 1
3,4-dimethylpyrazol-phosphate	0.8	
Mixture of 1H-1,2,4 Triazol and 3-methyl-pyrazol	0.2	Relation 2 : 1

8.3. Urease inhibitors

Any new urease inhibitor to be distributed in the form of an active ingredient for addition to urea by distributors or farmers has to undergo registration as a chemical substance. For stabilized fertilizers, e.g. urea stabilized by addition of a urease inhibitor, registration follows the fertilizer legislation.

For the European Commission 'urease inhibitors may offer a satisfactory solution' in the case of N fertilizer for which nitrification inhibitors may not be effective. It is recommended to include a urease inhibitor, such as NBPT, which was registered at the

EC-level in 2008, with a minimum content of 0.09% and a maximum content of 0.20% relative to the total urea-N content.

In Germany, N-(2-Nitrophenyl)-phosphorsäuretriamide (2-NPT) was registered in 2008. The minimum and maximum limits in relation to carbamide-N are of 0.04% and 0.15%, respectively.

The regulations under which a nitrification or urease inhibitor has to be registered have, of course, a significant influence on future research and the development of new nitrification and urease inhibitors because the costs involved may be a decisive factor.

9. Research

In Australia, Canada, China, Germany, France, India, Israel, Italy, Japan, the Netherlands, Russia, the United Kingdom and the United States, there are a number of research institutes, universities and industrial companies involved in research on slow- and controlled-release fertilizers, urease and nitrification inhibitors. Some investigations have also been carried out in the Czech Republic, Denmark, Egypt, Ghana, the Republic of Korea, Malaysia, the Philippines, Poland, South Africa, Spain and Thailand.

9.1. Slow- and controlled-release fertilizers

The use of slow- and controlled-release fertilizers is still very limited, due to their relatively high cost, despite the potential benefits (Shaviv, 2005).

Shaviv and Mikkelsen stated in 1993 (1993b) that there exist several other issues related to the efficient use of slow- and controlled-release fertilizers that deserve much more attention and deeper insight. If properly treated, these issues should lead to a more significant contribution of slow- and controlled-release fertilizers to agriculture and the environment. Among these issues are:

- Improvement and utilization of advanced technologies and development of new concepts for preparing more cost-effective slow-release fertilizers.
- Improved understanding of the mechanisms controlling the pattern and rate of release and the major environmental factors (e.g. temperature, moisture, microorganisms, acidity, soil type, etc.) that affect them.
- Improved assessment of expected benefits to the environment from using controlled-release fertilizers.
- Improved quantification of the economic advantages resulting from reduced losses of nutrients and savings in labour costs.
- Improved assessment of the economic benefits expected from reduced osmotic stress and specific toxicity as a result of synchronizing nutrient release with plant demand.
- Standardization of the tests for characterizing the release performance of slow- and controlled-release fertilizers in order to improve a user's decision, industrial quality control, and to assist regulatory efforts.
- Utilization of mechanical models for predicting the release of nutrients under laboratory and field conditions, and as a design tool for engineers.
- Exposing potential users to this knowledge in order to help them choose appropriate slow- and controlled-release fertilizers.

Achievements in these directions will greatly depend on organizing multi-disciplinary research and development (R&D) for dealing with such complex issues, and probably even more on the priority and support given to such work by our society.

Such research and development must include:

- Nitrogen use efficiency of conventional mineral fertilizers compared to controlled-release (sulphur-coated urea and encapsulated) fertilizers.

- Correlating data from laboratory testing and efficiency under field conditions.
- Assessment of the economic benefits resulting from the use of controlled-release fertilizers (value/cost ratio - VCR).
- Factors influencing nutrient release from sulphur-coated urea and encapsulated mineral fertilizers, such as type of coating, coating agents/coating process (polymerization coating processes), coating thickness, solvent agents, etc.
- Also very important are the physical characteristics of the substrate on which the coating is applied. These include particle size, shape and surface irregularity, prills, which often have holes on their surface, or granules which can be smooth or rough and irregular depending on whether the granulation process was agglomeration or compaction.
- Factors and mechanisms influencing nutrient release from sulphur-coated urea and encapsulated mineral fertilizers. Soil factors include soil type, humus content, acidity, microbial activity, temperature, and soil moisture (irrigation).
- Decomposition/degradationby biological, physical or chemical methods of the coating materials, particularly polymeric coatings, under specific soil and climatic conditions.
- Effect of controlled-release fertilizers on nitrate leaching, ammonia volatilization and emissions of N_2O and NO_x.
- Development of standard methods for the evaluation of nutrient release rates from controlled-release fertilizers.
- Development of new coating and encapsulating materials, specifically of more rapidly degradable synthetic materials/polymers.
- Development of new, improved, lower-cost and environment-friendly technologies in coating/encapsulating processes.

