

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

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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 (N₂O) emissions from fertilizer nitrogen (N), cattle urine and cattle slurry applications to land. Measurements were also made of the impact on ammonia (NH₃) volatilization, nitrate (NO₃⁻) leaching, crop yield and crop N offtake. DCD proved to be very effective in reducing direct N₂O 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 N₂O emission reductions observed from the limited assessments of the other nitrification inhibitors. Generally, there were no impacts of the nitrification inhibitors on NH₃ volatilization, NO₃⁻ leaching, crop yield or crop N offtake. Use of DCD could give up to 20% reduction in N₂O emissions from UK agriculture, but cost-effective delivery mechanisms are required to encourage adoption by the sector. Direct N₂O 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 (N₂O) 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 N₂O 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 N₂O 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 (NH₄⁺) to nitrite, and thus to nitrate (NO₃⁻), by deactivating the



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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 $15 \text{ kg DCD ha}^{-1}$. 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 $<4^\circ\text{C}$ 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 ($2 \times 2 \text{ m}$) 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 $40 \text{ m}^3 \text{ ha}^{-1}$ at Sampford Chapple and Gleadthorpe, respectively, and cattle slurry plus DCD (CS+DCD). The DCD was pre-mixed 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 m²) 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 N₂O. 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 N₂O 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 N₂O 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 m² of the treated plot area at a constant speed of 1 m s⁻¹. Absorption flasks containing 0.02 M orthophosphoric acid were used to measure the concentration of NH₃-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 NO₃⁻ 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 NO₃⁻-N and NH₄⁺-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 N₂O 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 m² of the 4 m² 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 N₂O and NH₃ emissions, cumulative NO₃⁻ leaching and crop yields and N offtakes within each experiment.

3. Results

3.1. Fertilizer experiments

Cumulative annual N₂O emissions from fertilizer applications were significantly greater than from the control treatment in

Table 4. Cumulative nitrous oxide emissions (kg N₂O-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 N₂O emission factors (EF), derived as the net N₂O-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 NH₃ 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 NH₃ 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 NH₃ 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 N₂O 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 ($^{\circ}\text{C}$) [†]
Sampford	Autumn	0.65	2.73	1.82	1.26	0.348	14.0
Chapple	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; [†]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 N₂O 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 N₂O 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 N₂O 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 N₂O emissions from ASN when combined with DMPP.

The mean N₂O 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 and 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 NO₃⁻ leaching from cattle urine. Dicyandiamide is mobile in soil water and downward movement with drainage water could separate DCD from the adsorbed soil NH₄⁺. However, the results of our present study would suggest that DCD can give significant and substantial reductions in N₂O emissions from cattle urine deposited to grassland during the grazing season.

The pyrazole derivatives did not give any significant reduction in N₂O 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 N₂O 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 N₂O, with emission reductions of between 20 and 90% being reported (e.g. Aita *et al* 2014, Li *et al* 2014, Mejjide *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 N₂O 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 NH₃ 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 N₂O emission and

therefore emission reduction. A good example of this is the practice of slurry injection, which can be very effective at reducing NH₃ emissions, but thereby increase the potential for N₂O emissions (depending on soil conditions). Aita *et al* (2014) reported DCD to give N₂O emission reductions of 28 and 66% when included with surface broadcast and injected pig slurry, respectively, where injection gave a 70% reduction in NH₃ emission. A number of studies in Spain and the UK have also shown DMPP to be effective in reducing N₂O 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 NH₃ emission, 26 studies reporting an increase and six studies reporting a decrease in NH₃ emissions. The meta-analysis suggested that use of nitrification inhibitors will lead to a significant increase in NH₃ emissions, depending on soil properties including pH and CEC. Results from the present study would not support this, where we found that DCD affected NH₃ 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 NO₃⁻ 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 NO₃⁻ 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 NH₄⁺ 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 N₂O losses is very small (even when factoring in associated NO and N₂ losses 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 NO₃⁻ 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 N₂O 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 N₂O 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 N₂O 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 N₂O 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 N₂O 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 nitrification 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 N₂O emissions from soils under the rates and conditions of the experiments. There was very little evidence of any effect of the inhibitors on NH₃ volatilization, NO₃⁻ leaching, crop yield or crop N offtake. Based on the reduction efficiencies derived from the present study, an approximate 20% reduction in N₂O emissions from UK agriculture is technically feasible with little risk of increasing NH₃ 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.

