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The effect of cattle slurry in combination with nitrate and the nitrification inhibitor dicyandiamide on in situ nitrous oxide and dinitrogen emissions

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Abstract

A field study was conducted to determine the effect of the nitrification inhibitor dicyandiamide (DCD) on N_2O and N_2 emissions after cattle slurry (CS) application in the presence of nitrate fertiliser on seven different occasions (between March 2009 and March 2011).

N_2O emissions from CS in the presence of NO_3 fertiliser were very high (0.4–8.7 % of applied N) over a 20 day period, under mild moist conditions. Emissions were significantly larger from the CS treatment compared to an NH_4^+-N source, supplying the same rate of N as in the slurry. This study supports the view that organic fertilisers should not be applied at the same time as nitrate based fertilisers, as significant increases in N_2O emissions occur. The average N_2O mole fraction ($N_2O/(N_2O = N_2)$) over all seven application dates was 0.34 for $CSNO_3$ compared to 0.24 for the NH_4ClNO_3 treatment, indicating the dominance of N_2 emissions.

The rate of nitrification in $CSNO_3$ was slower than in NH_4ClNO_3 and DCD was found to be an effective nitrification inhibitor in both treatments. However, as N_2O emissions were found to be predominantly associated with the NO_3 pool, the effect of DCD in lowering N_2O emissions is limited in the presence of a NO_3 fertiliser. To obtain the maximum cost-benefit of DCD in lowering N_2O emissions, under mild moist conditions, its application should be restricted to ammonium based organic or synthetic fertilisers.

1 Introduction

Ammonium nitrate or calcium ammonium nitrate are the dominant forms of fertiliser applied to grassland in UK and Ireland. Ammonium nitrate (AN) contains nitrogen as NH_4^+-N and NO_3^--N and calcium ammonium nitrate (CAN) contains in addition dolomite or limestone. Fertiliser usage for grassland has been declining since the mid 1980s by 38 % in UK and 33 % in Ireland. Increasing fertiliser prices (CSO, 2012) and nitrate regulations have mostly caused the observed decline. There is now more of an incentive to use organic fertilisers as a valuable supply of nitrogen (N) in a nutrient management plan on farms and cattle slurry is by far the most common form of organic fertiliser. On farm nutrient management planning encourages the integrated use of both cattle slurry and inorganic fertilisers. Therefore the practice of cattle slurry being applied in the presence of NO_3^- is regionally relevant.

Reviews of field studies where N_2O emissions were measured suggested that mineral N fertilisers plus organic manures resulted in higher losses than with mineral N fertilisers alone (Bouwman, 1990; Granli and Bøckman, 1994). Field studies have shown that whenever fertiliser containing NO_3 and CS are applied together, or within a few days of each other, the potential exists for enhanced N_2O and N_2 emissions. In moist soil conditions, cumulative N_2O emissions were up to 4 times greater from NH_4NO_3 followed by CS than from NH_4NO_3 alone (McTaggart et al., 1997). When CS was supplemented with NH_4NO_3, the loss of N_2O was 2.2 % compared with 1.2 % for NH_4NO_3 alone (Clayton et al., 1997). In studies conducted on four occasions in 1997 cattle slurry increased the flux of N_2O by an average factor of 3 (Stevens and Laughlin, 2001a). Lampe et al. (2006) found that the combined application of slurry and mineral fertiliser increased N_2O emissions by between 30 to 150 % compared to emissions from CAN alone. It has been reported that denitrifying bacteria are capable of utilising the volatile fatty acids (VFAs) (acetate, propionate and butyrate) present in slurry as C sources (Paul et al., 1989).

Nitrification is the general term for the aerobic oxidation of reduced nitrogen (NH_3) to NO_2^- and further to NO_3^- by autotrophic or heterotrophic microorganisms (Coyne and Frye, 2005). Autotrophic nitrification is a two step process carried out by chemolithotrophic bacteria, which obtain energy by oxidizing NH_3 to NO_3^-. The first step is carried out by *Nitro*-bacteria and involves the sequential oxidation of NH_3 to hydroxylamine and then to NO_2^-. The second step is the oxidation of NO_2^- to NO_3^- by *Nitro*-bacteria.

