Environmental Research Letters

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To cite this article: T H Misselbrook *et al* 2014 *Environ. Res. Lett.* **9** 115006

OPEN ACCESS
IOP Publishing
Environmental Research Letters
Environ. Res. Lett. **9** (2014) 115006 (11pp)
doi:10.1088/1748-9326/9/11/115006

# An assessment of nitrification inhibitors to reduce nitrous oxide emissions from UK agriculture

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Received 31 July 2014, revised 14 October 2014
Accepted for publication 14 October 2014
Published 11 November 2014

**Abstract**

A trial was conducted consisting of 14 experiments across sites in England of contrasting soil type and annual rainfall to assess the effectiveness of nitrification inhibitors (predominantly dicyandiamide (DCD) but limited assessment also of 3, 4-dimethylpyrazole phosphate (DMPP) and a commercial product containing two pyrazole derivatives) in reducing direct nitrous oxide ($N_2O$) emissions from fertilizer nitrogen (N), cattle urine and cattle slurry applications to land. Measurements were also made of the impact on ammonia ($NH_3$) volatilization, nitrate ($NO_3^-$) leaching, crop yield and crop N offtake. DCD proved to be very effective in reducing direct $N_2O$ emissions following fertilizer and cattle urine applications, with mean reduction efficiencies of 39, 69 and 70% for ammonium nitrate, urea and cattle urine, respectively. When included with cattle slurry a mean, non-significant reduction of 56% was observed. There were no $N_2O$ emission reductions observed from the limited assessments of the other nitrification inhibitors. Generally, there were no impacts of the nitrification inhibitors on $NH_3$ volatilization, $NO_3^-$ leaching, crop yield or crop N offtake. Use of DCD could give up to 20% reduction in $N_2O$ emissions from UK agriculture, but cost-effective delivery mechanisms are required to encourage adoption by the sector. Direct $N_2O$ emissions from the studied sources were substantially lower than IPCC default values and development of UK country-specific emission factors for use in inventory compilation is warranted.

Keywords: nitrous oxide, nitrification inhibitor, fertilizer, cattle urine, cattle slurry

## 1. Introduction

Nitrous oxide ($N_2O$) is a powerful greenhouse gas, with a global warming potential of approximately 300 times that of carbon dioxide (IPCC 2007). Agricultural soils are the major source of $N_2O$ emissions to the atmosphere, arising primarily as a result of the soil microbial processes of nitrification and denitrification (Firestone and Davidson 1989). In common with many countries, the UK has committed to challenging greenhouse gas emission reduction targets and that will require the implementation of mitigation strategies to all sectors of the economy, including agriculture. With increasing global demand for food and other food security issues, it is important that mitigation strategies are not at the expense of productivity but are aimed at reducing the greenhouse gas intensity of products.

Nitrification inhibitors offer potential to reduce $N_2O$ emissions from agricultural soils (de Klein and Eckard 2008). Nitrification inhibitors slow down the rate of the first step of the nitrification process, the conversion of ammonium ($NH_4^+$) to nitrite, and thus to nitrate ($NO_3^-$), by deactivating the

**Table 1.** Experimental sites.

| Site name | Location | 30-year mean annual rainfall (mm) | Soil texture | Year[a] | Crop | Soil organic carbon (%) | N applied (kg ha$^{-1}$) |
|---|---|---|---|---|---|---|---|
| Fertilizer experiments | — | — | — | — | — | — | — |
| Gleadthorpe | Central England | 760 | Sandy loam | 2010 | Winter wheat | 2.3 | 160 |
| North Wyke | SW England | 1040 | Clay loam | 2010 | Grass–1st cut silage | 4.6 | 120 |
| Newark | N England | 820 | Clay loam | 2011 | Grass–1st cut silage | 2.6 | 120 |
| Sampford Chapple | SW England | 1040 | Sandy clay loam | 2011 | Grass–1st cut silage | 2.3 | 120 |
| Boxworth | E England | 550 | Clay | 2012 | Winter wheat | 2.1 | 200 |
| Cockle Park | NE England | 640 | Clay loam | 2012 | Winter barley | 2.6 | 160 |
| Cattle urine experiments | — | — | — | — | — | — | — |
| Gleadthorpe | Central England | 760 | Sandy loam | 2011 | Grass | 2.9 | 625 |
|  | — | — | — | 2011 | Grass | 2.5 | 488 |
| Sampford Chapple | SW England | 1040 | Sandy clay loam | 2012 | Grass | 3.0 | 470 |
|  | — | — | — | 2012 | Grass | 3.0 | 365 |
| Cattle slurry experiments | — | — | — | — | — | — | — |
| Sampford Chapple | SW England | 1040 | Sandy clay loam | 2010 | Grass | 3.2 | 181 |
|  | — | — | — | 2011 | Grass | 3.2 | 167 |
| Gleadthorpe | Central England | 760 | Sandy loam | 2011 | Grass | 2.4 | 106 |
|  | — | — | — | 2012 | Grass | 2.6 | 146 |

[a] Month given is month of treatment application (for fertilizer experiment, the month of the first application).

