

Prospects of improving efficiency of fertiliser nitrogen in Australian agriculture: a review of enhanced efficiency fertilisers

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Abstract. Fertiliser nitrogen use in Australia has increased from 35 Gg N in 1961 to 972 Gg N in 2002, and most of the nitrogen is used for growing cereals. However, the nitrogen is not used efficiently, and wheat plants, for example, assimilated only 41% of the nitrogen applied. This review confirms that the efficiency of fertiliser nitrogen can be improved through management practices which increase the crop's ability to compete with loss processes. However, the results of the review suggest that management practices alone will not prevent all losses (e.g. by denitrification), and it may be necessary to use enhanced efficiency fertilisers, such as controlled release products, and urease and nitrification inhibitors, to obtain a marked improvement in efficiency. Some of these products (e.g. nitrification inhibitors) when used in Australian agriculture have increased yield or reduced nitrogen loss in irrigated wheat, maize and cotton, and flooded rice, but most of the information concerning the use of enhanced efficiency fertilisers to reduce nitrogen loss to the environment has come from other countries. The potential role of enhanced efficiency fertilisers to increase yield in the various agricultural industries and prevent contamination of the environment in Australia is discussed.

Additional keywords: controlled release, urease inhibitors, nitrification inhibitors, mitigation, greenhouse gases.

Introduction

As the intensity of agricultural production in Australia increases to keep pace with population growth, the need for food and fibre, and maintaining profit margin, fertiliser nitrogen use has increased from 35 Gg N in 1961 to 972 Gg N in 2002 (FAO 2007; Fig. 1). This fertiliser nitrogen is used mostly on cereals (702 Gg N), sugarcane, pasture, horticulture, cotton, and oilseeds. Rates of application varied from 2.5 to 229 kg N/ha (Table 1).

However, when fertiliser nitrogen is applied to soil it is not used efficiently, and the plant seldom assimilates >50% of the nitrogen added. Plant uptake for a range of crops and pastures in Australia varies from 6 to 59% of the nitrogen applied (Table 2). In general, bananas and flooded rice were the least efficient of the crops studied (6–17%). The mean recovery of applied nitrogen in Australian dryland wheat was 41% (22–59%), which is marginally better than the estimated worldwide efficiency of nitrogen for cereals of 33% (Raun and Johnson 1999).

One of the main reasons for the poor efficiency of fertiliser nitrogen use is that much of the nitrogen applied (up to 92%) can be lost from the plant–soil system (Table 3). Fertiliser nitrogen can be lost by ammonia volatilisation, during nitrification, and by leaching, erosion, runoff, and denitrification, and the relative importance of these processes can vary widely depending on the agroecosystem, fertiliser form, and method of application.

For example, ammonia volatilisation was important when urea was applied to sugarcane fields covered with plant residues, while denitrification was the major loss process when anhydrous ammonia was drilled into irrigated cotton (Table 3). In most of the systems studied in Australia, erosion and runoff were controlled and leaching was small.

Lost nitrogen represents a serious economic loss to farmers, but the impact of the lost nitrogen on the environment and human health is equally, if not more, important. As pointed out above gaseous emissions of nitrogen via ammonia volatilisation, nitrification, and denitrification are the dominant mechanisms for the loss of fertiliser nitrogen from Australian agroecosystems. These processes result in the release of ammonia, nitric oxide, and the greenhouse gas nitrous oxide into the atmosphere. Agriculture is the main source of nitrous oxide in Australia, contributing 67 Gg in 2005 (AGO 2007); using IPCC (1997) guidelines it is calculated that 21 Gg of this comes from fertiliser nitrogen. In addition to the effect on global warming, the nitrogen gases produced from fertiliser can acidify soils, eutrophy lakes, rivers, and estuaries, decrease biodiversity in terrestrial ecosystems, affect atmospheric visibility, reduce the stratospheric ozone layer that protects the Earth from harmful ultraviolet radiation, and increase ozone concentrations in the troposphere with consequent health effects (Peoples *et al.* 2004).

Mitigation strategies aimed at reducing nitrogen loss are variable and can range from management practices through to

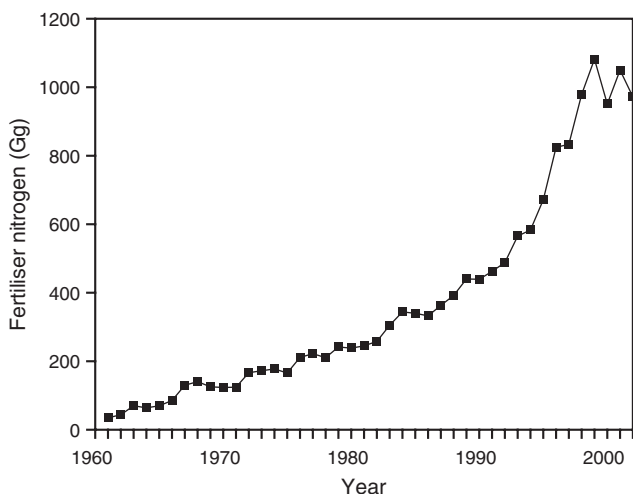


Fig. 1. Fertiliser used in Australia during the period 1960–2002.