Heterotrophic nitrification is the oxidation of organic N and NH_3 to NO_3^- by chemoheterotrophic bacteria and fungi who gain their energy from organic C instead of CO_2.

Oxidation of NH_4^+ is a key process in the N cycle having implications for the environment as non mobile NH_4^+ is converted to mobile NO_3^-, which if produced in excess to plant needs is either leached out of the root zone or is denitrified to produce N-gases (NO, N_2O and N_2). Nitrification inhibitors are available that are thought to act specifically on the enzyme ammonium mono-oxygenase, by blocking the site where ammonium is converted to NO_2^-. This slows down the microbial conversion of NH_4^+ to NO_3^- and hence reduces NO_3^- build-up and associated loss processes. The rate of degradation and hence the efficacy of nitrification inhibitors are affected by soil temperature (Zerulla et al., 2001; Edmeades, 2004), pH (Keeney, 1986), moisture content (Hendrikson and Keeney, 1979; Puttanna et al., 1999) and soil organic matter content (Briggs, 1975). The mobility of nitrification inhibitors in soil may also be a factor affecting their efficacy. DCD being highly water soluble can be leached through the profile (Zerulla et al., 2001).

Denitrification can be a major N loss process in grassland soils. Although the final product of denitrification is the benign atmospheric gas N_2, this process does not always go to completion and variable amounts of N_2O, a potent greenhouse gas (GHG), can be produced. Physical, chemical and biological factors influence the reduction of N_2O to N_2 (Weier et al., 1993) including soil moisture content (Davidson, 1991; Ruser et al., 2006), pH (Simek and Cooper, 2002; Cuhel et al., 2010), temperature (Bailey, 1976; Keeney et al., 1979), C supply (Parkin, 1987; Mathieu et al., 2006), soil redox conditions (Firestone and Tiedje, 1979; Tiedje, 1988) and management (Frolking et al., 1998; Liu et al., 2007).

Most attention over the last decade has been concentrated on the intermediate gaseous products of denitrification, NO and N_2O, because of their importance in tropospheric and stratospheric processes of ozone production and consumption, and radiative forcing (Davidson et al., 2000; Hall et al., 1996; Seitzinger and Kroeze, 1998). The anthropogenic inputs of reactive N from food and energy production has been increasing during the last few decades and reactive N has been accumulating in the environment. The largest gap in knowledge is the amount of reactive N converted back to N_2 by denitrification. Without this information it is impossible to determine the rate of accumulation of reactive N in all environmental reservoirs. At present reliable quantification of N_2 produced in the field is rare and estimates of how much reactive N is denitrified are highly uncertain.

In this study we used the ^{15}N gas flux method in the field to determine the effect of CS and DCD in the presence of nitrate on N_2 and N_2O emissions on seven occasions between March 2009 and March 2011.

2 Materials and methods

2.1 Study site characteristics

The experimental grassland site was located at Hillsborough, County Down, Northern Ireland (54° 46′ N; 6° 08′ W), where experiments were conducted on seven different occasions (March 2009, July 2009, October 2009, March 2010, June 2010, October 2010 and March 2011). A new area of grassland was used for each of the seven experimental applications. The sward was dominated by perennial ryegrass (*Lolium perenne* L.). White clover (*Trifolium repens*) and broad-leaved docks (*Rumex obtusifolius*) were removed from the swards using an appropriate herbicide prior to each treatment application. The long-term (1995–2010) average rainfall and daily temperature for the site were 916 mm and 9.3 °C, respectively (AFBI Climatological Database, 2012). The soil is a sandy clay loam with moderate drainage. The site was managed as a low N input system to maintain the same sward for all experiments. A basal dressing of P, K and S was applied prior to each experiment so that these major nutrients were not limiting grass growth.