**Table 2.** Mean air temperature and cumulative rainfall over the duration of each experiment (12 months) and drainage data for those experiments where nitrate leaching was measured.

| Experiment | Treatment application date[a] | Mean air temperature (°C) | Cumulative rainfall (mm) | Start of drainage | End of drainage | Cumulative drainage (mm) |
|---|---|---|---|---|---|---|
| Fertilizer experiments | — | — | — | — | — | — |
| Gleadthorpe | 16 March 2010 | 9.0 | 541 | 02 October 2010 | 01 March 2011 | 149 |
| North Wyke | 13 April 2010 | 9.7 | 673 | ND | ND | ND |
| Newark | 22 February 2011 | 11.1 | 332 | ND | ND | ND |
| Sampford Chapple | 14 April 2011 | 10.8 | 931 | ND | ND | ND |
| Boxworth | 13 March 2012 | 9.1 | 756 | ND | ND | ND |
| Cockle Park | 13 March 2012 | 8.3 | 1247 | ND | ND | ND |
| Urine experiments | — | — | — | — | — | — |
| Gleadthorpe summer | 09 June 2011 | 9.9 | 592 | 04 April 2012[b] | 10 May 2012 | 107 |
| Gleadthorpe autumn | 15 September 2011 | 9.9 | 714 | 04 April 2012[b] | 10 May 2012 | 107 |
| Sampford Chapple spring | 16 March 2012 | 10.3 | 1488 | ND | ND | ND |
| Sampford Chapple autumn | 04 September 2012 | 9.5 | 1158 | 24 September 2012 | 26 March 2013 | 566 |
| Slurry experiments | — | — | — | — | — | — |
| Sampford Chapple autumn | 22 September 2010 | 9.6 | 781 | 08 December 2010 | 07 March 2011 | 155 |
| Sampford Chapple spring | 09 March 2011 | 10.7 | 911 | ND | ND | ND |
| Gleadthorpe autumn | 17 August 2011 | 9.8 | 707 | 04 April 2012[b] | 10 May 2012 | 107 |
| Gleadthorpe spring | 22 February 2012 | 9.1 | 917 | ND | ND | ND |

[a] For fertilizer experiments date refers to first application, dates of subsequent applications are given in the text.

[b] A very dry autumn and winter 2011/12 at Gleadthorpe followed by a very wet spring 2012; ND, not determined as no leaching measurements were undertaken at these sites.

responsible enzyme (Amberger 1989). Many chemicals have been tested as nitrification inhibitors, but only a few are commercially available, of which dicyandiamide (DCD) and 3, 4-dimethylpyrazole phosphate (DMPP) are the most common. Initial interest in nitrification inhibitors was mainly concerned with minimizing $NO_3^-$ leaching losses following applications of fertilizer N, livestock slurry or urine returns from grazing livestock, as N is retained on soil exchange surfaces in the $NH_4^+$ form rather than leached as $NO_3^-$. However, $N_2O$ emissions from both nitrification and denitrification will also be reduced by inhibiting nitrification, offering a potential mitigation strategy for greenhouse gas emissions from agriculture. A growing body of research has demonstrated that significant reductions in emissions can be achieved through their use, particularly from New Zealand where, based on the work of Clough *et al* (2007) an emission reduction factor has been included in the national greenhouse gas inventory for emissions from cattle grazing urine returns where DCD is applied. However, the efficacy of nitrification inhibitors at reducing emissions may be influenced by factors including soil temperature (e.g. Kelliher *et al* 2008), soil texture (Barth *et al* 2001, Bronson *et al* 1989) and rainfall (Shepherd *et al* 2014), and proof of effectiveness for one soil type and climatic region cannot necessarily be extrapolated to others.

The objective of this study therefore was to assess the effectiveness of nitrification inhibitors in reducing direct $N_2O$ emissions from applied nitrogen fertilizers, livestock slurries and cattle grazing urine returns across sites of contrasting soil type and annual rainfall in England. By retaining the N in the $NH_4^+$ form, reductions in $N_2O$ emission and $NO_3^-$ leaching might be expected as noted above, but other N pathways might also be influenced including a potential increase in ammonia ($NH_3$) volatilization (e.g. Zaman *et al* 2009) and impacts on plant N uptake. Very few studies to date have assessed potential impacts on all of these pathways within the same study. A secondary objective of this study was therefore to assess the impact of the use of nitrification inhibitors on other nitrogen pathways, including $NH_3$ volatilization, $NO_3^-$ leaching and crop yield and N offtake.

## 2. Methods

### 2.1. Experimental sites and treatments

Ten experiments were conducted at six sites across England using small field plots and a randomized block experimental design (three replicates of each treatment), covering a range of soil types and annual rainfall (table 1). For the fertilizer application experiments, treatments included an untreated control (C), ammonium nitrate fertilizer at recommended rates and timings for the crop (AN), ammonium nitrate plus DCD (AN + DCD), urea fertilizer at recommended rates and timings for the crop (U) and urea plus DCD (U + DCD). At two of the sites (Sampford Chapple and Boxworth) two additional treatments were included: ammonium sulphate nitrate fertilizer at recommended rates and timings for the crop (ASN) and ammonium sulphate nitrate plus DMPP (ASN + DMPP). The DCD was applied as a 2% solution and sprayed onto the plots immediately after each fertilizer application at a rate of 15 kg DCD $ha^{-1}$. Post-application spraying is unlikely to be an economic delivery method, but at the time of the study there were no combined AN + DCD or U + DCD fertilizer products available, so the compromise solution of post-application spraying was used. The DMPP was included with the ASN fertilizer (26% N) for the ASN + DMPP treatment at each application, with a DMPP content of 0.15%. Fertilizer was applied to the whole plot area.

