

The science behind inhibitors

AHDB

from theory
to field

There's a debate going on about the mandatory use of nitrogen inhibitors for urea fertilisers. Last year, AHDB reviewed the literature to reveal the science behind them and how they could be used to reduce emissions. CPM investigates.

By Lucy de la Pasture

Many things in politics are uncertain, but it's a sure thing that life will soon change as farming is shaped by the new Agriculture Bill. With clean air and clean water very much a focus of the government's 25-year environment plan, ensuring efficient use of organic and inorganic fertilisers will likely be a key priority.

The way change will be implemented is yet to be fully revealed, but there will be a focus on a greener environment, says AHDB resource management scientist, Dr Sajjad Awan. "Approximately 88% of ammonia (NH_3) emissions in the UK are from agriculture, so farming practices that mitigate these losses will be necessary."

The arable sector loses nitrogen gases from its soils to the atmosphere — as NH_3 , nitrous oxide and other nitrogenous oxides (produced through nitrification/denitrification processes) — as well as losing nitrates into water through leaching.

"Nitrogenous gases contribute to particulate matter which can cause respiratory problems in humans, with current levels in the air estimated to cost billions to the NHS. These emissions also affect the environment and nitrous oxide is a powerful greenhouse gas," he explains.

Ammonia emissions

"Denmark and Holland have succeeded in reducing their ammonia emissions considerably since the 1990s (by 40% and 64% respectively), whereas the UK has only achieved a 10% reduction in the same timeframe. To meet targets under UK policy, we only have 10 years left to reduce ammonia emissions substantially."

The main inorganic form of nitrogen fertiliser responsible for losses of NH_3 to the air is urea ($\text{CH}_4\text{N}_2\text{O}$), which according to the latest British Survey of Fertiliser Practice (2018) accounts for just over 10% of total N applied to cereal crops and 15% to oilseed rape.

The trend in tillage practices towards a no-till approach has multiple benefits to soil health, but also has an influence on ammonia emissions, points out Sajjad. "There's some evidence that soil organic matter and crop residues can increase urease concentrations in the top few centimetres of soil, hence under no-till and/or higher stubble environments, losses from urea could be higher, with increased ammonia production."

Germany has recently taken the step to ban the application of straight urea this year, allowing only inhibited forms to be applied to crops. Even though nitrogen inhibitors have

been available for a couple of decades in the UK, their use hasn't been widely adopted for economic reasons. But recently there's been a rapid rise in their use, with a 10-fold increase in area treated reported between 2010 and 2015.

The changing emphasis in farming, with its keen focus on the environment, prompted AHDB to conduct an internal review of the available scientific literature last year. The aim was to understand the problems caused by nitrogen losses and look at the possible solutions, particularly the science behind urease and nitrification inhibitors.

"Nitrogen losses from solid urea application can range from 10-58%, averaging around 26%, and are strongly influenced by factors such as soil water, organic matter, soil temperature, pH and urea concentration," he says.

"Significant losses of urea into the atmosphere could be due to high surface temperature, usually observed in the UK

“Nitrogen losses from solid urea application can range from 10-58%.”



Sajjad Awan explains that to meet targets under UK policy, there's only 10 years left to reduce ammonia emissions substantially.

Factors affecting NBPT efficacy

Factor/condition	Efficacy of NBPT (N-butyl) thiophosphoric triamide
Soil type	Efficiency usually higher in clay or silty soils with high cation exchange capacity
Soil moisture	Highly effective at field capacity or slightly above, reduced efficiency under water-logged conditions
Soil pH	Efficiency improves with increase in the pH, higher efficiency in alkaline conditions
Soil temperature	Duration of NBPT activity decrease with increasing temperature
Concentration (wt/wt)	Increasing concentration from 0.01 to 0.12% can significantly increase NBPT efficiency

Source: 'Use of nitrogen inhibitors to mitigate greenhouse gas emissions in the UK arable agriculture.' AHDB internal review, 2020.

Pros and cons of using different nitrification inhibitors

Nitrification inhibitor	Pros	Cons
DCD (Dicyandiamide)	<ul style="list-style-type: none"> <input type="checkbox"/> Could be cheaper compared DMPP <input type="checkbox"/> Less volatile <input type="checkbox"/> Better water solubility 	<ul style="list-style-type: none"> <input type="checkbox"/> May be ecotoxic as high concentration are required <input type="checkbox"/> Efficacy reduces under hot conditions
DMPP (3, 4 - dimethylpyrazol phosphate)	<ul style="list-style-type: none"> <input type="checkbox"/> Higher efficacy at low concentration <input type="checkbox"/> Could be less toxic 	<ul style="list-style-type: none"> <input type="checkbox"/> Currently expensive to use <input type="checkbox"/> Mode of action not fully understood
Nitrapyrin (2-chloro-6-(trichloromethyl) pyridine)	<ul style="list-style-type: none"> <input type="checkbox"/> Slow degradation under temperate conditions and heavy soils <input type="checkbox"/> Effective at lower concentrations (inhibition at 1ppm) <input type="checkbox"/> No substantial loss across wide ranges in pH 	<ul style="list-style-type: none"> <input type="checkbox"/> Volatile, hence, works best when soil injected <input type="checkbox"/> Degrades quickly in bright and wet conditions and in coarser soils low in organic matter

Source: 'Use of nitrogen inhibitors to mitigate greenhouse gas emissions in the UK arable agriculture.' AHDB internal review, 2020.