Table 1. Fertiliser nitrogen used for crops and pasture in Australia in 2000 (FAO, IFA, IFDC, IPI, PPI 2002)

Commodity	Fertiliser consumption (Gg N)	Application rate (kg N/ha)
Cereals	702	42.9
Sugarcane	96	229.1
Pasture	75	2.5
Horticulture	71	187.8
Cotton	56	121.2
Oilseeds	55	12.8
Total	1055	

the development of new technologies. New technologies include the use of products such as controlled release fertilisers and urease and nitrification inhibitors. Many of these products have been in some use for decades, with controlled release fertilisers commonly used in the nursery industry and inhibitors used for research purposes, yet their use in agricultural situations is relatively new and of particular interest in light of current concerns regarding greenhouse gas emissions.

The objective of this paper is to provide a review of the current literature on improving the efficacy of nitrogen fertilisers through the use of controlled release coatings and urease and nitrification inhibitors, concentrating specifically on work carried out in Australia.

Approaches to improve efficiency

The processes that generate nitrogen loss from soil are controlled directly by factors such as nitrogen availability and moisture, and indirectly by environmental or management factors (Granli and Bøckman 1994). Some of the factors that control loss such as soil type, rainfall, radiation, and temperature are outside the farmer’s control, but there are others that the farmer can influence. These manageable factors include fertiliser type, amount, method and time of application, water status (controlled by irrigation and drainage), soil pH (adjusted by

application of lime), and soil compaction (tillage and trafficking).

In general, nitrogen loss can be decreased by management practices which increase the crop’s ability to compete with the loss processes (Minami 1997). The approaches that have been suggested for improving the efficiency of fertiliser nitrogen include the following:

- (i) using soil and plant testing to make best use of indigenous nitrogen (Johnkutty and Palaniappan 1996; Dobermann and Cassman 2004);
- (ii) using the optimal form, rate, method and time of application of the fertiliser (Strong *et al.* 1992; Smith *et al.* 1997);
- (iii) incorporation or deep placement of fertiliser (De Datta *et al.* 1989; Cai *et al.* 2002; Roy and Hammond 2004);
- (iv) using split applications—several applications of small amounts of fertiliser during the growing season are more effective than one large dose at the beginning of the season (Hooper 2004);
- (v) minimising application in the wet season to reduce leaching and denitrification (McTaggart *et al.* 1994);
- (vi) delaying the supply of fertiliser until a substantial canopy has developed (Humphreys *et al.* 1988),
- (vii) using foliar application (Smith *et al.* 1991); and
- (viii) using inter seasonal cover crops to minimise the accumulation of nitrate during fallow periods (McLenaghan *et al.* 1996; Wagner-Riddle and Thurtell 1998; Cameron *et al.* 2002).

Where denitrification is likely to be the main process responsible for nitrogen loss, nitrate forms of fertiliser should not be used. Thus, matching the type of fertiliser with rainfall and moisture conditions in the soil could result in appreciable reductions in nitrogen loss (McTaggart *et al.* 1994). This is likely to be more beneficial and easier to manage than attempting to maintain a balance between appropriate water management and limiting denitrification or nitrate leaching. For example, trickle or drip irrigation systems which allow delivery of nitrogen to the area of maximum crop uptake enable the application rate to be matched to the plants’ requirements. With careful operation, trickle systems can reduce deep percolation, runoff, and denitrification (Doerge *et al.* 1991). The aim of better water management should be to reduce denitrification by ensuring that the water-filled pore space of the soil does not exceed 60% (Smith *et al.* 1997; Mosier *et al.* 2002).

Returning crop residues to the soil instead of burning them allows reuse of the nitrogen contained in the residues. Incorporated residues can also improve soil structure, and reduce ammonia volatilisation by influencing the conditions of the underlying soil, and by acting as a medium through which ammonia must pass before being lost to the atmosphere (Aulakh *et al.* 1991; Freney *et al.* 1992b). Incorporating residues with high C/N ratio into soils will immobilise mineral nitrogen which can become available later when mineralised (Aulakh *et al.* 1991).

Optimising plant growth and uptake of nitrogen through management of the plant’s total nutrient requirements is another means of increasing nitrogen use efficiency. The supply of one nutrient affects the absorption, distribution, or

Table 2. Recovery of fertiliser nitrogen by crops and pastures in Australia

Crop and location	Recovery (% of applied)			References
	Plant	Soil	Plant + soil	
Bananas: East Palmerston, Qld	15	60	75	Prasertsak <i>et al.</i> (2001a)
Cotton (irrigated): Narrabri, NSW	27–29	8–28	8–57	Freney <i>et al.</i> (1993), Humphreys <i>et al.</i> (1990)
Pasture: Millaa Millaa, Qld	42	18	60	Prasertsak <i>et al.</i> (2001b)
Rice (flooded): Griffith, NSW	6–17	37–48	44–60	Simpson <i>et al.</i> (1984, 1985), Keerthisinghe <i>et al.</i> (1993)
Sugarcane:				
Mackay, Qld	14–38	23–41	38–61	Chapman <i>et al.</i> (1991)
South Johnstone, Qld	19–29	22–25	41–54	Prasertsak <i>et al.</i> (2002)
Sunflowers: Tatura, Vic.	35	30	65	Smith <i>et al.</i> (1988)
Wheat (dryland): Hanwood, Murrumbidgee, Widgee, Willerah, Wumbulgal, Yanco, NSW; Birchip, Chinkapook, Elmore, Wunghnu, Diggers Rest, Vic.	22–59	20–54	60–88	Bacon and Freney (1989), P. E. Bacon, J. R. Freney, unpublished data
Wheat (irrigated): Tatura, Vic.	25	25	50	Freney <i>et al.</i> (1992a)