Application dates of the first fertilizer split are given in table 2. For the cereal sites, fertilizer was applied in three splits: at Gleadthorpe, 40, 60 and 60 kg N $ha^{-1}$ applied on 16th March, 29th March and 26th April; at Boxworth, 40, 80 and 80 kg N $ha^{-1}$ applied on 13th March, 11th April and 9th May; at Cockle Park, 40, 60 and 60 kg N $ha^{-1}$ applied on 13th March, 26th March and 7th May. For the grassland sites (North Wyke and Newark), fertilizer was applied in two splits each of 60 kg N $ha^{-1}$, with the second split being applied approximately one month after the first.

For the cattle urine experiments, treatments included an untreated control (C), cattle urine applied at 5 L $m^{-2}$, cattle urine plus DCD (Urine + DCD) and cattle urine plus an additive containing two pyrazole derivatives (Urine + PD): 1H-1,2,4-triazole and 3-methylpyrazole at inclusion rates of approximately 3.1 and 1.6%, respectively. At each of the two sites, a spring or summer and autumn applications of each treatment were made. Urine was collected from lactating dairy cows at Reading University, kept refrigerated at <4 °C and applied within two days of collection. Nitrogen content of the urine varied between experiments, with respective values of 12.5, 9.8, 9.4 and 7.3 g $L^{-1}$ for Sampford Chapple spring and autumn and Gleadthorpe summer and autumn applications. The nitrification inhibitors were pre-mixed with the urine prior to application to give application rates of 15 kg N $ha^{-1}$ and 5 L $ha^{-1}$ for the DCD and the pyrazole derivatives, respectively. Pre-mixing was used as spraying the nitrification inhibitor as an additional operation was thought to be unlikely to be a cost-effective practice, and introduction of the nitrification inhibitor through the animal and directly into the urine is being studied as a possible delivery mechanism (Welten *et al* 2013). Cattle urine was applied to five 1 $m^2$ areas of the plot for $N_2O$ emission measurements and to a separate 4 $m^2$ area (2 × 2 m) for ammonia emission, $NO_3^-$ leaching and crop yield determination.

For the cattle slurry experiments, treatments included an untreated control (C), cattle slurry (CS) surface broadcast applied at 50 and 40 $m^3$ $ha^{-1}$ at Sampford Chapple and Gleadthorpe, respectively, and cattle slurry plus DCD (CS + DCD). The DCD was premixed with the cattle slurry immediately prior to application to give a rate of 15 kg $ha^{-1}$. At each site, autumn and spring applications of each treatment were made. Characteristics of the cattle slurries applied are given in table 3. Cattle slurry was applied to the whole plot area.

The mean ambient air temperature and cumulative rainfall were recorded at each of the experimental sites over the

**Table 3.** Characteristics of the applied cattle slurries.

| Site | Year | Dry matter content (%) | pH | Total N content (g kg$^{-1}$) | Total ammoniacal N content (g kg$^{-1}$) |
|---|---|---|---|---|---|
| Sampford Chapple | 2010 | 7.1 | 7.4 | 3.6 | 1.5 |
| Sampford Chapple | 2011 | 6.7 | 7.0 | 3.3 | 1.8 |
| Gleadthorpe | 2011 | 6.7 | 6.6 | 2.7 | 1.3 |
| Gleadthorpe | 2012 | 7.8 | ND[a] | 3.6 | 1.9 |

[a] ND, not determined.

12 month monitoring period from the treatment application date (table 2). There was little contrast in mean air temperature, ranging from 8.3 to 11.1 °C, but cumulative annual rainfall varied greatly, from 332 to 1488 mm.

### 2.2. Nitrous oxide emissions

Nitrous oxide emissions were measured using the static chamber technique (Mosier 1989), with five chambers (each covering 0.16 m$^2$) per plot to account for spatial variability. Sampling was conducted according to Chadwick *et al* (2014) whereby the chambers were closed to allow headspace accumulation of $N_2O$. After 40 min, gas samples were taken from each chamber and stored in pre-evacuated vials. Initial chamber concentration was assumed to be the same as for ambient air, for which ten samples were taken on each sampling occasion at chamber height. Linearity of headspace accumulation of $N_2O$ was confirmed by taking additional samples from selected chambers at four or five intervals over a 60 min closure time. Sampling was conducted over a period of 12 months from treatment application (from the first application for fertilizer experiments), with a total of 35–50 sampling occasions (depending on experiment) and samples being taken more frequently in the weeks directly after treatment application when greatest fluxes were expected. Samples were always taken between 10 am and 2 pm. Gas samples were analysed as soon as possible after collection using gas chromatographs fitted with an electron-capture detector and an automated sample injection system. The $N_2O$ flux for each chamber at each sampling occasion was determined from the increase in headspace concentration. Cumulative emissions between two sampling occasions were calculated as the product of the mean plot flux for the two occasions and the time interval between.