Reducing nitrogen losses from fertilisers has the added benefit that more nitrogen is available to the crop, improving nitrogen use efficiency.

during summer, moist soil conditions also promote urea conversion to ammonia, and wet conditions reduce these losses.

"It's not a bad idea to apply urea if rain is imminent, up to 10mm of rainfall soon after fertiliser application increases urea efficacy and can reduce ammonia losses by up to 80%. A soil pH above 7.5 also promotes urea hydrolysis which could result in greater losses as ammonia. Urease inhibitors can be added to urea to slow down this process and consequently reduce volatilisation," he says.

Within the review Sajjad has identified a ►



Under no-till and/or higher stubble environments, losses from urea could be higher, with increased ammonia production.

► range of substances that have a urease inhibitor effect and the majority of these are phosphoramidate compounds, such as NBPT (n-butyl-thiophosphoric triamide) and NPPT (N(n-propyl) thiophosphoric triamide).

In autumn 2019, a new urease inhibitor containing both NBPT and NPPT (known as 2-NPT) became available for the first time and in trials has been shown to reduce ammonia emissions by up to 98%, which

is in part due to its polymer formulation, claimed to be unique.

“The review focuses on NBPT as this is the most widely used in the UK and brings the performance of urea on a par with ammonium nitrate fertilisers, reducing ammonia losses on average to 7.8%,” he explains.

“How NBPT renders urease unable to function is debated within the scientific literature, so isn’t yet fully understood. But it’s clear that its efficacy can be affected by storage period, low soil moisture and the concentration applied to the urea granules (see table on p37).”

Even though the more wholesale use of urease inhibitors would have a positive effect on reducing ammonia emissions, Sajjad believes that within the literature there can also be found a cautionary note which may warrant further exploration.

“Urease is an enzyme that’s produced by up to 30% of the soil bacterial population. In bacteria it has an extracellular function, but

in other organisms there’s evidence that it has a role within the cell in ATP synthesis.

“The literature highlighted that NBPT-treated plants also had an over-accumulation of urea and a decrease in ammonium concentration, reinforcing the hypothesis that NBPT is involved in the inhibition of urea transportation and remobilisation in plants,” he explains.

“Because there’s evidence that the vast majority of microorganisms rely on urease for various cellular functions, it’s important to understand whether there are any long-term implications from the widespread use of urease inhibitors in the UK, applying them to the same field year after year,” he cautions.

Sajjad also notes that from the literature reviewed, there was no evidence to suggest the application of inhibitors has any negative effect on non-target bacterial populations.

The second type of inhibitors that can help reduce nitrogen losses to the environment are nitrification inhibitors. This is the process where ammonium ions are

Regulation could solve one problem and create another

January saw the new introduction of the revised Agriculture Bill, hailed by Environment Secretary Theresa Villiers as “the most important environmental reforms for many years, rewarding farmers for the work they do to safeguard our environment and helping us meet crucial goals on climate change and protecting nature and biodiversity.”

Within the Bill, there’s the power for government to ‘effectively regulate the fertiliser industry, including updating the definition of a fertiliser to take account of the latest technological advances.’ Behind closed doors, there’s certainly a lot of discussion going on with DEFRA, says Peter Scott, chair of the AIC fertiliser sector and technical director at Origin fertilisers.

One of the big questions is whether the UK will follow Germany’s lead and legislate for the use of inhibited urea products as part of its strategy to tackle NH₃ emissions. “AIC’s view is that, while urease inhibitors are one of the potential mitigators for NH₃, regulating to solve one problem can produce unintended consequences,” says Peter.

“We’d prefer to see inhibitors as one tool in a menu of options to reduce emissions available to growers. If government mandate the use of inhibited urea, then we are likely to see an increase in AN fertiliser with higher potential for nitrous oxide emissions — solving one problem and creating another.”

The situation in Germany illustrates just how complex it is to draft legislation that’s fit for purpose. “The Germans have mandated the use

of inhibited urea in 2020 but didn’t get the definitions nailed down properly in the legislation. This has allowed companies to formulate urea products with less than 46% N to get around the new rules,” explains Peter.

Peter acknowledges that a lot of questions are being raised about whether enough is known about the long-term effects of urease inhibitors on the soil and the environment. While the fertiliser industry isn’t complacent, he points out that the three EU urease inhibitors have all been registered under REACH, so have demonstrated compliance with the regulations.