Producers in Japan and in Israel, as well as the leading manufacturers in North America, are working intensively on the development of new lower-cost controlled-release fertilizer products. In Japan, another particular field of research is the degradation of polymeric coating materials.

Though there are no fundamental changes to be expected, improved and more economic products may enter the market within the next few years, particularly in China, Japan and the United States.

9.2. Nitrification and urease inhibitors

Kiss and Simihaian (2002) summarised the extensive research carried out for more than a decade on urease inhibitors. A similar review on the development and testing of nitrification inhibitors has been done by Subbarao *et al.* (2006).

Further research is required on the relationship between nitrification inhibitors and methane flows (Gutser 1999a; Wozniak *et al.*, 1999) because they apparently have a positive effect on methane fluxes (Amberger, 2008b; Bouwman, 1995; Ottow *et al.*, 1999; Weiske *et al.*, 2001b, 2001c; Zerulla *et al.*, 2001a).

There is also a need for data on the effects of nitrification and urease inhibitors over a period of several years to prove that these compounds have no adverse effects on the soil microbial population (e.g. a build up of resistance) and on crop productivity (Suter *et al.*, 2006). Factors that influence the degradation of nitrification and urease inhibitors in the soil, such as soil type, pH, humus content, temperature, moisture (irrigation) require further study. It would also be useful to study the efficiency of nitrification and urease inhibitors after repeated application over many years. A three-year study on 15 different sites indicated that repeated applications of NBPT did not diminish its efficiency in inhibiting volatilization (Watson *et al.*, 1998). The urease inhibitory effect of NBPT is associated with the activity of its derivative, the oxygen analogue, N-(n-butyl)phosphoric triamide (NBPTO) but there is as yet little information on the biotic and abiotic factors affecting the rate of conversion to NBPTO and its subsequent stability in the soil (Watson *et al.*, 2008).

With the increased use of nitrification inhibitors and the delayed transformation of ammonium to nitrate, more research is needed on the consequences of ammonium-nutrition on the growth and physiology of plants. In particular, attention should be paid to the positive effect of late ammonium-nutrition (Gerendás and Sattelmacher, 1995).

There are indications that replacing three N fertilizer dressings with one starter application with a nitrification inhibitor for winter wheat may result in a lower crude protein content of the grain. Therefore, research is required to test AN-based fertilizers with and without a nitrification inhibitor to find ways of achieving large grain yields with satisfactory protein content (Pasda *et al.*, 2001a and 2001b).

The ease of absorption of a nitrification inhibitor by soil components affects its ability to inhibit nitrification of ammonium. Research is required to evaluate which soil properties are effective so that the short-term inhibitory effect of nitrification inhibitors can be predicted (Barth *et al.*, 1999, 2001). Also the efficiency of nitrification and urease inhibitors under tropical conditions needs further study (Azam *et al.*, 2001).

Subbarao *et al.* (2006) suggest the need for a new generation of nitrification inhibitors, especially ones that are efficient, cost-effective and suitable for both tropical and temperate production systems and whether larger concentrations are required under tropical conditions (Watson, 2005). More detailed information on the mode of action of nitrification and urease inhibitors for irrigated rice would be useful.

For grassland, long-term trials are required to quantify the effects of nitrification and urease inhibitors and their repeated use on soil and water quality, and human and animal health (Edmeades, 2004), including effects on the soil microbial population and ammonium oxidizing bacteria especially (Varel *et al.*, 1999). There is also the question whether the continued use of DCD (or other nitrification inhibitors) will induce resistance in ammonium-oxidizing bacteria making DCD ineffective in the long term, and induce other changes in soil microbial population dynamics. Although no detectable levels of DCD have been found in animal muscles after ingestion by grazing animals and only very low levels of DCD have been found in milk, more research is needed on the effect of DCD and other nitrification inhibitors on grazing animals. Further research is also required on the mitigation potential of nitrification inhibitors on nitrous oxide emissions from slurry.

Regarding the use of urease inhibitors in Western Europe, it is essential to ensure that these products do not increase the risk of urea loss to surface waters because this could increase ammonium-N concentrations above the EC standard for freshwater (Watson, 2005).