### 2.3. Ammonia emissions

Ammonia emissions were measured using a system of small wind tunnels (Lockyer 1984), with one tunnel placed at the upwind edge of each of the treated plots. The tunnels employ a fan to draw the air through a transparent canopy (2 × 0.5 m) covering 1 m$^2$ of the treated plot area at a constant speed of 1 m s$^{-1}$. Absorption flasks containing 0.02 M othrophosphoric acid were used to measure the concentration of $NH_3$-N in the air at the inlet and outlet of the canopy. Flux was determined as the product of the net air concentration (outlet minus inlet) and the volume of air drawn through the tunnel divided by the sampling time. Emission measurements were made for seven days following application of cattle slurry or urine, with absorption flasks replaced at 1, 3, 6 and 24 h after application and then every subsequent 24 h. Measurements were made for 21 days following application of fertilizer, with absorption flasks changed every 24 h.

### 2.4. Nitrate leaching

Measurements of $NO_3^-$ leaching losses were conducted in the experiments on sandy loam or sandy clay loam soils (with the exception of the Sampford Chapple fertilizer to grassland experiment). Porous ceramic cups were installed (six per plot) to a depth of 90 cm and samples of soil water were collected every two weeks or after every 50 mm of drainage, whichever occurred first. Drainage for each site was estimated using IRRIGUIDE (Bailey and Spackman 1996). The start and end dates of drainage and cumulative drainage amount are given in table 2. Samples were analysed for $NO_3^-$-N and $NH_4^+$-N, using automated colorimetry.

### 2.5. Crop yield and nitrogen offtake

Grain and grass yields together with crop N offtakes were measured from a representative proportion of each plot area (avoiding edges and areas used for $N_2O$ emission measurements, using a plot combine harvester for the cereal experiments and a small plot grass harvester (Haldrup) for the fertilizer and slurry to grassland experiments. Fresh weight was recorded in the field and a subsample taken from each plot for dry matter and total N analysis (Dumas). For the urine to grassland experiments, the central 1 m$^2$ of the 4 m$^2$ yield area was harvested manually and fresh weight recorded. This was sub-sampled for dry weight and N analysis as for the other experiments.

### 2.6. Statistical analyses

One-way analysis of variance was used (Genstat v16, VSN International) to compare treatment means for cumulative $N_2O$ and $NH_3$ emissions, cumulative $NO_3^-$ leaching and crop yields and N offtakes within each experiment.

## 3. Results

### 3.1. Fertilizer experiments

Cumulative annual $N_2O$ emissions from fertilizer applications were significantly greater than from the control treatment in

**Table 4.** Cumulative nitrous oxide emissions (kg $N_2O$-N ha$^{-1}$) from the fertilizer experiments over a 12 month period following first application; control (C), ammonium nitrate (AN), urea (U), ammonium nitrate with the nitrification inhibitor DCD (AN + DCD) and urea with the nitrification inhibitor DCD (U + DCD).

| Site | C | AN | U | AN + DCD | U + DCD | s.e.d. | *P* value | Mean soil temperature (°C)† |
|---|---|---|---|---|---|---|---|---|
| Gleadthorpe | $0.26^{a}$ | $0.46^{b}$ | $0.52^{b}$ | $0.39^{a,b}$ | $0.27^{a}$ | 0.07 | 0.014 | 8.0, 8.9, 10.8 |
| North Wyke | 0.45 | 1.81 | 1.28 | 1.21 | 0.88 | 0.37 | 0.054 | 10.6, 11.1 |
| Newark | $0.16^{a}$ | $1.47^{c}$ | $0.71^{b}$ | $0.82^{b}$ | $0.22^{a}$ | 0.11 | <0.001 | 5.7, 10.0 |
| Sampford Chapple | −0.10 | −0.31 | −0.28 | −0.19 | 0.03 | 0.18 | 0.402 | 10.8, 13.3 |
| Boxworth | $0.76^{a}$ | $3.72^{c}$ | $2.38^{b}$ | $3.22^{c}$ | $0.88^{a}$ | 0.22 | <0.001 | 8.4, 8.6, 12.7 |
| Cockle Park | $0.61^{a}$ | $2.85^{c}$ | $2.12^{b,c}$ | $1.68^{b}$ | $1.32^{a}$ | 0.33 | 0.001 | 8.3, 7.7, 9.8 |

*Notes*: s.e.d, Standard error of difference of the means; †mean soil temperature for the three weeks following each application; within rows, values with different superscripts differ significantly ($P < 0.05$).

**Table 5.** Cumulative nitrous oxide emissions (kg ha$^{-1}$) from the cattle urine experiments over a 12 month period following first application; control (C), urine and urine with the nitrification inhibitors DCD (urine + DCD) or pyrazzole derivatives (urine + PD).

| Site | Season | C | Urine | Urine + DCD | Urine + PD | s.e.d. | *P* value | Mean soil temperature (°C)† |
|---|---|---|---|---|---|---|---|---|
| Gleadthorpe | Summer | $0.41^{a}$ | $2.41^{c}$ | $1.38^{b}$ | $2.23^{c}$ | 0.26 | <0.001 | 16.0 |
| | Autumn | $0.38^{a}$ | $1.94^{b}$ | $1.85^{b}$ | $2.30^{b}$ | 0.51 | 0.037 | 14.2 |
| Sampford Chapple | Spring | $-0.04^{a}$ | $1.57^{b}$ | $0.21^{a}$ | $1.19^{b}$ | 0.27 | 0.003 | 8.7 |
| | Autumn | $0.40^{a}$ | $2.79^{b}$ | $0.32^{a}$ | $2.08^{a,b}$ | 0.77 | 0.042 | 14.5 |