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References

- Abalos D, Jeffery S, Sanz-Cobena A, Guardia G and Vallejo A 2014 Meta-analysis of the effect of urease and nitrification inhibitors on crop productivity and nitrogen use efficiency *Agric. Ecosyst. Environ.* **189** 136–44
- Aita C, Gonzatto R, Miola E C C, dos Santos D B, Rochette P, Angers D A, Chantigny M H, Pujol S B, Giacomini D A and Giacomini S J 2014 Injection of dicyandiamide-treated pig slurry reduced ammonia volatilization without enhancing soil nitrous oxide emissions from no-till corn in Southern Brazil *J. Environ. Qual.* **43** 789–800
- Akiyama H, Yan X and Yagi K 2010 Evaluation of effectiveness of enhanced-efficiency fertilizers as mitigation options for N₂O and NO emissions from agricultural soils: meta-analysis *Glob. Change Biol.* **16** 1837–46
- Amberger A 1989 Research on dicyandiamide as a nitrification inhibitor and future outlook *Commun. Soil Sci. Plant Anal.* **20** 1933–55
- Bailey R J and Spackman E 1996 A model for estimating soil moisture changes as an aid to irrigation scheduling and crop water-use studies: 1. Operational details and description *Soil Use Manage.* **12** 122–8
- Barneze A S, Minet E P, Cerri C C and Misselbrook T 2014 The effect of nitrification inhibitors on nitrous oxide emissions from cattle urine depositions to grassland under summer conditions in the UK *Chemosphere* **119** 122–9
- Barth G, von Tucher S and Schmidhalter U 2001 Influence of soil parameters on the effect of 3,4-dimethylpyrazole-phosphate as a nitrification inhibitor *Biol. Fertil. Soils* **34** 98–102
- Bronson K F, Touchton J T and Hauck R D 1989 Decomposition rate of dicyandiamide and nitrification inhibition *Commun. Soil Sci. Plant Anal.* **20** 2067–78
- Chadwick D R *et al* 2014 Optimizing chamber methods for measuring nitrous oxide emissions from plot-based agricultural experiments *Eur. J. Soil Sci.* **65** 295–307
- Clough T J, Di H J, Cameron K C, Sherlock R R, Metherell A K, Clark H and Rys G 2007 Accounting for the utilization of a N₂O mitigation tool in the IPCC inventory methodology for agricultural soils *Nutr. Cycl. Agroecosyst.* **78** 1–14
- Cui M, Sun X C, Hu C X, Di H J, Tan Q L and Zhao C S 2011 Effective mitigation of nitrate leaching and nitrous oxide emissions in intensive vegetable production systems using a nitrification inhibitor, dicyandiamide *J. Soils Sediments* **11** 722–30
- de Klein C A M and Eckard R J 2008 Targeted technologies for nitrous oxide abatement from animal agriculture *Aust. J. Exp. Agric.* **48** 14–20
- de Klein C, Novoa R S A, Ogle S, Smith K, Rochette P, Wirth T C, McConkey B G, Mosier A and Rypdal K 2006 N₂O emissions from managed soils, and CO₂ emissions from lime and urea application 2006 IPCC Guideline for National Greenhouse Inventories. Intergovernmental Panel on Climate Change (Paris, France: IPCC/OECD/IEA) chapter 11