Finally, there is a need to assess the economic benefits for the farmers resulting from the use of nitrification or urease inhibitors – value/cost ratio (VCR). The same assessment must be made for the expected benefits to the environment and society. Grant (2005) claimed that there was still a significant need for research to define and value the advantages associated with the use of slow- and controlled-release and stabilized fertilizers. It is important to quantify possible decreases in the amount of fertilizer to be applied when slow- and controlled-release and stabilized fertilizers are used so that producers can recover a portion of the extra cost of these products by using a smaller amount. Identification of the benefits possible in terms of reduced lodging, reduced disease incidence, controlled maturity, enhanced protein and trace element content, changes in oil content and quality, will be important.

Although the possible agricultural and environmental benefits arising from the chemical control of nitrification have been known since the 1960s very little effort has been devoted to the development of the next generation of nitrification inhibitors (Subbarao *et al.,* 2006). They suggested further intensive research on the development of Biological Nitrification Inhibition (BNI) as a primary task of universities and official research centers/institutions.

Developing nitrification and urease inhibitors is significantly more difficult than that of new coating technologies and coated/encapsulated fertilizers. Manufacturers developing such materials must consider the cost because of the requirements for testing (i.e. toxicity on rats, mice, etc., decomposition of the active ingredient, decomposition and toxicity of metabolites, crop residue studies) before seeking registration as a pesticide, as a fertilizer, or as a soil amendment. The majority of fertilizer manufacturers have neither the research facilities nor the capital needed. The profitability of nitrification and urease inhibitors to producers is too small to justify R&D efforts. The cost and time involved in the development of new acceptable nitrification and urease inhibitors are equal to, or even greater than, for the development of a new crop protection product while the financial return that may be expected is more or less in the range of that of conventional fertilizers. There are more opportunities for acceptable economic returns from investing in herbicides, insecticides, fungicides and conventional fertilizers than in nitrification or urease inhibitors. Consequently, worldwide, there are only three or four companies which, at present, have developed nitrification and urease inhibitors that meet the numerous requirements for registration and practical application. These companies concentrate their efforts in promoting precise, safe and efficient use of their products.

Future developments must give priority to an eco-efficiency analysis to harmonize economy and ecology. Only when observing such eco-efficiency, will sustainable development be possible (Saling *et al.*, 2005) but it should ensure increased crop production and environmental protection for the benefit of both agriculture and the society at large. If the benefits to society are substantial, some costs should be transfered to society, possibly through subsidies or incentives for adoption, and support for developmental and adaptive research (Grant, 2005).

Addendum. Manufacturers and distributors of slow- and controlled-release fertilizers and nitrification and urease inhibitors

In North America, the leading producers and/or suppliers of slow- and controlled-release fertilizers are: Agrium Inc. (including Pursell Technologies Inc. and Nu-Gro Corp.), Georgia-Pacific, Growth Products, Helena Chemicals, Kugler Company, Lebanon Seaboard Corp., Lesco Inc, Tessenderlo Kerley and The Scotts Company.

The leading manufacturers and/or suppliers in Western Europe are: Aglukon (Germany), BASF (Germany), Compo (Germany), Scotts Europe (The Netherlands), Puccioni (Italy) and Sadepan Chimica (Italy).

In Israel the leading manufacturer and supplier is Haifa Chemicals.

The leading manufacturers and/or suppliers in Japan are: Central Union Fertilizer, Chissoasahi Fertilizer[11], Co-op Chemical, Katakura Chikkarin, Mitsubishi Chemical, Sumitomo Chemical, Taki Chemical and Ube Agri-Materials.

In China, the leading manufacturers are: Hanfeng Evergreen, Shandong Kingenta Ecological Engineering and Shikefeng Chemical Industry.

1. Urea reaction products/slow-release fertilizers

North America	
Liquid products	
Georgia-Pacific	Nitamin® 30L – UF fertilizer
Tessenderlo Kerley	Formolene-Plus® and several Trisert® - urea-triazone formulations
Helena Chemicals	CoRoN® – UF solution
Kugler Company	KQ XRN 28-0-0 – UF solution
Growth Products	Nitro-30 – UF solution 30-0-0
Granular products	
Agrium (former Nu-Gro)	Nitroform® – UF formulation Nutralene® – methylene urea IB Nitrogen - IBDU

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[11] *Chissoasahi Kasai Chemicals and Mitsubishi Chemical have reached a joint venture agreement for their affiliates Chissoasahi Fertlizer Co. and Mitsubishi Chemical Agri., Inc. The new company is called JCAM Agri Co., Ltd. and should have started operation on 1 October 2009.*