*Notes*: s.e.d, Standard error of difference of the means; †mean soil temperature for the three weeks following application; within rows, values with different superscripts differ significantly ($P < 0.05$).

four of the six experiments (table 4), being not quite significant for the North Wyke experiment where variability in measurements was very high, and there being effectively no emissions from any treatment in the Sampford Chapple experiment which was subject to very dry soil conditions following fertilizer application. Cumulative emissions were numerically lower from U than AN in four of the experiments, although only significantly so in two experiments (Newark and Boxworth). The use of DCD with AN gave numerical reductions in cumulative emissions compared with AN alone in all experiments except for Sampford Chapple, but only statistically significant for two experiments. The use of DCD with U compared with U alone also gave numerical reductions in cumulative emissions in all experiments except for Sampford Chapple, being statistically significant in four of the experiments. Emissions from U + DCD were not significantly greater than from the control in any experiment.

The mean $N_2O$ emission factors (EF), derived as the net $N_2O$-N emission (treatment value minus control value) expressed as a percentage of the fertilizer N applied, across the six experiments were 0.80, 0.47, 0.49 and 0.17% for AN, U, AN + DCD and U + DCD, respectively. Thus the mean reduction in emission achieved with DCD was 38 and 64% when applied with AN and U, respectively. Excluding the Sampford Chapple experiment where no emissions were observed, mean reduction efficiencies were 39 and 69% for AN and U, respectively. There are insufficient data to draw firm conclusions regarding the influence of soil texture or soil temperature, but there did not appear to be a consistent effect of either on the reduction efficiency of the DCD (tables 1 and 4).

The DMPP had no significant effect at the Sampford Chapple site, where no significant emissions were measured from ASN or ASN + DMPP, or from the Boxworth site, where mean EF were 1.12 and 1.05% of applied N for ASN and ASN + DMPP, respectively.

There was no significant effect ($P > 0.05$) of DCD on $NH_3$ emissions from U or AN fertilizers (data not shown), with the exception of the Gleadthorpe site where emission from U + DCD was significantly greater (5.4% of applied N compared with 1.3% of applied N from U). Ammonia emissions from urea at this site were very much lower than at the other five sites, most likely because of rainfall events following each application. Mean $NH_3$ emissions across the six experiments, expressed as a percentage of the fertilizer N applied, were 1.9 and 2.0% for AN and AN + DCD and 24.7 and 26.2% for U and U + DCD, respectively. DMPP had no significant effect ($P > 0.05$) on $NH_3$ emissions from ASN fertilizer, with mean emissions over the two experiments where DMPP was used of 0.8 and 0.4% of the applied fertilizer N for ASN and ASN + DMPP, respectively.

Nitrate leaching at the Gleadthorpe site was not significantly influenced ($P > 0.05$) by the addition of DCD to U or AN fertilizers (data not shown), with an amount equivalent to 18.4 and 14.0% of the applied N leached from the U and AN treatments (with and without DCD), respectively.

There was no significant effect of DCD or DMPP on crop yield or N offtake across all six sites (data not shown), with the exception of at Sampford Chapple where the U + DCD treatment had a 20% lower dry matter grass yield than the U ($P < 0.050$).

### *3.2. Cattle urine experiments*

Application of cattle urine to the soil resulted in significant emissions of $N_2O$ in all four experiments (table 5), with EF

**Table 6.** Cumulative nitrous oxide emissions (kg ha$^{-1}$) from the cattle slurry experiments over a 12 month period following first application; control (C), cattle slurry (S) and cattle slurry with the nitrification inhibitor DCD (S + DCD).

| Site | Season | C | S | S + DCD | s.e.d. | *P* value | Mean soil temperature (°C)$^{\dagger}$ |
|---|---|---|---|---|---|---|---|
| Sampford Chapple | Autumn | 0.65 | 2.73 | 1.82 | 1.26 | 0.348 | 14.0 |
| | Spring | 0.39 | 0.77 | 0.42 | 0.21 | 0.252 | 8.3 |
| Gleadthorpe | Autumn | 0.54 | 0.75 | 0.66 | 0.18 | 0.541 | 16.3 |
| | Spring | 0.77 | 0.83 | 0.65 | 0.21 | 0.711 | 6.8 |

*Notes*: s.e.d, Standard error of difference of the means; $^{\dagger}$mean soil temperature for the three weeks following application; within rows, values with different superscripts differ significantly ($P < 0.05$).

ranging from 0.32 to 0.66% and a mean of 0.41% of urine-N applied. Inclusion of DCD with the urine gave significant reduction in cumulative $N_2O$ emission compared with urine alone in three of the experiments (not for the Gleadthorpe autumn application), while inclusion of the pyrazole derivatives (PD) had no significant effect. Mean EF for the Urine + DCD and Urine + PD treatments were 0.12 and 0.35% of the applied urine N, respectively, a 70% reduction for Urine + DCD compared with Urine.

There was no significant effect ($P > 0.05$) of DCD or the pyrazole derivatives (PD) on $NH_3$ emissions from the urine applications to grassland (data not shown). Mean emission across the four experiments and all treatments was 25.5% of the applied urine N (25.2, 25.0 and 26.2 for Urine, Urine + DCD and Urine + PD, respectively).