Table 3. Nitrogen lost from agricultural systems in Australia (% of applied)

Crop and location	Loss			References
	Volatilised	Denitrified	Total	
Bananas: East Palmerston, Qld	20	5	25	Prasertsak <i>et al.</i> (2001a)
Cotton (irrigated): Narrabri, NSW	0	43–92	43–92	Freney <i>et al.</i> (1993), Humphreys <i>et al.</i> (1990)
Pasture:				
Millaa Millaa, Qld	20	20	40	Prasertsak <i>et al.</i> (2001b)
Ellinbank, Vic.	32–57	13–15	47–70	Eckard <i>et al.</i> (2003)
Rice (flooded): Griffith, NSW	0–11	15–56	40–56	Simpson <i>et al.</i> (1984, 1985), Keerthisinghe <i>et al.</i> (1993)
Sugarcane:				
Mackay, Qld	0	39–62	39–62	Chapman <i>et al.</i> (1991)
South Johnstone, Qld	6–37	22–40	46–59	Prasertsak <i>et al.</i> (2002)
Sunflowers: Tatura, Vic.	6	29	35	Smith <i>et al.</i> (1988)
Wheat (dryland): Hanwood, Murrumbidgee, Widgee, Willerah, Wumbulgal, Yanco, NSW; Birchip, Chinkapook, Elmore, Wunghnu, Diggers Rest, Vic.	1–24	2–27	12–40	Bacon and Freney (1989), P. E. Bacon, J. R. Freney, unpublished data
Wheat (irrigated): Tatura, Vic.	0	50	50	Freney <i>et al.</i> (1992a)

function of another nutrient, so that insufficient amounts of plant-available phosphorus, sulfur, potassium, or other nutrient will reduce nitrogen use efficiency. For example, nitrogen recovery in phosphorus-deficient corn was <40%, whereas it was 75% when adequate phosphorus was supplied (Oberle and Keeney 1990).

Site-specific nitrogen management is used to synchronise the supply and demand of nitrogen, and it can be used to manage nitrogen in labour-intensive, small-scale farming or highly mechanised, large-scale production fields (Dobermann and Cassman 2004). Optimum nitrogen rates vary spatially and seasonally; thus, diagnostic tools are required to assess soil or crop nitrogen status during the growing season to make decisions on the amount of nitrogen to be applied (Schröder *et al.* 2000). One diagnostic measure is leaf greenness, and several techniques exist to measure this, including near-infrared leaf nitrogen analysis, chlorophyll meters, leaf colour charts, crop canopy reflectance sensors, and remote sensing (Giller *et al.*

2004). Significant increases in nitrogen use efficiency have been achieved through reductions in nitrogen use.

Decision support systems (DSS), based on comprehensive and process-based agro-ecosystem models, for optimum nitrogen fertiliser management have also been used recently. The advantage of such systems is the ability to integrate biophysical variables/interacting processes and management practices and economical–environmental considerations. The best management practices can be identified by simulating the combination of different management practices, such as interaction of nitrogen application rates and time with irrigation rate and time, and trade-off between economical and environmental interests. The GIS-based DSS for fertiliser application and irrigation for North China Plain, derived from the Water and Nitrogen Management Model (WNMM), has significantly assisted the dissemination of the best management fertiliser nitrogen practices with substantial economical impact (Chen *et al.* 2006).

Enhanced efficiency fertilisers

While the techniques described above have the potential to increase the effectiveness of applied nitrogen, considerable N losses still occur. For example, in flooded rice the time of application had a big effect on the agronomic efficiency of fertiliser nitrogen and ammonia volatilisation, but even with the best system devised, around 40% of the applied nitrogen was still lost by ammonia volatilisation, denitrification, or leaching (Bacon and Heenan 1987; Humphreys *et al.* 1988). In order to further reduce loss by these processes, alternative fertilisation techniques, such as the use of controlled release fertilisers, urease inhibitors, and nitrification inhibitors, need to be considered. These can be collectively referred to as enhanced efficiency fertilisers.

There have been numerous studies on enhanced efficiency fertilisers, either used alone or in combination in agroecosystems, with highly variable efficiencies demonstrated (Smith *et al.* 1997; Trenkel 1997; Zerulla *et al.* 2001; Drost *et al.* 2002; Singh *et al.* 2004; Watson 2005). The high variability in effectiveness is often due to a lack of understanding of the interaction of these chemicals with soil and environmental variables (Mosier *et al.* 2002). For example, the nitrification inhibitor dicyandiamide (DCD) was shown to be a very effective nitrification inhibitor under cold climatic conditions, but is less effective in warm/hot and wet climates due to its rapid decomposition (Zerulla *et al.* 2001; Singh *et al.* 2004; Di and Cameron 2004b; Hatch *et al.* 2005). Most field studies have concentrated on the effect on production (grain yield or biomass) and few have considered gaseous nitrogen loss and nitrate leaching. While many studies have been carried out in other countries, few have been conducted in Australia. Thus, there is a need to evaluate the effectiveness of various formulations and strategies under conditions applicable to Australia's major agroecological zones for fertiliser manufacturers and farmers.

Controlled release fertilisers

The supply of nitrogen by a single application of slow or controlled-release fertiliser should satisfy plant requirements and maintain low concentrations of mineral nitrogen in the soil throughout the growing season. As a result, labour and application costs should be low, nitrogen loss should be minimised, nitrogen use efficiency should increase, and yields should be improved.