- Delgado J A and Mosier A R 1996 Mitigation alternatives to decrease nitrous oxides emissions and urea-nitrogen loss and their effect on methane flux *J. Environ. Qual.* **25** 1105–11
- Di H J and Cameron K C 2004 Effects of temperature and application rate of a nitrification inhibitor, dicyandiamide (DCD), on nitrification rate and microbial biomass in a grazed pasture soil *Aust. J. Soil Res.* **42** 927–32
- Ding W X X, Yu H Y Y and Cai Z C C 2011 Impact of urease and nitrification inhibitors on nitrous oxide emissions from fluvo-aquic soil in the North China Plain *Biol. Fertil. Soils* **47** 91–9
- Dittert K, Bol R, King R, Chadwick D and Hatch D 2001 Use of a novel nitrification inhibitor to reduce nitrous oxide emission from N-15-labelled dairy slurry injected into soil *Rapid Commun. Mass Spectrom.* **15** 1291–6
- Dobbie K E and Smith K A 2003 Impact of different forms of N fertilizer on N₂O emissions from intensive grassland *Nutr. Cycl. Agroecosyst.* **67** 37–46
- Firestone M K and Davidson E A 1989 Microbiological basis of NO and N₂O production and consumption in soil ed M O Andea and D S Schimel *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere* (Chichester: Wiley) pp 7–21
- IPCC 2007 Climate change 2007 *The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* ed S Solomon, D Qin, M Manning, Z Chen, M Marquis, K B Averyt, M Tignor and H L Miller (Cambridge: Cambridge University Press) p 996
- Kelliher F M, Clough T J, Clark H, Rys G and Sedcole J R 2008 The temperature dependence of dicyandiamide (DCD) degradation in soils: a data synthesis *Soil Biol. Biochem.* **40** 1878–82
- Kim D-G, Saggat S and Roudier P 2012 The effect of nitrification inhibitors on soil ammonia emissions in nitrogen managed soils: a meta-analysis *Nutr. Cycl. Agroecosyst.* **93** 51–64
- Li J, Shi Y, Luo J, Zaman M, Houlbrooke D, Ding W, Ledgard S and Ghani A 2014 Use of nitrogen process inhibitors for reducing gaseous nitrogen losses from land-applied farm effluents *Biol. Fertil. Soils* **50** 133–45
- Linzmeier W, Gutser R and Schmidhalter U 2001 Nitrous oxide emission from soil and from a nitrogen-15-labelled fertilizer with the new nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) *Biol. Fertil. Soils* **34** 103–8
- Lockyer D R 1984 A system for the measurement in the field of losses of ammonia through volatilization *J. Sci. Food Agric.* **35** 837–48
- Luo J, van der Weerden T, Hoogendoorn C and de Klein C 2009 Determination of the N₂O emission factor for animal dung applied in spring in three regions of New Zealand *Report for the Ministry of Agriculture and Forestry* (Wellington: Ministry of Agriculture and Forestry)
- Macadam X M B, del Prado A, Merino P, Estavillo J M, Pinto M and Gonzalez-Murua C 2003 Dicyandiamide and 3,4-dimethyl pyrazole phosphate decrease N₂O emissions from grassland but dicyandiamide produces deleterious effects in clover *J. Plant Physiol.* **160** 1517–23