Similarly, $NO_3^-$ leaching (data not shown) was not significantly affected at the Gleadthorpe site, accounting for an amount equivalent to 20.7 and 15.1% of the applied urine N for the summer and autumn applications, respectively. Leaching losses were very low from the autumn application at the Sampford Chapple site, but were significantly reduced by DCD, with an amount equivalent to 1.5, 0.1 and 1.1% of the applied N being leached from the Urine, Urine + DCD and Urine + PD treatments, respectively.

The nitrification inhibitors had no significant effect ($P < 0.05$) on grass yield or N offtake compared with the Urine treatment for any of the urine experiments (data not shown).

### 3.3. Cattle slurry experiments

There were no significant differences in cumulative $N_2O$ emissions among treatments across all four experiments (table 6). Numerically, emissions from S and S + DCD were much greater than from C in the Sampford Chapple autumn experiment, but variability among replicates was very high in this experiment. For the experiments, emissions were numerically in the order S > S + DCD > C. While not statistically significantly different from the control, EFs were derived as 0.41 and 0.18% of applied slurry N for S and S + DCD, respectively, but these values are heavily influenced by the Sampford Chapple autumn application results.

Inclusion of DCD in the slurry resulted in a 30% increase in $NH_3$ emissions for the autumn application at Sampford Chapple, but had no significant effect ($P > 0.05$) for any other application. Mean emissions across the four experiments were 22.1 and 23.8% of the applied slurry N for S and S + DCD, respectively.

There was no impact of DCD on $NO_3^-$ leaching from the autumn-applied slurries (data not shown), with mean losses equivalent to 1.9 and 2.9% of applied slurry N for the Sampford Chapple and Gleadthorpe sites, respectively, across S and S + DCD treatments. Similarly, there was no effect of DCD on grass dry matter yield or N offtake in any of the four experiments (data not shown).

## 4. Discussion

### 4.1. Nitrous oxide emissions

The EF for AN and U derived from the present study were lower than the IPCC default EF of 1% of applied N, although within the uncertainty range of 0.3–3.0% (de Klein *et al* 2006). Although measurements were conducted over a 12 month period, most of the $N_2O$ emissions from fertilizer applications occurred within the first three months of the application (typically 80 to 95% where significant emissions were measured), as noted by others (Dobbie and Smith 2003, Smith *et al* 2012). Smith *et al* (2012) reported a wide range in seasonal EF (not full 12 month measurements) from fertilizer experiments conducted across a number of UK sites, ranging from 0.07 to 3.93% of applied N for AN and calcium ammonium nitrate (CAN) and from 0.08 to 1.76% for U. The mean for AN or CAN and U from their experiments was 0.99 and 0.77% of applied N, respectively. They reported that while the EF for U was often lower than that for AN/CAN, taking into account the indirect $N_2O$ emission by applying the default IPCC EF of 1% to the volatilized $NH_3$ (greater from U) resulted in similar overall emissions. Our results from the present study agree with this and, indeed, if the EF are expressed as a percentage of the N remaining after $NH_3$ volatilization, they are also similar for AN and U (0.83 and 0.66%, respectively). For inventory compilation purposes therefore, if fertilizer types are to be treated differently it is important to use an N mass flow approach including appropriate EF for both $NH_3$ and $N_2O$.

A meta-analysis of 35 studies assessing the effect of nitrification inhibitors with fertilizers as a mitigation option for $N_2O$ emissions from agricultural soils conducted by Akiyama *et al* (2010) reported an average reduction of 38% (95% confidence interval of 31–44% reduction). Specifically for DCD use with urea, our mean reduction of 69% was higher than this and at the higher end of the range from the literature (35–82%; e.g. Cui *et al* 2011, Delgado and Mosier 1996, Ding *et al* 2011, McTaggart *et al* 1997). We have found only one previous study of the effect of DCD with AN on $N_2O$ emissions, where McTaggart *et al* (1997) reported a 35% reduction in annual emission for grassland, very similar to our mean reduction for AN, but no effect for fertilizer application to spring barley. Merino *et al* (2001) reported a 42% reduction in $N_2O$ emission from calcium ammonium nitrate application to grassland when DCD was used at 25 kg $ha^{-1}$. From our limited assessment of DMPP with ASN fertilizer, we found no significant effect on $N_2O$ emissions albeit that at one site no significant emissions were observed from any of the treatments. This is in contrast to the findings of Weiske *et al* (2001), Linzmeier *et al* (2001) and Macadam *et al* (2003) who all reported significant reductions (range 20–58%) in $N_2O$ emissions from ASN when combined with DMPP.

The mean $N_2O$ EF for urine applications from the present study was 0.41%, within the range of 0.02–1% reported by Yamulki *et al* (1998) from measurements on the heavier-textured North Wyke soil, but considerably lower than the IPCC default EF of 2% for cattle excreta, suggesting that the UK should develop country-specific EF for cattle urine and dung for use in the UK greenhouse gas inventory in a similar way to New Zealand which derived values of 1 and 0.25% for cattle urine and dung, respectively (Luo *et al* 2009). Qiu *et al* (2010) reported higher EF for winter than summer urine applications (1.27 and 0.78%, respectively) in a study in New Zealand. In the UK, winter grazing generally does not occur so a representative EF should integrate spring, summer and autumn conditions. From the four experiments in the present study, the first three in table 5 from summer, autumn and spring all gave EF of approximately 0.3% whereas for the final autumn experiment the EF was 0.65%. In another UK study by Barneze *et al* (2014), cumulative emissions over two months following a summer application at North Wyke represented 0.65% of the applied urine N.