Many different controlled release forms of nitrogen have been suggested (Peoples *et al.* 1995), and considerable advances have been made in the formulation of these materials. Shaviv (2005a, 2005b) has classified these fertilisers into 3 main types:

- (i) inorganic low solubility compounds (e.g. magnesium ammonium phosphate);
- (ii) organic low solubility compounds (e.g. urea formaldehyde and isobutylidenediurea);
- (iii) coated materials in which a physical barrier controls the release (e.g. granules coated with hydrophobic polymers, or matrices in which the soluble fertiliser is dispersed so the dissolution of the fertiliser is restricted).

The coated fertilisers can be further divided into those coated with inorganic material (e.g. sulfur-coated urea), sulfur-coated fertiliser, which is further coated with an organic polymer (e.g. polymer-coated sulfur-coated urea), and those coated with organic polymers, viz. thermosetting resin-coated fertilisers and thermoplastic polymer-coated fertilisers.

Sulfur-coated urea was developed in the 1960s by the National Fertilizer Development Center and used with mixed success in a variety of applications, e.g. flooded rice (Prasad and De Datta 1979) and wheat (Mason 1985). Sulfur coatings provide highly variable nitrogen release patterns depending upon coating damage that might occur, and as much as one-third can be released instantaneously. Addition of a polymer coating to sulfur-coated urea significantly improved its performance. Polymer sulfur-coated urea has improved ryegrass and bluegrass quality in 2 Pacific north-west climates (Miltner *et al.* 2004) and reduced leaching loss to only 1.7% of the applied nitrogen after application to turf lawn in southern New England (Guillard and Kopp 2004).

The main thermosetting resin-coated fertilisers are the alkyd-type resins (e.g. Osmocote) and those with polyurethane-like coatings such as Polyon, and Multicote (Trenkel 1997; Shaviv 2005a). Nutrient release from these materials is controlled by the coating thickness (Trenkel 1997; Shaviv 2005a). According to Shoji and Gandeza (1992), the most accurate controlled release of nutrients is provided by the polyolefin thermoplastic-coated fertilisers (e.g. Meister) developed by Chisso-Asahi Fertilizer Co., Japan. Fertiliser release is controlled by coating fertiliser particles with polyolefins, such as polyethylene and polypropylene, which have low water permeability, and ethylene vinyl acetate, which has high water permeability.

The pattern of nutrient release from coated fertilisers can be parabolic, linear, or sigmoidal and long- or short-term (Shaviv 2005a). Nitrogen uptake of seasonal crops and perennial species is generally sigmoidal (Shoji and Kanno 1994; Shoji *et al.* 2001; Shaviv 2005a). Because of the variety of polyolefin-coated fertilisers available it is now possible to use computers to program fertiliser release patterns to match the specific requirements of a crop, and Shoji (2005) illustrates how this can be used to supply nitrogen at the times of peak demand for flooded rice.

Use of polyolefin-coated urea instead of uncoated fertiliser has resulted in increased yields and nitrogen use efficiency in a range of crops including potatoes, rice, and direct-seeded onions (Mikkelsen *et al.* 1994; Shoji and Kanno 1994; Shoji *et al.* 2001; Drost *et al.* 2002; Fashola *et al.* 2002; Shoji 2005; Wu *et al.* 2005). Large reductions in the emission of nitrous oxide have also been achieved using polyolefin-coated ammonium nitrate (Minami 1994), polyolefin-coated ammonium sulfate (Nutricote; Smith *et al.* 1997), and polyolefin-coated urea (Shoji *et al.* 2001) instead of uncoated nitrogen fertiliser. However, no yield effect was found in irrigated cotton in Australia by using polyolefin-coated urea, although there were significant impacts on N uptake and mineral N (urea, ammonium, and nitrate) dynamics (Chen *et al.* 2008). Ammonium-based fertilisers have been coated with polyolefins for use in vegetable growing to prevent the build-up of nitrate, which affects quality and may constitute a health risk (Matsumoto 1991; Takebe *et al.* 1996; Shoji 2005;

Wang *et al.* 2005). A further decrease in nitrate uptake by vegetables was achieved by adding the nitrification inhibitor DCD to the fertiliser before coating the mixture with polyolefin (Mimaki 2003).

However, it has been pointed out that use of controlled release fertilisers may result in nitrogen, in excess of the crop's requirements, remaining in the soil after harvest. This nitrogen may then be lost to the environment in the same manner as uncoated fertiliser (Delgado and Mosier 1996).

The use of controlled-release fertilisers in agriculture is still limited in spite of the technological developments and availability. Only about 10% of the total production is consumed in agriculture, and the remainder is used for lawns, golf courses, fruit trees, and vegetables (Shaviv 2005a). The main reason for the limited use seems to be the high cost, which may be 3–10 times the cost of conventional fertiliser (Shaviv 2000).

Urease inhibitors

Urea has become the most widely used form of fertiliser nitrogen, because it is the least expensive form of fertiliser available, and its high nitrogen content (46%) means lower transportation costs. Globally in developed countries urea consumption has stabilised at around 30 Mt, while in developing countries consumption is still increasing dramatically and was around 55 Mt in 2002 (IFA 2006). However, it has the disadvantage that considerable losses of nitrogen can occur if the urea is not incorporated into soil soon after application. Losses have ranged from negligible amounts to >50% of the nitrogen applied, depending upon fertiliser practice and environmental conditions (Peoples *et al.* 1995; Cai *et al.* 2002). The loss occurs by ammonia volatilisation after the urea is converted to ammonia at the soil surface by reaction with the enzyme urease. One approach to decreasing ammonia volatilisation is to find compounds that inhibit urease activity, thus allowing the urea to move into the soil before hydrolysis. The ammonia then released would be retained by the soil.