- McCarty G W and Bremner J M 1990 Evaluation of 3-methylpyrazole-1-carboxamide as a soil nitrification inhibitor *Biol. Fertil. Soils* **9** 252–6
- McTaggart I P, Clayton H, Parker J, Swan L and Smith K A 1997 Nitrous oxide emissions from grassland and spring barley, following N fertiliser application with and without nitrification inhibitors *Biol. Fertil. Soils* **25** 261–8
- Meijide A, Diez J A, Sanchez-Martin L, Lopez-Fernandez S and Vallejo A 2007 Nitrogen oxide emissions from an irrigated maize crop amended with treated pig slurries and composts in a mediterranean climate *Agric. Ecosyst. Environ.* **121** 383–94
- Menendez S, Merino P, Pinto M, Gonzalez-Murua C and Estavillo J M 2006 3,4-dimethylpyrazol phosphate effect on nitrous oxide, nitric oxide, ammonia, and carbon dioxide emissions from grasslands *J. Environ. Qual.* **35** 973–81
- Merino P, Estavillo J M, Besga G, Pinto M and Gonzalez-Murua C 2001 Nitrification and denitrification derived N₂O production from a grassland soil under application of DCD and Actilith F2 *Nutr. Cycl. Agroecosyst.* **60** 9–14
- Merino P, Menendez S, Pinto M, Gonzalez-Murua C and Estavillo J M 2005 3,4-dimethylpyrazole phosphate reduces nitrous oxide emissions from grassland after slurry application *Soil Use Manage.* **21** 53–7
- Mkhabela M S, Gordon R, Burton D, Madani A, Hart W and Elmi A 2006 Ammonia and nitrous oxide emissions from two acidic soils of Nova Scotia fertilised with liquid hog manure mixed with or without dicyandiamide *Chemosphere* **65** 1381–7
- Mosier A 1989 Chamber and isotope techniques ed M Andrea and D Schimmel *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere. Life Sciences Research Report 47* (Chichester: Wiley) pp 175–87
- Pasda G, Hahndel R and Zerulla W 2001 Effect of fertilizers with the new nitrification inhibitor DMPP (3,4-dimethylpyrazole phosphate) on yield and quality of agricultural and horticultural crops *Biol. Fertil. Soils* **34** 85–97
- Pereira J, Fanguero D, Chadwick D R, Misselbrook T H, Coutinho J and Trindade H 2010 Effect of cattle slurry pre-treatment by separation and addition of nitrification inhibitors on gaseous emissions and N dynamics: a laboratory study *Chemosphere* **79** 620–7
- Qiu W H, Di H J, Cameron K C and Hu C X 2010 Nitrous oxide emissions from animal urine as affected by season and a nitrification inhibitor dicyandiamide *J. Soils Sediments* **10** 1229–35
- Saggar S, Jha N, Deslippe J, Bolan N S, Luo J, Giltrap D L, Kim D-G, Zaman M and Tillman R W 2013 Denitrification and N₂O:N₂ production in temperate grasslands: processes, measurements, modelling and mitigating negative impacts *Sci. Total Environ.* **465** 173–95
- Shepherd M, Welten B, Wyatt J and Balvert S 2014 Precipitation but not soil texture alters effectiveness of dicyandiamide to decrease nitrate leaching from dairy cow urine *Soil Use Manage.* **30** 361–71
- Smith K A, Crichton I J, McTaggart I P and Lang R W 1989 Inhibition of nitrification by dicyandiamide in cool temperate conditions ed J A Hansen and K Henriksen *Nitrogen in Organic Wastes Applied to Soils* (London, UK: Academic) pp 289–303
- Smith K A, Dobbie K E, Thorman R, Watson C J, Chadwick D R, Yamulki S and Ball B C 2012 The effect of N fertilizer forms on nitrous oxide emissions from UK arable land and grassland *Nutr. Cycl. Agroecosyst.* **93** 127–49
- Vallejo A, Garcia-Torres L, Diez J A, Arce A and Lopez-Fernandez S 2005 Comparison of N losses (NO₃⁻, N₂O, NO) from surface applied, injected or amended (DCD) pig slurry of an irrigated soil in a Mediterranean climate *Plant Soil* **272** 313–25
- Webb N, Broomfield M, Brown P, Buys G, Cardenas L, Murrells T, Pang Y, Passant N, Thistlethwaite G and Watterson J 2014 UK greenhouse gas inventory, 1990–2012 *Annual Report for Submission Under the Framework Convention on Climate Change* (Didcot: Ricardo-AEA)
- Weiske A, Benckiser G, Herbert T and Ottow J C G 2001 Influence of the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) in comparison to dicyandiamide (DCD) on nitrous oxide emissions, carbon dioxide fluxes and methane oxidation during 3 years of repeated application in field experiments *Biol. Fertil. Soils* **34** 109–17
- Welten B G, Ledgard S F, Schipper L A, Waller J E, Kear M J and Dexter M M 2013 Effects of prolonged oral administration of dicyandiamide to dairy heifers on excretion in urine and efficacy in soil *Agric. Ecosyst. Environ.* **173** 28–36
- Yamulki S, Jarvis S C and Owen P 1998 Nitrous oxide emissions from excreta applied in a simulated grazing pattern *Soil Biol. Biochem.* **30** 491–500
- Zaman M, Saggar S, Blennerhasset J D and Singh J 2009 Effect of urease and nitrification inhibitors on N transformation, gaseous emissions of ammonia and nitrous oxide and N uptake in grazed pasture systems *Soil Biol. Biochem.* **41** 1270–80