


Infinite **nutrient stewardship**



# Nitrogen fertilization: Inhibitors





An inhibitor is a compound added to a nitrogen-based fertilizer to reduce losses when the fertilizer has been applied to the crop. By extending the time the active nitrogen component of the fertilizer remains in the soil as either urea-N or ammonium-N, an inhibitor can improve nitrogen use efficiency (NUE) and reduce environmental emissions.

There are two main types of inhibitor that are added to nitrogen fertilizers:

- Urease inhibitors (UI), which inhibit the hydrolytic action of the urease enzyme on urea.
- Nitrification inhibitors (NI), which inhibit the biological oxidation of ammonium to nitrate.

# Urease inhibitors

ON A GLOBAL SCALE, UREA IS THE MOST WIDELY PRODUCED AND USED NITROGEN FERTILIZER. IT IS COMPARATIVELY EASY TO MANUFACTURE AND HAS A HIGH NITROGEN CONTENT. AS A RESULT, PER UNIT OF NITROGEN ITS TRANSPORTATION AND STORAGE COSTS ARE LOW.

It is hard, however, for a urea fertilizer to be directly absorbed by crops. Before it can be used as a source of nitrogen, it must first be converted into ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ). Urease enzymes in the soil are responsible for the first step of the conversion process.

Urea is unstable in the presence of water, so the transformation process usually starts immediately. But the transformation into ammonium is not direct; urea is first converted into ammonia and carbamic acid, which itself then spontaneously decomposes into ammonia and carbon dioxide (Fig. 1).

The pH of the soil determines whether the water it contains transforms the resulting ammonia into ammonium. The urease reaction creates an alkaline zone around the urea granule which induces a pronounced localized pH peak (Fig. 2). This shifts the equilibrium of the reaction towards the formation of ammonia (Fig. 1: red arrow) and subsequent gaseous emissions.

The ammonium conversion rate and ammonia losses depend on a number of factors of which soil temperature and moisture are the most important. Other influences include the amount of crop residue on the soil surface, the soil's cation exchange capacity and soil pH. High ammonia losses, therefore, tend to occur in light soils and in no-till zones.

Although ammonia losses of up to 80% have been recorded in laboratory trials, an average ammonia loss by volatilization of 24% (20% ammonia-N) is assumed (EEA, 2013)<sup>1</sup>.

FIG. 1: CONVERSION OF UREA IN THE SOIL

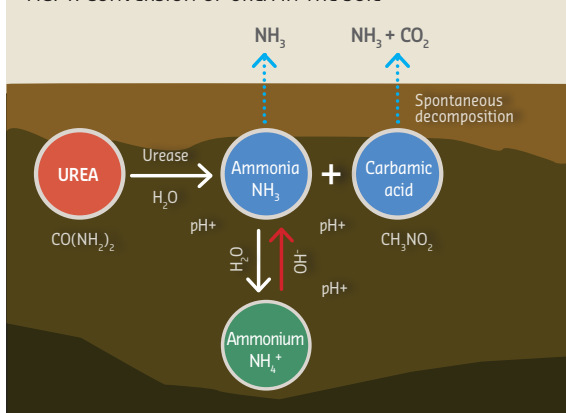
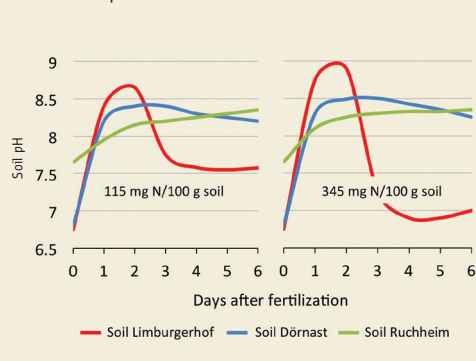


FIG. 2: SOIL pH DURING HYDROLYZATION OF UREA





## Reducing ammonia losses

Gaseous losses of ammonia can be significantly reduced if urea is washed into the soil by rain, irrigation water or if it is directly incorporated into the soil. However, under many circumstances this is not possible (e.g. with winter crops, grassland, lack of irrigation, drylands, no-till zones, etc.).

The first and most obvious option to reduce ammonia emissions is to use an ammonium-nitrate based fertilizer. This is also recommended by the UNECE Task Force on Reactive Nitrogen (United Nations Economic Commission for Europe 2015)<sup>2</sup>.

Another means of reducing ammonia loss is to treat urea-based fertilizers with urease inhibitors. This effectively delays their conversion into ammonia and carbamic acid for approximately two weeks by blocking the action of the urease enzyme (Fig. 3).