A large number of compounds with differing characteristics have been tested for their ability to inhibit urease activity (Medina and Radel 1988; Watson 2000, 2005; Kiss and Simihaian 2002). Some inhibit the enzyme by reacting with active sites on the enzyme or a key functional group elsewhere in the molecule, or by changing the conformation of the active site. Many organic and inorganic compounds and metal ions inhibit urease by reacting with the sulfhydryl groups in the enzyme (e.g. mercapto compounds), others by complexing with nickel in the active site (e.g. hydroxamates), some by reacting with the carboxylic acid group (e.g. arylorganoboron compounds), and others because they are structural analogues of urea (e.g. thiourea, methyl urea, and phosphoryl di- and triamides) (Medina and Radel 1988).

The most effective compounds for the inhibition of urease activity appear to be the phosphoryl amides (e.g. N-(*n*-butyl) phosphoric triamide and cyclohexylphosphoric triamide (Chai and Bremner 1987; Keerthisinghe and Blakely 1995; Byrnes and Freney 1995), although hydroquinone and 2, 5-dimethyl p-benzoquinone can provide inhibition at high concentrations (Tomlinson 1970; Xu *et al.* 2005).

A host of natural products have been tested for their ability to inhibit urease activity, including coal and peat; humic substances; lignins and tannins; plant residues and extracts containing polyphenols and saponins; neem cake, oil, and extracts; karanja cake and mahua cake; and microbial products (Kiss and Simihaian 2002). In India the press cake from the production of neem (*Azadirachta indica*) oil has been shown to inhibit urease activity (Trenkel 1997), and when it was used to coat urea it reduced loss of nitrogen and improved nitrogen use efficiency (John *et al.* 1989). Patra *et al.* (2006) showed that the natural essential oil, dementholised oil, and terpenes of peppermint (*Mentha spicata*) significantly retarded soil urease activity. Natural inhibitors of urease activity have also been found in *Artemisia annua* (Patra *et al.* 2002), *Ranunculus repens* (Khan *et al.* 2006), and *Aspergillus ochraceus* (Lin *et al.* 1997).

The compound which has been most widely tested for its capacity to reduce ammonia loss from urea is N-(*n*-butyl) thiophosphoric triamide (Trenkel 1997; Singh *et al.* 2004; Watson 2005). However, like the other thiophosphoryl triamides it is not a urease inhibitor. The thio compounds are the precursors of oxygen analogues which are the actual inhibitors. Numerous tests of the pure thio compounds *in vitro* have shown their total ineffectiveness. The thio compounds have to be converted to the oxygen analogues on contact with soil or other material before inhibition can occur (McCarty *et al.* 1989; Creason *et al.* 1990). It might seem to be more logical to market the oxygen analogue of N-(*n*-butyl) thiophosphoric triamide (viz. N-(*n*-butyl) phosphoric triamide), but the oxygen analogue is not sufficiently stable for it to be packaged and distributed for commercial application (Incitec Pivot, pers. comm.). N-(*n*-butyl) thiophosphoric triamide, on the other hand, seems to be quite stable (Hendrickson and Douglass 1993) although its effectiveness is controlled by temperature (Chai and Bremner 1987; Carmona *et al.* 1990). The results of Carmona *et al.* (1990) indicate that higher concentrations of N-(*n*-butyl) thiophosphoric triamide will be required to prevent ammonia loss from warm soils than for temperate soils.

Watson *et al.* (1994a, 1994b) found N-(*n*-butyl) thiophosphoric triamide very effective at low concentrations (0.01% of applied urea nitrogen) for reducing ammonia volatilisation (by ~50%) in field trials on temperate grassland. Its use also significantly delayed and reduced ammonia and nitrous oxide emissions from soil after application of urea, urine, and urea ammonium nitrate (Bronson *et al.* 1989b; Schlegel 1991; Grant *et al.* 1996; Wang and Douglas 1996; Singh *et al.* 2004) and produced significant improvements in nitrogen use efficiency of corn following application of urea ammonium nitrate (Fox and Piekielek 1993). In 21 upland field experiments, treating urea with N-(*n*-butyl) thiophosphoric triamide increased grain yields of maize by an average of 750 kg/ha (Bronson *et al.* 1989b). An additional 80 kg N/ha would need to be applied to obtain that increase in yield (Byrnes and Freney 1995). Similar positive results were reported by Hendrickson (1992) for maize fertilised with urea or urea ammonium nitrate in 78 trials conducted in the USA between 1984 and 1989.

Both N-(*n*-butyl) thiophosphoric triamide and cyclohexyl phosphoric triamide have been used successfully to control ammonia emission from animal wastes, to prevent environmental damage, and to produce a more balanced nitrogen/phosphorus fertiliser from manure (Varel 1997; Varel *et al.* 1999).

Nitrification inhibitors

Maintaining nitrogen in the ammonium form in soil would prevent its loss by both nitrification and denitrification. One method of doing this is to add a nitrification inhibitor with the fertiliser. This prevents or slows the microbial conversion of ammonium to nitrate and hence the leaching of nitrate and production of nitric oxide, and nitrous oxide by both nitrification and denitrification. While this technique does not always produce increased crop yields it does provide a tool for managing nitrate leaching and nitrous oxide production (Edmeades 2004).