There have been many studies, from New Zealand in particular, assessing the effectiveness of DCD in reducing emissions from grazed pastures, with emission reductions of up to 91% being reported (de Klein and Eckard 2008). However, many of these were lysimeter studies, representing a single urine patch and may overestimate the effectiveness compared with use on grazed pasture where losses will be driven by a number of grazing events. A more conservative emission reduction factor of 50% was suggested for inclusion in the New Zealand agricultural emission inventory to reflect adoption of this mitigation measure (Clough *et al* 2007). Qiu *et al* (2010) showed DCD to be more effective at reducing emissions from urine applications to grassland in New Zealand in the higher-emitting winter season (mean 69% reduction) than in summer (mean 40% reduction). It is known that the microbial degradation of DCD in soil is temperature dependent (Kelliher *et al* 2008) and maximum nitrification inhibition has been reported to occur at soil temperatures ⩽10 °C (Di and Cameron 2004, Smith *et al* 1989). Soil temperature may therefore be expected to be a limiting factor on the effectiveness of DCD in reducing emissions from cattle urine under UK grazing conditions. However, this was not apparent from the present study, there being no correlation between soil temperature and reduction efficiency, and DCD gave an apparent reduction in EF of 70% (although in the Gleadthorpe autumn experiment there was only a 6%, non-significant reduction in net emission). Barneze *et al* (2014) reported a much lower, non-significant reduction efficiency for their summer urine application of 33% with DCD under higher soil temperature (mean of c. 20 °C for the first three weeks following application). This lower reduction efficiency may also have been associated with the heavier soil texture; there are a number of studies in which nitrification inhibitor performance is reported to be higher for lighter textured soils (e.g. Barth *et al* 2001, Bronson *et al* 1989, Pasda *et al* 2001). Shepherd *et al* (2014) found rainfall to be more important than soil texture from a lysimeter study in New Zealand assessing the effectiveness of DCD to decrease $NO_3^-$ leaching from cattle urine. Dicyandiamide is mobile in soil water and downward movement with drainage water could separate DCD from the adsorbed soil $NH_4^+$. However, the results of our present study would suggest that DCD can give significant and substantial reductions in $N_2O$ emissions from cattle urine deposited to grassland during the grazing season.

The pyrazole derivatives did not give any significant reduction in $N_2O$ emissions from cattle urine. This is in agreement with Barneze *et al* (2014) who also reported no significant effect of the same pyrazole derivatives, but did report a numerical but non-significant reduction when included at the much higher rate of 80 L $ha^{-1}$ (3.8 kg $ha^{-1}$ of the combined active ingredients). There are few literature reports of the effectiveness of such pyrazole derivatives, but our results are in contrast to those of McCarty and Bremner (1990) who reported that 3-methylpyrazole-1-carboxamide reduced nitrification in a laboratory study by 50%.

We observed numerical, non-significant reductions in $N_2O$ emissions following the cattle slurry applications when DCD was included in the slurry, with a 56% reduction in EF. For the Sampford Chapple autumn experiment, where emissions were relatively large (EF for slurry of 1.15%), the lack of significance was because of very large variability in measured emissions between replicates. For the remaining three experiments, emissions were relatively low (EF of 0.04 to 0.23% for the slurry treatment) and therefore more difficult to detect significant changes with the measurement technique and number of replicates used. From the literature it is evident that in general, inclusion of DCD with pig or cattle slurry at field application results in lower emissions of $N_2O$, with emission reductions of between 20 and 90% being reported (e.g. Aita *et al* 2014, Li *et al* 2014, Meijide *et al* 2007, Merino *et al* 2001, Vallejo *et al* 2005). However, there are at least two reported laboratory studies where DCD had no effect on $N_2O$ emissions from applied slurry (Mkhabela *et al* 2006, Pereira *et al* 2010). One factor which may impact the relative effectiveness of the DCD is the proportion of N lost by $NH_3$ volatilization after slurry application. If a large proportion of the readily available N is lost very soon after application, then there is a much lower potential for $N_2O$ emission and therefore emission reduction. A good example of this is the practice of slurry injection, which can be very effective at reducing $NH_3$ emissions, but thereby increase the potential for $N_2O$ emissions (depending on soil conditions). Aita *et al* (2014) reported DCD to give $N_2O$ emission reductions of 28 and 66% when included with surface broadcast and injected pig slurry, respectively, where injection gave a 70% reduction in $NH_3$ emission. A number of studies in Spain and the UK have also shown DMPP to be effective in reducing $N_2O$ emissions following slurry applications to land (Dittert *et al* 2001, Macadam *et al* 2003, Menendez *et al* 2006, Merino *et al* 2005).

### *4.2. Ammonia emissions, nitrate leaching and crop effects*

A recent meta-analysis on the effect of nitrification inhibitors on soil ammonia emissions (Kim *et al* 2012) stated that studies conducted so far provide conflicting results, with 14 studies reporting no change in $NH_3$ emission, 26 studies reporting an increase and six studies reporting a decrease in $NH_3$ emissions. The meta-analysis suggested that use of nitrification inhibitors will lead to a significant increase in $NH_3$ emissions, depending on soil properties including pH and CEC. Results from the present study would not support this, where we found that DCD affected $NH_3$ emissions in only two out of the 14 experiments, and although more limited in their assessment, there was no impact of DMPP or the pyrazole derivatives.

