1,2,3-Triazoles as Nitrification Inhibitors for Australian Soils

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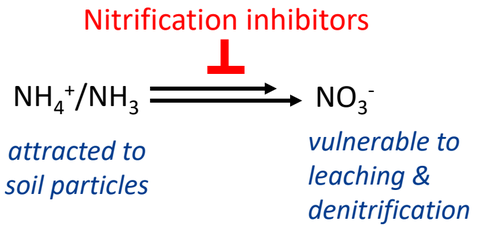
Key Finding

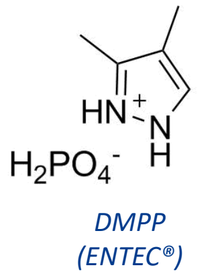
A number of readily-accessible substituted **1,2,3-triazoles** were found to **stabilise soil nitrogen** in the ammonium form to **an equal or greater extent** than the commercial nitrification inhibitor **DMPP**.

Introduction

Nitrification is the multi-step oxidation of ammonium (NH_4^+) to nitrate (NO_3^-). Nitrification inhibitors (NIs) can be used to reduce nitrogen losses from synthetic fertiliser application, by slowing the microbial conversion of nitrogen from the more stable NH_4^+ form.

Commercial NIs including 3,4-dimethyl pyrazole phosphate (DMPP) provide variable results under Australian field conditions.[1] 1,2,3-Triazoles were investigated as a new class of NIs that are synthetically accessible in few steps, and may provide more consistent efficacy in Australian soils, under varied climatic and edaphic conditions.

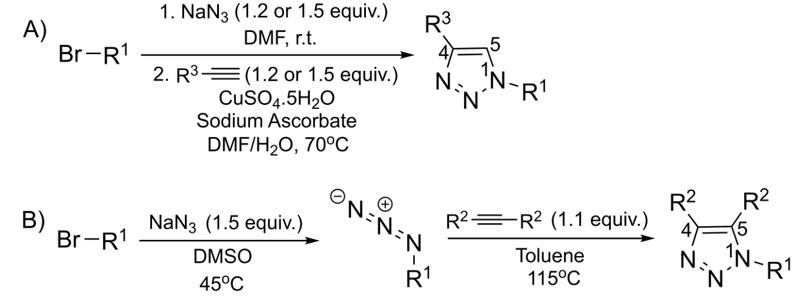




Methods

A library of 23 di- and tri-substituted 1,2,3-triazoles (**N001** – **N023**)‡ were synthesised via thermal or Cu(I)-catalysed click reactions (see Scheme 1).[2]

Soils sourced from five different locations in eastern Australia, with pH_{water} ranging from 5.0 to 8.8, were used in microcosm incubations conducted at either 25°C or 35°C in the dark, over 28 days. Soils were treated with $(NH_4)_2SO_4$ alone or combined with an inhibitor (*n = 3*). Following 2M KCl extraction at 6 time points, NH_4^+-N and (NO_2^- + NO_3^-)-N concentrations were analysed by segmented flow analysis (Skalar SAN++).



Scheme 1: *Examples of A) the Cu(I)-catalysed synthetic pathway to give 1,4-disubstituted 1,2,3-triazoles, and B) the thermal Huisgen synthetic route to 1,4,5-trisubstituted 1,2,3 triazoles.*‡,[2]

Results

- 23 substituted 1,2,3-triazoles assessed as NIs in laboratory incubations
- Triazoles containing smaller, more lipophilic substituents exhibited promising NI activity: slowed NH_4^+-N losses when compared to treatment with $(NH_4)_2SO_4$ alone (Fig. 2A and B).
- Triazole NH_4^+-N stabilising ability appears to be less affected than DMPP when temperature is increased (25°C vs 35°C).

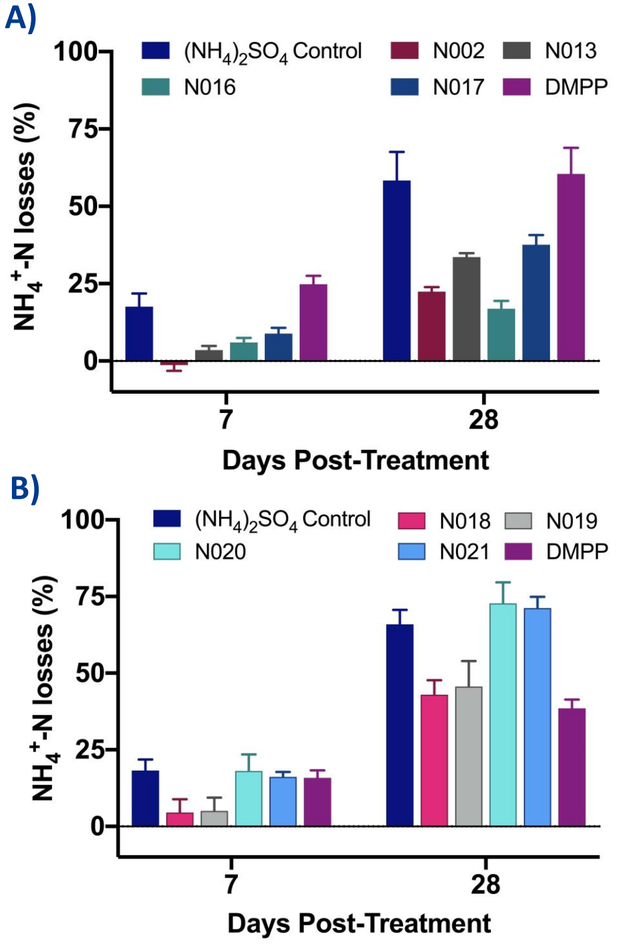


Fig. 2: Ammonium loss percentages calculated 7 and 28 days after treatment with $(NH_4)_2SO_4$ or $(NH_4)_2SO_4$ + inhibitor (either DMPP or 1 of synthesised 1,2,3-triazoles N001 to N023). *Clay soil collected from Dahlen, Victoria Australia (pH 7.3), tests conducted at 35°C, errors presented are standard errors of the mean (n = 3). $(NH_4)_2SO_4$ was applied at 100 mg N kg^{-1} soil with inhibitors applied at 10 mol % of $(NH_4)_2SO_4$-N.*

‡ Complete triazole structures have been withheld for confidentiality reasons.

References

1. a) Nauer *et al.*, *Agric. Ecosyst., Environ.*, 2018, 253, 82-89; b) Dougherty *et al.*, *Soil Res.*, 2016, 54, 675-683. **2.** a) Huisgen, R., *Angnew. Chem. Int. Ed., 1963, 2, 565-598;* b) Sharpless *et al.*, *Angew. Chem. Int. Ed.*, **2002**, *41*, 2596 - 2599; c) Meldal *et al.*, *J. Org. Chem.*, **2002**, *67*, 3057 - 3064