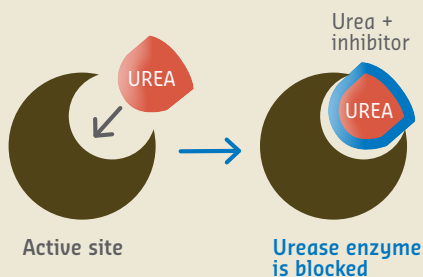


The pH peak around the urea particles is avoided and the formation of ammonia reduced.

The intensity of delaying urea hydrolysis depends on the amount of urease inhibitor applied. The maximum ammonia loss reduction is approximately 80% and UNECE estimates that the technology can reduce ammonia losses by an average of 70%. (S. Bittman et al. 2013)<sup>3</sup>.



FIG. 3: ACTION OF UREASE INHIBITORS



Urease inhibitors, however, can have limited stability, particularly when applied together with other plant nutrients, such as sulphur.

# Nitrification inhibitors

DEPENDING ON TEMPERATURE, THE AMMONIUM IN UREA AND AMMONIUM NITRATE FERTILIZERS IS RAPIDLY TRANSFORMED AFTER THEIR APPLICATION INTO NITRATE VIA NITRIFICATION. THE USE OF FERTILIZERS WITH NITRIFICATION INHIBITORS CONSIDERABLY REDUCES THE RISK OF NITRATE LEACHING.

A nitrification inhibitor delays the microbial conversion in the soil of ammonium nitrogen to nitrate by temporarily suppressing the action of the enzyme ammonium-mono-oxygenase in the soil bacteria *Nitrosomonas* ssp., which is responsible for the first step of the nitrification process (conversion of ammonium to nitrite).

The length of time nitrification can be inhibited primarily depends on the ambient temperature. At low soil temperatures, the period is quite long while it is comparatively short at higher temperatures, although still several weeks.

## Nitrate leaching

During the growing season, nitrate leaching can occur under particular conditions such as sandy soils, high water input and shallow rooting crops. Incomplete cation exchange during the formation of the soil colloids gives the soil a negative charge. A negatively charged ion such as nitrate, therefore, can easily move within the soil if too much rain or irrigation water leads to its dislocation.

As a positively charged ion, ammonium is far less mobile because it is bound to the cation exchangers in the soil colloids. Nitrification inhibitors therefore reduce the conversion rate of the less mobile ammonium into nitrate, reducing leaching potential (Fig. 5).

FIG. 4: SOIL NITRIFICATION AND ACTION OF NITRIFICATION INHIBITORS

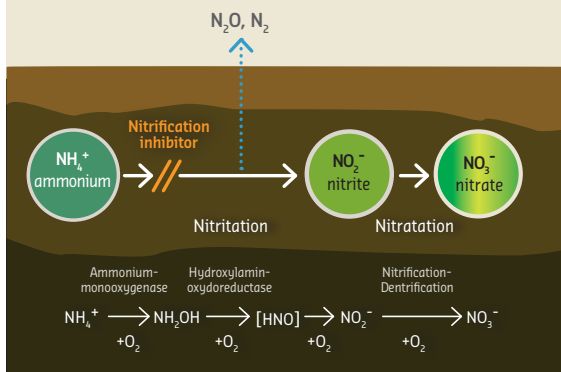
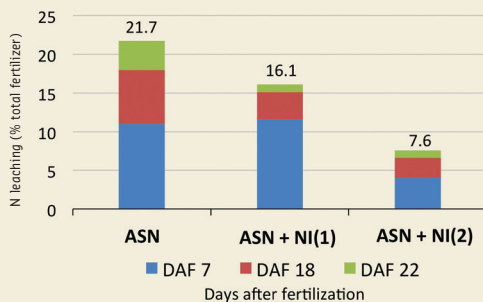


FIG. 5: LEACHING TRIAL WITH TWO NITRIFICATION INHIBITORS\*

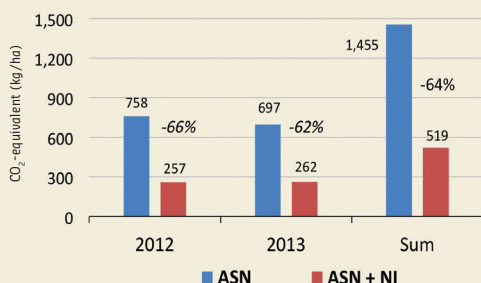


\*Trial with spinach in Mitscherlich pots; leaching forced by 3x20mm irrigation in excess of water retention capacity.

## Reduced greenhouse gas emissions

Nitrification of ammonium and denitrification of nitrate are sources of nitrous oxide ( $\text{N}_2\text{O}$ ), which is an important greenhouse gas and agriculture's main contribution to climate change.