Reliable data on the use of nitrification inhibitors in different crops and regions are not available. Surveys of USA farmers indicate that at present about 9% of the national maize area is treated with nitrification inhibitors, and this proportion has remained unchanged in recent years (Christensen 2002).

Many chemicals have been tested as nitrification inhibitors, but few are commercially available (Table 4) or have proven to be agronomically and economically effective (Slangen and Kerkhoff 1984; Prasad and Power 1995; McCarty 1999; Frye 2005). The persistence and behaviour of nitrification inhibitors in soil is determined by diffusion into the atmosphere, decomposition or degradation, differential movement in soils, sorption on clay or organic matter (Slangen and Kerkhoff 1984), and by environmental and edaphic factors, such as temperature, moisture, and soil texture (Prasad and Power 1995). While progress is being made towards understanding the mode of action of many inhibitors of ammonia oxidation, little is known about the action of others such as the heterocyclic nitrogen compounds (McCarty 1999).

Of the inhibitors listed in Table 4, the most extensively studied products are nitrapyrin, DCD, and more recently 3,4-dimethylpyrazole phosphate (Goos and Johnson 1999; Dittert *et al.* 2001; Pasda *et al.* 2001; Weiske *et al.* 2001a, 2001b; Zerulla *et al.* 2001; Calderon *et al.* 2005; Chao *et al.* 2005; Islam *et al.* 2007a, 2007b).

Nitrapyrin is often ineffective because of sorption on soil colloids, hydrolysis, and loss by volatilisation (Hoeft 1984; Liu *et al.* 1984), but it has reduced nitrogen losses and resulted in

increased plant nitrogen uptake (Fillery and De Datta 1986; Chen *et al.* 1998a, 1998b). When Wolt (2004) evaluated the performance of nitrapyrin across research trials conducted in diverse environments over many years in Midwestern USA, he found that, on average, nitrapyrin increased corn yield by 7% and soil retention of nitrogen by 28%. It also decreased nitrogen leaching by 16% and nitrous oxide emission by 51%.

Dicyandiamide inhibited nitrification when ammoniacal fertilisers were applied to field crops and vegetables (Frye *et al.* 1989; Frye 2005) with the result that nitrogen remained longer in the soil in the ammonium form (Irigoyen *et al.* 2003). Yield increases have been obtained when DCD was applied to pastures (Di and Cameron 2002; Smith *et al.* 2005) and various cropping systems, e.g. maize (Ball-Coelho and Roy 1999), wheat (Rao 1996; Sharma and Kumar 1998; Rao and Popham 1999), and maize-wheat (Sharma and Prasad 1996). However, application of DCD does not always lead to yield increases (Mason 1987; Dachler 1993; Frye 2005) and in some cases can have deleterious effects on plant growth (Macadam *et al.* 2003). Yield increases usually occurred at low fertiliser application rates (Frye 2005).

Leaching of nitrate can be significantly reduced by addition of DCD (Ball-Coelho and Roy 1999; Serna *et al.* 2000; Di and Cameron 2002, 2004a). Treatment of urine patches on a fine sandy loam in New Zealand with DCD reduced nitrate leaching losses from 85 to 20–22 kg N/ha.year (Di and Cameron 2002, 2004a). The beneficial effect of the DCD was increased beyond the saving of nitrogen because it also reduced leaching of the cations associated with nitrate, calcium by 38–56% and magnesium by 21–42% (Di and Cameron 2004a, 2004c).

Because DCD effectively retards nitrification, when it is added to soil along with ammonium based fertilisers, emissions of nitric oxide and nitrous oxide are substantially reduced compared with fertiliser alone (Majumdar *et al.* 2000; Shoji *et al.* 2001; Vallejo *et al.* 2001; Singh *et al.* 2004; Hatch *et al.* 2005; Merino *et al.* 2005;). For example, Skiba *et al.* (1993) showed that addition of DCD reduced nitric oxide emission by about 92% and nitrous oxide emission by 40%. Significant reductions have also been reported for DCD-treated pig slurry (Vallejo *et al.* 2005) and DCD-treated animal urine patches in grazed perennial ryegrass-white clover pastures (Di and Cameron 2003). Di and Cameron (2003) showed that repeated applications of DCD offered no advantage over a single application of DCD immediately after urine deposition.

However, the effect of DCD on reducing the rate of nitrification in soil is variable and in some cases no effect on nitrate leaching was obtained (Davies and Williams 1995;

Table 4. Compounds produced commercially as nitrification inhibitors (modified from Nelson and Huber 2001)

Chemical name	Common or trade name	Manufacturer
2-Chloro-6-(trichloromethyl)-pyridine	Nitrapyrin, N-Serve	Dow Chemical Co.
5-Ethoxy-3-trichloromethyl-1, 2, 4-thiadiazole	Dwell, Terrazole, Etradiazo	Uniroyal Chemical
Dicyandiamide	DCD	SKW Trostberg AG
3,4-Dimethylpyrazole phosphate	DMPP (ENTEC)	BASF AG
2-Amino-4-chloro-6-methyl-pyrimidine	AM	Mitsui Toatsu Co.
2-Mercapto-benzothiazole	MBT	Onodo Chemical Industries
2-Sulfanilamidothiazole	ST	Mitsui Toatsu Co.
Thiourea	TU	Nitto Ryuso

Beckwith *et al.* 1998). The effectiveness of DCD in soil is controlled by temperature, texture, and moisture content (Prasad and Power 1995; Irigoyen *et al.* 2003). With increasing temperature the inhibiting effect of DCD is greatly decreased (Bronson *et al.* 1989a; Irigoyen *et al.* 2003; Di and Cameron 2004b). Bronson *et al.* (1989a) found that the half-life of DCD in a sandy loam was reduced from 52 to 14 days when the temperature was increased from 8°C to 22°C, and Di and Cameron (2004b) observed a greater reduction in a silt loam.

