Investigating the fate and behaviour of nitrification inhibitors in soil systems

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Introduction

Increased use of synthetic nitrogen-based (N-based) fertilisers has become a common practice to achieve higher crop yields. However, a large proportion of the applied N is lost to the surroundings via ammonia volatilisation, nitrate leaching and denitrification.[1] Addition of nitrification inhibitors (NIs) has been recommended as a strategy to minimise N-losses and improve overall N-use efficiency. Current NIs have some limitations and their effectiveness varies greatly depending on environmental conditions and soil properties. However, there is a little understanding behind these inconsistent responses.

Objective

To investigate the efficiency, fate and behaviour of commercial and newly synthesised NIs in soil systems through degradation studies.

Experimental Methods

❖**Accelerated Weathering Studies:** NIs were subjected to various alternating cycles of UV light (in the range that stimulates natural sunlight) and moisture at controlled, elevated temperatures and then analysed for any structural changes by LC-MS (Liquid Chromatography – Mass Spectrometry) and HRMS (High Resolution Mass Spectrometry).

❖**Extraction and Quantification:** Optimised methods were developed for extraction of each NI from soil and quantification by HPLC (High Performance Liquid Chromatography).

❖**Soil Incubation Experiments:** Following method optimisation, soil incubation experiments were conducted to study degradation of NI and identify possible degradation products. Degradation products are identified through isolation and spectroscopic characterisation.

Results

Commercial NIs (Figure 1a)

➢**Accelerated Weathering**

DMP dimer formation was observed in LC-MS analysis for DMPG formulation. This was further confirmed by HRMS analysis where a species with *m/z* 191.1292 was observed (Figure 1b).

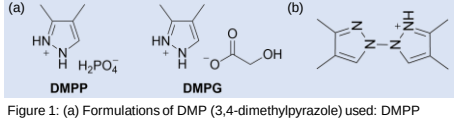

Figure 1: (a) Formulations of DMP (3,4-dimethylpyrazole) used: DMPP (3,4-dimethylpyrazole phosphate) and DMPG (3,4-dimethylpyrazole glycolate); (b) Proposed structure of the dimer (*m/z* = 191.1292)

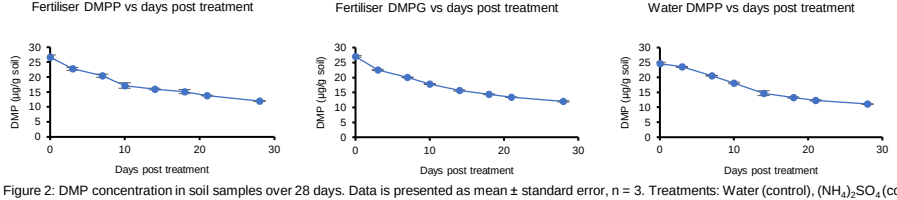

Figure 2: DMP concentration in soil samples over 28 days. Data is presented as mean ± standard error, n = 3. Treatments: Water (control), $(NH_4)_2SO_4$ (control), $(NH_4)_2SO_4$ + DMPP, $(NH_4)_2SO_4$ + DMPG, water + DMPP, water + DMPG. $(NH_4)_2SO_4$ was applied at 100 mg N/kg soil and NI was applied at 5 mol% of fertiliser-N. The experiment was conducted at 25 °C, 60% water-filled pore space. (Water DMPG graph not shown here).

➢**Soil Incubation Experiment**

Extraction procedure from literature was modified to allow consistent recovery of DMP from soil.[2] Optimised procedure allows ~ 80% to 90 recovery of DMP over a range of concentrations tested. Rate of degradation was similar irrespective of the formulation of DMP with or without fertiliser indicating that the degradation occurs on a similar rate for the active component DMP in all treatments (Figure 2).

New NIs

Synthesised NIs are 1,2,3-triazoles derivatives with various substitution patterns and satisfy the observation that adjacent ring N increase nitrification activity.[3]

➢**Accelerated Weathering**

Initial studies have shown the possibility of oxidation and loss of small molecules from R^1 and R^2, when exposed to UV light and moisture at controlled, elevated temperature in the weathering machine.

➢**Extraction and Quantification**

An optimised procedure for extraction of 1,2,3-triazole derivatives (Figure 3) and HPLC analysis has been developed.

➢**Soil Incubation Experiment**

A 14-day incubation experiment using one of the synthesised NIs (Figure 4) to test effectiveness of the optimised method was conducted (25 °C, 60% water-filled pore space). Treatments: $(NH_4)_2SO_4$ (control), $(NH_4)_2SO_4$ + NI-001 (1 mol%), $(NH_4)_2SO_4$ + NI-001 (5 mol%).

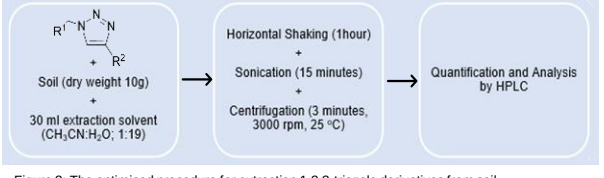

Figure 3: The optimised procedure for extraction 1,2,3-triazole derivatives from soil.

Future works

❖Longer incubation experiments at higher NI application rate will be performed to allow sufficient formation of degradation products to enable spectroscopic characterization.

❖Soil incubation studies for a range of soils to ascertain the influence of soil type, pH, temperature and water content on inhibition activity and degradation behaviour of new NIs.

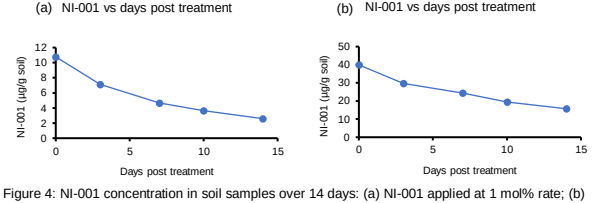

Figure 4: NI-001 concentration in soil samples over 14 days: (a) NI-001 applied at 1 mol% rate; (b) NI-001 applied at 5 mol% rate. Data is presented as mean ± standard error, n = 3.

Acknowledgements

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References

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