FIG. 6:  $\text{N}_2\text{O}$  EMISSIONS AFTER APPLICATION OF A NITRIFICATION INHIBITOR TO ASN FERTILIZER\*



\*Net  $\text{N}_2\text{O}$  emissions after annual fertilization with 180 kg/ha N from ASN with and without nitrification Inhibitor (Guzman, 2013, whole year field measurements). Background emissions without N fertilization: 1.577 kg/ha  $\text{CO}_2$ -eq in two years.



$\text{N}_2\text{O}$  has a mean atmospheric lifetime of 114 years and it also impacts ozone depletion. The global warming potential of  $\text{N}_2\text{O}$  is 298 times higher than that of  $\text{CO}_2$ .

Because of delayed nitrification and the reduced amount of  $\text{NO}_3^-$  during the inhibition process, the emission of  $\text{N}_2\text{O}$  is substantially reduced if nitrification inhibitors are added to fertilizers (Fig. 6)

## Partial ammonium nutrition

In addition to nitrate, ammonium can also be a direct source of nitrogen for crops. However, unlike nitrate, it is only poorly translocated to the rhizosphere which prevents its rapid uptake by plant root-soil systems. Nitrification inhibitors favour partial ammonium nutrition of plants.

A side effect of crop ammonium nutrition is an improved uptake of phosphorus. When plant roots take up ammonium ions, protons ( $\text{H}^+$ ) are excreted to maintain charge equilibration in the roots.



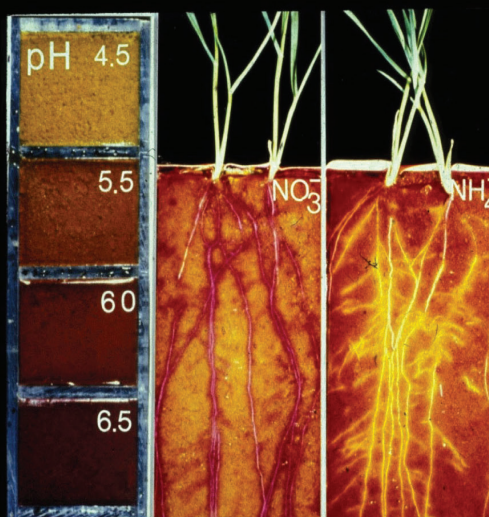


The pH of the rhizosphere is decreased (up to two units; Fig. 7), which supports the mobilization of phosphorus in the soil (Curl and Truelove, 1986). The same is also valid for the mobility and uptake of some micronutrients such as Mn (Marschner, 1986).

The effect on phosphate and micronutrient mobilization is intensified with the addition of a nitrification inhibitor, which extends the ammonium uptake phase. However, nutrients with a positive charge (e.g.  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{K}^{+}$ ) benefit from nitrate uptake because of their synergetic uptake with nitrate anions ( $\text{NO}_3^-$ ).

In contrast to urea, the application of nitrification inhibitors to ammonium and ammonium nitrate-based fertilizers does not usually lead to higher emissions of ammonia. Higher emissions have only been observed in particular cases (such as in high pH soils).

FIG. 7: PH IN THE RHIZOSPHERE OF CEREALS AFTER NUTRITION WITH  $\text{NO}_3^-$  VERSUS  $\text{NH}_4^+$ .



Prevailing  $\text{NO}_3^-$  absorption leads to alkalinization of the rhizosphere; prevailing  $\text{NH}_4^+$  absorption leads to acidification.

<sup>1</sup> EEA 2013 - EMEP/EEA Air Pollutant Emission Inventory Guidebook 2013, Technical report no 12/2013, Technical guidance to prepare national emission inventories, Chapter 3D: Crop production and agriculture. [www.eea.europa.eu/publications/emep-eea-guidebook-2013](http://www.eea.europa.eu/publications/emep-eea-guidebook-2013).

<sup>2</sup> United Nations Economic Commission for Europe, 2015: Framework Code for Good Agricultural Practice for Reducing Ammonia Emissions ([www.unece.org/environmental-policy/conventions/envlrapwelcome/publications.html](http://www.unece.org/environmental-policy/conventions/envlrapwelcome/publications.html)).

<sup>3</sup> S. Bittman, M. Dedina, C.M. Howard, O. Oenema and M.A. Sutton, 2014: Options for ammonia mitigation, Guidance from the UNECE Task Force on Reactive Nitrogen, Centre for Ecology and Hydrology, Edinburgh, UK. [www.clrtap-tfrn.org/content/options-ammonia-abatement-guidance-unece-task-force-reactive-nitrogen](http://www.clrtap-tfrn.org/content/options-ammonia-abatement-guidance-unece-task-force-reactive-nitrogen).






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