Western Europe	
Aglukon	Plantosan® - granular Methylene-urea - Azolon® granular and Azolon® fluid / Methylene-urea - PlantoDur® - NPK fertilizer, N based on UF
BASF (producer) Compo (distributor)	CDU (imported from Japan) - Triabon®- NPK fertilizer based on CDU Floranid® - N-, NK- and NPK-fertilizers, N based on IBDU
Puccioni (Italy)	Nutritop® - Nutritop® N, Smartfert® Top - NPK and NP fertilizers, based on UF
Sadepan Chimica (Italy)	Sirflor™ N38, based on UF Sazolene™ - granular and liquid methylene-urea

China	
Hanfeng Evergreen	UF

Japan	
Chissoasahi Fertilizer	CDU nitrogen 'UBER' - controlled-mineralization CDU (called 'Hyper CDU' in Japan) NPK fertilizer based on CDU
Mitsubishi Chemical	IBDU nitrogen 'Good-IB' and 'Super-IB', based on IBDU NPK fertilizer - based on IBDU
Sun Agro	UF NPK fertilizer based on UF

2. Coated/encapsulated controlled-release fertilizers

North America	
Polymer-coated products	
The Scotts Company	Agroblen® - polymer-coated N, NK and NPK fertilizers Osmocote® - polymer-coated NPK fertilizers
Agrium (former Pursell Technologies)	ESN® Duration® CR - clay-coated PCU Polyon® PCU - polymer-coated urea Polyon® coated potassium nitrate, MAP and NPK fertilizers
Sulphur-coated urea (SCU)	
Agrium (former Nu-Gro)	SCU®
Polymer/sulphur-coated products	
Agrium (former Pursell Technologies)	TriKote® - several polymer, sulphur-coated fertilizer types

Western Europe and Israel	
Polymer-coated products	
Aglukon	Plantacote® - polymer-coated NPK fertilizers
Compo	Basacote® - polymer-coated NPK fertilizers Basatop® - partly polymer-coated N- and NPK-fertilizers
Haifa Chemicals	Multicote® - polymer-coated NPK-, NP- and NK- fertilizers CoteN™ – polymer-coated urea Mulitcote® Agri – coated NPK-fertilizers for open field crops and fruit trees Multigreen® – controlled-release turf fertilizers Multigro® – controlled-release fertilizer blends for agriculture and horticulture

China	
Sulphur-coated products	
Shandong Kingenta Ecological Engineering	Syncote®- sulphur-coated urea and NPK-fertilizers
Hanfeng Evergreen	
Shikefeng Chemical	
Polymer/sulphur-coated products	
Shandong Kingenta Ecological Engineering	Syncote®- polymer/sulphur-coated urea
Polymer-coated products	
Shandong Kingenta Ecological Engineering	Syncote® - polymer-coated NPK-fertilizers and urea

Japan	
Sulphur-coated products	
Sun Agro	S-Coat®- sulphur-coated NPK- fertilizers and urea
Polymer-coated products	
Chissoasahi Fertilizer	Meister®- polymer-coated urea (called 'LP-cote' in Japan) Nutricote® - polymer-coated NPK fertilizer, magnesium sulphate or calcium nitrate Pile Nutricote® - Nutricote® in paper pile 'Naebako-makase' - special Meister® for single basal application in nursery boxes of rice 'Ikubyou-makase' – special Nutricote®- for single basal application in nursery pots of horticultural crops
Mitsubishi Chemical	M-coat® - polymer-coated urea

Taki Chemical	Taki-coat® - polymer-coated urea
MC Ferticom	U-coat® - polymer-coated urea
Central Union Fertilizer	Cera-coat®- polymer-coated urea
Co-op Chemical	Co-op coat®- polymer-coated NPK fertilizers
Katakura Chikkarin	Sigma-coat® - polymer-coated urea and NPK fertilizers
Sumitomo Chemical	'SR-coat' - polymer-coated urea

3. Nitrification inhibitors

North America	
DowAgro Sciences	Producer of nitrapyrin, which is distributed under the trade name N Serve®
Conklin Company.	DCD under the name Guardian® Guardian® - DF, also DCD + ATS under the name Guardian®- DL
Freeport-McMoran Res. Partners Terra Nitrogen	Distributor of N fertilizers amended with DCD, which are all imported into the United States from China, Norway and Germany
Nutra-Flo	ATS
Tessenderlo Kerley.	ATS

Western Europe	
AlzChem Trostberg (Germany)	Manufacturer of DCD for industrial use
SKW Piesteritz	Producer of DCD, urea with DCD + 1H-1,2,4-Triazole (Alzon® 46) AN-urea-solution with Triazole + 3MP (Alzon liquid) and other stabilized N-fertilizers Liquid combination of the active ingredients Triazole + 3MP (Piadin®)
BASF	Former manufacturer and distributor of N and NPK fertilizers stabilized with DCD: Nitrophos® stabil, Nitrophoska® stabil and Basammon® stabil. Since 1999, various N fertilizers amended with DMPP under the name Entec®, distributed through Compo. Also formulated as Entec® liquid
ODDA Smelteverk (Norway)	Manufacturer of DCD for industrial and agricultural use.