A number of studies have shown that nitrification inhibitors can be very effective in reducing $NO_3^-$ leaching; Clough *et al* (2007) reported a mean reduction from grazed pastures of 61% from a number of studies in New Zealand using DCD (although largely based on lysimeter studies of single urine patches, which may overestimate effect as noted above) and Cui *et al* (2011) reported reductions of 36–58% in intensive vegetable production in China. However, the timing of the inhibitor application in relation to the main period of $NO_3^-$ leaching is important and, for our studies, it is likely that the DCD had degraded in the soil prior to the onset of leaching. For many of the New Zealand studies (Clough *et al* 2007), where there was strong evidence of effect, urine applications tended to be made later in the season and there may have been 2–3 applications of DCD over the drainage season. As discussed above, leaching of DCD, moving it away from the adsorbed soil $NH_4^+$ may also explain lack of effect (Shepherd *et al* 2014).

We found no significant effect of the use of nitrification inhibitors on crop yields or N offtakes in the present study. This is perhaps not surprising as the amount of N saved through reducing $N_2O$ losses is very small (even when factoring in associated NO and $N_2$ loses via denitrification) compared to the total N applied to the field (Saggar *et al* 2013) and therefore very difficult to detect in yield and plant uptake measurements. However, many studies have reported yield improvements through the use of nitrification inhibitors. In a recent meta-analysis, Abalos *et al* (2014) give an average yield increase of 6% (95% confidence limits 2.5–10%) for DCD based on 40 comparisons from 10 studies. In some of these studies there will be a greater benefit than observed in our study of reductions in $NO_3^-$ leaching, for example in pasture systems in New Zealand over the winter season.

### *4.3. Potential impact of nitrification inhibitors on emissions from UK agriculture*

This study has shown that significant reductions in $N_2O$ emissions from fertilizer, cattle slurry and cattle urine applications to soil can be achieved under UK soil and climatic conditions. While further measurements are required to develop robust emission reduction efficiencies (and country-specific EF), the mean reduction efficiencies derived from this study can be used to provide an assessment of the potential magnitude of emission reduction across UK agriculture. From the UK greenhouse gas inventory for 1990–2012 (Webb *et al* 2014), total $N_2O$ emission for the UK was estimated as 116.3 Gg for 2012, with the total from agriculture accounting for 83% (96.2 Gg). The relevant N inputs for 2012 were 1.01 million tonnes of N fertilizer, of which 49% was AN and 24% as urea-based N, 375 000 tonnes of cattle excreta N at grazing and approximately 130 000 tonnes of N as livestock slurry applied to land. Maximum potential reductions (assuming 100% adoption of DCD) would give 8.9, 8.2 and 1.0 Gg reduction in emissions for fertilizer applications (across urea and AN), cattle urine returns and slurry applications, respectively, representing a 19% reduction in total $N_2O$ emission from UK agriculture.

To achieve adoption of nitrification inhibitors by the UK agricultural sector requires the development of practical, cost-effective delivery mechanisms. For fertilizers, combined products in which the inhibitor is applied in combination with the fertilizer is the most likely approach. For cattle and pig slurries, inclusion in the slurry store while mixing during store emptying, or automated addition to the slurry during spreading are potential options. For grazed pastures, routine spraying of the inhibitor to the pasture as has been practised in New Zealand is unlikely to be practical or cost-effective under UK grazing management systems where larger areas are grazed during a given time period. Development of systems whereby the inhibitor is introduced through the animal, in feed or drinking water, is a potential delivery mechanism currently being researched (e.g. Welten *et al* 2013).

## 5. Conclusions

The nitrification inhibitor DCD was shown to be effective in reducing direct $N_2O$ emissions following application to land of fertilizer N (urea and ammonium nitrate), cattle urine and cattle slurry under a range of contrasting soil types and annual rainfall in England. Mean reduction efficiencies of 39, 69, 70 and 56% were derived for AN, urea, cattle urine and cattle slurry, respectively (although non-significant for the cattle slurry). Mean $N_2O$ EF derived from the study for the different N sources were all substantially lower than IPCC default values and development of UK country-specific values for inventory compilation purposes is clearly warranted. From a much more limited assessment, the nitrifications inhibitors DMPP, included with ASN fertilizer, and a commercial product containing a combination of two pyrazole derivatives (1H-1,2,4-triazole and 3-methylpyrazole) included with cattle urine, proved ineffective at reducing direct $N_2O$ emissions from soils under the rates and conditions of the experiments. There was very little evidence of any effect of the inhibitors on $NH_3$ volatilization, $NO_3^-$ leaching, crop yield or crop N offtake. Based on the reduction efficiencies derived from the present study, an approximate 20% reduction in $N_2O$ emissions from UK agriculture is technically feasible with little risk of increasing $NH_3$ emissions. However, with little evidence of crop yield or N offtake benefit, routes to industry adoption may be difficult and the development of cost-effective delivery mechanisms is critical.

## Acknowledgements

This study was funded by the UK Department for Environment and Rural Affairs.

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