2.2 Experimental treatments

Cattle slurry ($33\,m^3, ha^{-1}$) amended with KNO_3 ($65\,kg\,N\,ha^{-1}$), with or without DCD (at 15 % NH_4^+-N content of the CS) was surface applied to grassland with either the NH_4^+

or the NO_3^- pool ^{15}N labelled ($^{15}CS^{14}NO_3$, $^{14}CS^{15}NO_3$) at 50 atom %, according to the procedure of Stevens et al. (1997). Ammonium chloride (NH_4Cl) amended with KNO_3 (65 kg, N, ha^{-1}), with or without DCD, with either the NH_4^+ or the NO_3^- pool ^{15}N labelled, served as controls for $^{14}CS^{15}NO_3$ and $^{15}CS^{14}NO_3$, respectively having the same amount of NH_4^+-N as the CS but no degradable carbon. In summary there were eight treatments: (i) $^{15}CS^{14}NO_3$ without DCD, (ii) $^{15}CS^{14}NO_3$ with DCD, (iii) $^{14}CS^{15}NO_3$ without DCD, (iv) $^{14}CS^{15}NO_3$ with DCD, (v) $^{15}NH_4Cl^{14}NO_3$ without DCD, (vi) $^{15}NH_4Cl^{14}NO_3$ with DCD, (vii) $^{14}NH_4Cl^{15}NO_3$ without DCD, and (viii) $^{14}NH_4Cl^{15}NO_3$ with DCD. The eight treatments were replicated four times in a randomised block design. Immediately prior to application aliquots of CS/NH_4Cl, KNO_3, and DCD/water were mixed together and uniformly applied directly inside the chamber (area of 0.16 m^2).

2.3 Slurry collection and analysis

Sufficient CS was collected prior to each of the seven treatment application dates. Anaerobic digested dairy cattle slurry was used at all times. The properties of the raw and amended CS and application rates for each of the seven application dates are detailed in Table 1. CS was amended by adding either unlabelled urea or urea enriched at 99 atom % and incubating the CS for 3 days at 35 °C to hydrolyse the urea to NH_4^+-N (Stevens and Laughlin, 2001a). Slurry dry matter content was determined by drying a representative slurry sample at 105 °C for 24 h. Total ammoniacal N in slurry was determined by steam distillation into boric acid solution, in the presence of magnesium oxide. The boric acid solution was titrated with 0.1 M sulphuric acid to determine the ammonium N in the sample. Slurry pH was determined by Orion pH meter Model 420A. Volatile fatty acids (VFAs) were determined directly by capillary gas-liquid chromatography and detected by a flame ionization detector. Total C was determined by the Dumas method with quantitative analysis by an Elementar Vario Max CN elemental analyser.

2.4 Flux measurement technique

Gaseous N_2 and N_2O emissions were measured using the static chamber method deploying square stainless steel chambers (0.4 m × 0.4 m wide and 0.1 m high). The chamber collar was inserted into the ground to a depth of ≥5 cm at least 3 days prior to commencing each experiment, and left in position for the duration of the experiment. The collars had a water-filled trough into which the chamber lid was placed when sampling, thus ensuring a gas-tight seal. Gas sampling occurred between 10:00 a.m. and 12:00 p.m. on 10 occasions over a 20 day period following treatment application. In order to detect evolved $^{15}N_2$, Stevens and Laughlin (1998) showed that a chamber closure time of 2 h was necessary. After 2 h, samples of the chamber headspace were taken through a silicone septa positioned on the centre of the chamber lid, using a 20 ml polypropylene syringe equipped with a 25 gauge luer lock needle (0.5 × 16 mm). The syringe was flushed once with headspace air before sampling. A 15 ml sample was withdrawn from the chamber and injected into a 12 ml pre-evacuated glass vials fitted with a 3 mm butyl rubber septa (Labco, UK). Linearity checks on N_2O were conducted on 104 occasions from the $CSNO_3$ without DCD treatment by sampling the chamber headspace four times over the chamber closure period. Chamber datasets were not examined for linearity if the T_{2h} sample was not significantly higher than the T_{0h} sample, or occasionally if apparent leaks occurred in the vials. From the 104 chamber datasets 27 % were discarded for these reasons. In Fig. 1 the percentage of data is depicted for ranges of linear co-efficient of determination (R^2) for the accepted datasets. Eighty-four percent of the accepted data had an R^2 of >0.85. As this experiment was a comparative study it was deemed suitable to apply a linear regression model to all data. Cumulative fluxes were calculated by linear interpolation between sampling times.