A relatively new nitrification inhibitor, 3, 4-dimethylpyrazole phosphate (DMPP), was developed by the German company BASF AG (BASF 1999; Zerulla *et al.* 2001). It is generally more effective and longer lasting than DCD in inhibiting nitrification, and inhibition was achieved with lower rates of application (0.5–1.5 kg DMPP/ha). DMPP has been found to reduce nitrate and nitrite levels in soil after application of ammonium-based fertilisers and cattle slurry, leading to significantly lower nitric oxide and nitrous oxide emissions, and nitrate leaching, and to improve crop yields (Dittert *et al.* 2001; Pasda *et al.* 2001; Zerulla *et al.* 2001; Chao *et al.* 2005; Menéndez *et al.* 2006). Weiske *et al.* (2001b) showed that DMPP reduced emission of nitrous oxide by 49% (averaged over 3 years), which was considerably more than DCD (average reduction 26%). European field trials demonstrated that addition of DMPP increased yields of winter wheat, wetland rice, maize, potatoes, sugar beets, carrots, lettuce, radish, cauliflower, and onions, allowed lower rates of nitrogen fertiliser, or permitted fewer applications to be used to attain the same yields as treatments without DMPP (Pasda *et al.* 2001).

The effectiveness of DMPP, like DCD, is influenced by temperature, soil texture, and moisture (Barth *et al.* 2001; Pasda *et al.* 2001; Merino *et al.* 2005). Merino *et al.* (2005) found that DMPP applied with cattle slurry was able to maintain soil mineral nitrogen in the ammonium form for 22 days and reduce nitrous oxide emission by 69% in autumn, but in spring its effect on soil mineral N lasted for only 7–14 days, and reduced nitrous oxide loss by 48%.

Other nitrification inhibitors that have been used successfully in field trials include acetylene, substituted acetylenes, etridiazole, and a natural product from the Neem tree (*Azadirachta melia*). Acetylene is a potent inhibitor of nitrification, but because it is a gas, it is difficult to add and keep in soil at the correct concentration to inhibit the oxidation of ammonium. Calcium carbide coated with layers of wax and shellac has been used to provide a slow-release source of acetylene to inhibit nitrification (Mosier 1994). This technique has increased the yield or recovery of nitrogen in irrigated wheat, maize, cotton, and flooded rice (Bronson and Mosier 1991; Bronson *et al.* 1992; Freney *et al.* 1992a, 1993; Zhang *et al.* 1992). Another product, a polyethylene matrix containing small particles of calcium carbide and various additives to provide controlled water penetration and acetylene release, has been developed as an alternative slow-release source of acetylene. In laboratory studies, this matrix inhibited nitrification for 90 days and considerably slowed the oxidation for 180 days (Freney *et al.* 2000). It also retarded nitrification in an irrigated corn field for at least 48 days (Randall *et al.* 2002). The substituted acetylenes

2-ethynylpyridine and phenylacetylene are very effective inhibitors of nitrification in the field (Freney *et al.* 1993; Chen *et al.* 1994, 1998a, 1998b), but their current price restricts their use by farmers.

Etridiazole (Terrazole, Dwell) was found to be a very effective nitrification inhibitor in laboratory investigations (Liu *et al.* 1984; Rafii *et al.* 1984; McCarty and Bremner 1990), and it has been shown to inhibit nitrification for prolonged periods in the field (Somda *et al.* 1989; Rochester *et al.* 1994) and to substantially improve yields for a variety of field and horticultural crops (Somda *et al.* 1990) and irrigated cotton (Rochester *et al.* 1994, 1996).

Various products (cake and oil) from the seeds of the Neem tree have been tested to determine whether they could be used as cheap nitrification inhibitors for resource-poor Indian farmers (Majumdar *et al.* 2000; Malla *et al.* 2005). Field experiments on the Indo-Gangetic plain showed that application of neem cake and neem oil with the fertiliser significantly reduced the emission of nitrous oxide. Addition of neem cake also significantly increased the yield of rice (Malla *et al.* 2005).

Unless care is taken to place ammonium-based fertilisers below the soil surface, use of nitrification inhibitors may result in increased ammonia volatilisation (Rodgers 1983; Chaiwanakupt *et al.* 1996).

Potential for use of enhanced efficiency fertilisers in Australia

Research suggests that the effectiveness of different controlled release fertilisers, and urease and nitrification inhibitors will depend upon crop, soil climate, and management factors. The broadacre agricultural industries in Australia which have been identified as high nitrogen users are those producing cereals, sugarcane, cotton, and pasture (Table 1). Some dairy pastures receive up to 300 kg N/ha.year (Eckard 2004). Horticultural cropping and turf production are also big users of nitrogen, but these industries are beyond the scope of this review. Each of these industries is likely to benefit from the use of the enhanced fertilisation techniques, but the best technique for each crop is likely to vary.