China
Several small producers of nitrification inhibitors

Japan	
Chissoasahi Fertilizer	'Dd-Meister' - polymer-coated urea with DCD

4. Urease inhibitors

United States	
Agrotain International	Urease inhibitor NBPT, distributed under the trade name Agrotain® 'Agrotain Plus' is a dry formulation of NBPT and DCD for UAN solutions 'SuperU' is a pre-treated granular urea containing NBPT and DCD

Western Europe	
SKW Piesteritz	N-(2-nitrophenyl)phosphoricacidtriamide (2-NPT)

China	
Hanfeng Evergreen	Hydroquinone (HQ)

Annex I. Methods used to test controlled-release fertilizers in Japan[12]

1. Laboratory methods

1.1. Release in water

Ten grams each of polyolefin-coated fertilizer (POCF) are put into net bags and the bags placed in plastic bottles containing 200 ml of water at temperatures ranging from 5 to 35°C. After given periods of dissolution the solution is taken for analysis.

1.2. Release in soil

In order to examine release of POCF in the soil, a variety of soils and soil conditions (moisture, pH, etc.) are selected. 2.5 to 5.0 grams of POCF is put in a plastic bottle of 200 ml containing the soil (100 g dry weight) which is subjected to the experimental conditions. The bottles are then maintained at temperatures ranging from 5 to 35°C for given periods. POCF particles separated from the soil are used for analysis. Release in the soil is compared with release in water.

2. Field method

2.5 to 5.0 grams of POCF mixed with 200 ml of sieved soil are placed in net bags and the net bags are placed in the ploughed layer of soil. The net bags are removed after given periods of time and POCF particles separated from the soil are used for analysis. The observed release of POCF is compared with the calculated release taking account of the soil temperature and other soil data for the ploughed layer.

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[12] *Given by Toshio Fujita, Director Fertilizer Institute Chisso Corp., Japan, (Fujita 1996a)*

Annex II. Laboratory methods used to test slow- and controlled-release fertilizers in China[13]

Chemical Industry Criterion

1. Extract at 25°C or 40°C

Ten grams of the fertilizer is put into a nylon net and placed in 250 ml glass or plastic bottles containing 200 ml water and sealed then put into a biochemistry constant temperature incubator at 25°C or 40°C.

Sampling is done after 24h and then after 3, 5, 7, 10, 14, 28, 42, 56, 84, 112, 140 and 168 days. Following the 168th day, sampling can be continued every 28 days. On each sampling occasion, the contents of the bottle are shaken and the solution transferred to a 250 ml flask, made up to volume and the solution analyzed. Another 200 ml of water is then added to the bottle which is sealed and returned to the incubator. This procedure is repeated until 80% of the total nutrient content has been released and the time taken to achieve this release is noted.

2. Extract at 100°C

Ten grams of the fertilizer is put into a stainless steel net, placed in a container to which 200 ml water is added. The container is then placed in a controlled-release fertilizer constant temperature extractor maintained at 100±1°C. After time intervals of 1h, 3h, 5h, 7h, 10h, 24h, 30h, 36h, 48h, 54h, 60h and 72h, all the liquid in the container is transferred into a 250 ml volumetric flask, made up to volume and the solution analyzed. Another 200 ml water is added and the extraction continued for the next time period.

3. Extract of some slow- and controlled-release fertilizers

Thirty grams of well blended fertilizer is put into a 250 ml plastic or glass bottle or conical flask. Add 200 ml water, seal and put into a biochemistry constant temperature incubator at 25°C. After 24h, shake the bottles and transfer the contents to a 500 ml volumetric flask through a 1.00 mm sieve. Wash the fertilizer on the sieve breaking up any soluble fertilizer with a glass rod and washing it into the flask. Make up to volume, then filter before analyzing for phosphorus and potassium.

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[13] *First draft by Liu Gang, Wan Lianbu, Zhang Min, Cao Yiping, Chen Hongkun and Yang Yi of the National Center for Quality Supervision and Testing of Chemical Fertilizers Shanghai, and Shandong Kingenta Ecological Engineering, under the supervision of the National Fertilizer and Soil Amendment Standard Technical Committee.*

Analysis for total nitrogen (N)
    Kjeldahl determination or GB/T 8572
Analysis for phosphorus (P)
    GB/T 8573-1999
Analysis for potassium (K)
    GB/T 17767.3-1999

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