“These require ecotox data to be submitted, which looks at effect of the substance on the ecology of soil and water. NBPT is not classified as environmentally hazardous and has been shown not to be a persistent bioaccumulative toxic substance,” he adds.

Peter also highlights that the amounts actually being applied are very small. “If a grower used a protected urea to supply the total N-requirement for a crop of winter wheat, over the season the amount of inhibitor active applied would amount to 0.02-0.03g/ha,” he explains.

On top of the work that’s been done on inhibitor products around the globe, studies are ongoing to provide reassurance that they pose no risk to the environment, water or food chain.

Under EU fertiliser regulations the concentration of urease inhibitors applied to urea has to reach a minimum value and it remains to be seen what will happen after Brexit. Under current GB regulations, there isn’t a specification



If protected urea becomes mandatory, a regulatory framework will be needed which supports the science behind the work on emissions factors, says Peter Scott.

for their concentration, he points out.

“If Defra decides to make protected urea mandatory, then it will need to take the time to draw up a regulatory framework which supports the science behind the work on emissions factors. For example, work by Teagasc shows that NBPT at 660ppm can reduce NH₃ emissions by 78%, but the current minimum concentration for NBPT is 414ppm (according to EU fertiliser regulations), which wouldn’t achieve the same level of reduction.

“So any regulation would need to be constructed to be certain the concentration of urease inhibitors in use can achieve the desired reduction in emissions, and that these levels can be effectively policed at the point of use.”

From Theory to Field

These articles are part of AHDB's delivery of knowledge exchange on grower-funded research projects. CPM would like to thank AHDB for its support and in providing privileged access to staff and others involved in helping put them together.

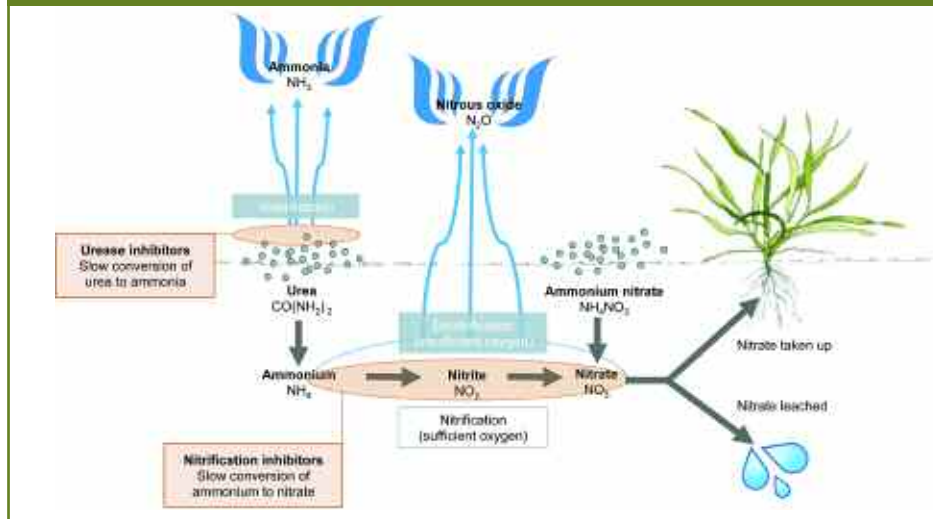
converted first to nitrite (NO_2) and then to nitrate (NO_3).

"Plants mostly take up nitrogen in nitrate form, but these can easily be lost to the environment through denitrification (losses of greenhouse gas — nitrous oxide) or leaching. The aim of a nitrification inhibitor is to keep nitrogen in the ammonium form for longer to prevent these losses from occurring," says Sajjad.

"Dicyandiamide (DCD) and nitrapyrin (2-chloro-6-(trichloromethyl) pyridine) are the most frequently used commercial nitrification inhibitors in agriculture. Each has pros and cons which should be considered when deciding which product to use (see table on p37).

Recent literature also suggests that using one type of nitrogen inhibitor may not be enough, adds Sajjad. "Using a urease inhibitor together with a nitrification inhibitor

How nitrogen inhibitors work



Source: AHDB, 2020.

may be a better way to reduce nitrogen losses by reducing volatilisation and retaining ammonium in the soil for longer, because both processes happen simultaneously."

Reducing nitrogen losses from fertilisers has the added benefit that more nitrogen is available to the crop, improving nitrogen use efficiency. In an economic analysis comparing the different forms of nitrogen,

the review found inhibited urea was a financially viable option for growers, providing an equivalent crop production cost (£/kg grain) as ammonium nitrate.

"Inhibitors can provide farmers with another tool to keep N in the root zone and improve its agronomic efficiency. The real benefit comes from a marked reduction in ammonia losses, especially under high-risk environments," he concludes. ■