The major wheat-producing regions are in southern Western Australia, New South Wales, South Australia, and western Victoria where the climate is temperate and the soils are mainly Chromosols, Sodosols, Vertosols, and Calcarasols (Isbell 1996). The pasture-producing areas that have high nitrogen inputs are the rainfed or irrigated dairying regions (Eckard 2004). Most of the dairy pastures are in Victoria, which is responsible for 64% of Australia's milk production (Dairy Australia 2006), and most of the dairy cattle are in the Western District (rainfed), Goulburn (irrigated), and Gippsland (ABS 2005). The main soils in these regions are, respectively, Chromosols, Sodosols, and Vertosols; Sodosols; and Dermosols and Ferrosols. The climate in these regions is temperate. Sugarcane is grown along a 2000-km strip of land on the east coast of Australia from northern New South Wales to north Queensland. About one-third of this crop is grown in north Queensland from Ingham to Mossman. This area has a humid tropical climate, and sugarcane is grown on soils formed from alluvial deposits, the deep red and yellow friable loams and the

krasnozems (Wood 1991). In the subtropical areas, the crop is grown on red loams around Bundaberg, and on acid sulfate soils in the coastal lowland regions. Cotton is grown throughout NSW and Queensland on alkaline heavy clay soils where the climate ranges from temperate to subtropical.

Urease inhibitors are expected to be most beneficial on soils where loss of ammonia from application of urea fertiliser is high. This is likely to be when urea is applied to the surface of pasture soils (e.g. in the dairy industry) or other soils which have high urease activity due to lack of cultivation or the accumulation of organic matter (e.g. sugarcane trash). Ammonia loss will also occur when incorporation of urea is difficult and there is little opportunity for the urea to move into the soil with infiltrating water (e.g. rainfed wheat). Nitrification inhibitors are likely to have the greatest benefit on soils where nitrogen losses due to leaching or denitrification are large. Leaching losses are more likely to occur on coarse-textured, free-draining soils under heavy rainfall (e.g. sugarcane soils in the tropics) than on fine-textured clay soils with low rainfall (cotton soils in western NSW). Losses due to denitrification are expected to be large in warm, flooded, or waterlogged soils (cotton and rice soils), in soils to which plant residues have been added (sugarcane and banana soils), and in dung and urine patches (pasture soils). Benefits from the use of controlled release fertilisers could potentially occur in all the agricultural industries, as their use should limit losses by all processes.

The choice of controlled release fertiliser, urease inhibitor, or nitrification inhibitor is likely to be determined more by factors such as price and availability rather than by degree of effectiveness, as many of the compounds shown to be very effective in the laboratory and small-scale trials are not available commercially. Available products which have the potential to increase yield, nitrogen use efficiency, or loss of nitrogen are described below.

Controlled release fertilisers

The controlled release fertilisers that appear to show the greatest potential for dryland and irrigated cropping, and pasture are (i) a polymer-coated urea (Environmentally Smart Nitrogen; Agrium 2006); (ii) a polyolefin-coated urea (Meister; Chisso Corporation 2006); and (iii) a humic-acid-coated urea (Black Urea; Advanced Nutrients Australia 2006).

Environmentally Smart Nitrogen has been extensively used in the USA and Canada and recently in trials in subtropical Queensland. It maximised nitrogen use efficiency and minimised nitrogen losses to the environment (Blaylock *et al.* 2005; Agrium 2006). Meister comes in several forms having different release types and times. Meister-SS15 shows a sigmoidal-type release, with a lag period of 70 days and a release period of 80 days (Shoji *et al.* 2001). This makes it ideal for dryland wheat, which requires nitrogen fertilisation approximately 80 days after sowing to supply nitrogen for grain-fill. Urea coated with humic acid has significantly reduced nitrogen loss and enhanced nitrogen uptake by dryland wheat in field trials at Quirindi, NSW, and increased dryland pasture yields compared with urea (Advanced Nutrients Australia 2006). Addition of humic acid to urea has

also reduced ammonia loss from acid soils (Garcia Serna *et al.* 1996; Siva *et al.* 2000).

Urease inhibitors

The most readily available compound, N-(*n*-butyl) thiophosphoric triamide, is sold in Australia as Agrotain, which contains 20–25% active ingredient (IMC-Agrico 1997). Agrotain is marketed by Incitec Pivot Ltd in the following formulations: (i) Green Urea 14, which contains 45.8% nitrogen as urea and Agrotain @ 5.0 L/t to reduce the loss of ammonia by volatilisation for up to 14 days; and (ii) Green Urea 7, which contains 45.9% nitrogen and Agrotain @ 3.0 L/t to reduce ammonia volatilisation for up to 7 days (Incitec Pivot Ltd 2006).

Nitrification inhibitors

The products which show the greatest potential for reducing nitrogen loss from agricultural industries in Australia are (i) DMPP (rainfed wheat and pasture), (ii) DCD (rainfed and irrigated pasture, wheat), and (iii) etridiazole (irrigated cotton). DMPP seems to be the best product because of its positive effects on yield and nitrogen loss at low concentrations, and because of its stability and lack of movement in soil. It may need to be applied at slightly higher concentrations in warm conditions. It is marketed as ENTEC by BASF and is distributed by Incitec-Pivot in Australia (Incitec Pivot Ltd 2006). DCD (marketed as Didin by SKW Trostberg, Germany) needs to be applied at higher rates than DMPP. It is unstable at high temperatures, and thus is likely to be more effective when used during winter and autumn.

Further testing of these materials under a range of conditions is required to select the best material for a particular industry in Australia, and to determine the economics of its use.

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