2.5 Analysis of N_2O and N_2

The concentration and ^{15}N content of N_2O and the ^{15}N content of the N_2 was determined by automated isotope ratio mass spectrometry (IRMS) as described by Stevens et al. (1993), using a Europa Scientific 20–20 Stable Isotope Analyser interfaced to a Europa Scientific Trace Gas Preparation System ANCA-TG (Crewe, UK) with Gilson autosampler (Anachem, Luton, UK). The ion currents (I) at *m/z* 44, 45, and 46 enabled concentrations and molecular ratios ^{45}R ($^{45}I/^{44}I$) and ^{46}R ($^{46}I/^{44}I$) to be calculated for N_2O. The sources of N_2O were then apportioned into the fraction (d'_D) derived from the denitrifying pool of enrichment a_D and the fraction $d'_N = (1 - d'_D)$ derived from the pool or pools at natural abundance (Arah, 1997). For N_2, the ion currents at *m/z* 28, 29 and 30 enabled molecular ratios ^{29}R ($^{29}I/^{28}I$) and ^{30}R ($^{30}I/^{28}I$) to be determined. Differences between the molecular ratios in enriched and normal atmospheres were calculated as $\Delta^{29}R$ and $\Delta^{30}R$. The flux of N_2 was calculated using $\Delta^{30}R$ data only and the equation of Mulvaney (1984), assuming that the enrichment of the denitrifying pool was a_D (Stevens and Laughlin, 2001b). This method of N_2 flux calculation improved the sensitivity of N_2 emission measurement by a factor of 16 and without this method we could not have detected the N_2 flux.

2.6 Statistical methods

Analyses was carried out using GenStat Version 14 software. Each of the seven application times were analysed separately. The experiment was analysed using analysis of variance as a randomised block experiment with a full factorial design incorporating two factors. The factors used were NH_4^+-N form (two levels: CS or NH_4Cl) and DCD (2 levels: with and without DCD). The ANOVA model was used to ascertain the significance of treatments on the cumulative fluxes of N_2O, N_2, and N_2O mole fraction, and on the values of d_D and a_D. A significance level of 0.05 was used, unless otherwise stated. Estimates of means, standard error of means, standard error of differences in means and Fisher's least significant difference (LSD) were calculated.

3 Results

3.1 Composition of applied cattle slurries

The NH_4^+-N contents of the amended slurries used over the course of this experiment varied considerably over the seven application times (Table 1). The rate of NH_4^+-N applied varied between 73.9 to 140.6 kg N ha^{-1}. The same rate of NO_3^--N was applied on each occasion to give a rate of 65 kg N ha^{-1}. The slurries used had a mean dry matter content of 4.6 % and the pH ranged from 7.14 to 8.27 (Table 1).

3.2 Rainfall and soil temperature

Daily rainfall and soil temperature at 5 cm were collected at a weather station located within 1 km of the site. Figure 2 shows the daily data for 20 days post treatment application for each of the seven application times. The total rainfall for five days post application ranged from 0.0 mm in June 2010 to 33.0 mm in July 2009, indicating a wide range of rainfall conditions.

3.3 Overview of chamber fluxes

The N_2O and N_2 emitted over each measurement period showed a similar pattern, with peak emissions occurring in the first five days after treatment application. Figures 3 and 4 illustrate a typical pattern of emissions for July 2009 for nitrous oxide and dinitrogen, respectively. On each of the seven application times N_2O fluxes were higher for the $CSNO_3$ treatment than the NH_4ClNO_3 treatment. Fluxes were considerably lower in June 2010 compared to other measurement periods, probably due to lower soil moisture contents, as there was no rainfall for 10 days post treatment application.

3.4 Cumulative emissions

The cumulative fluxes of N_2O-N and N_2-N and the mole fraction of N_2O ($N_2O/(N_2O + N_2)$) for each measurement period are given in Table 2. The flux of N_2O was independent of the ^{15}N labelling, therefore fluxes from treatments with either the NH_4^+ or the NO_3^- pool ^{15}N labelled (e.g. $^{15}CS^{14}NO_3$, $^{14}CS^{15}NO_3$) were averaged. It was only possible to measure the flux of N_2 from treatments where the $^{15}NO_3$ pool was labelled.

Cumulative N_2O emissions over 20 days in the $CSNO_3$ without DCD treatment ranged from 0.76 kg N ha^{-1} in June 2010 to 17.28 kg N ha^{-1} in March 2009; $CSNO_3$ with DCD treatment ranged from 0.88 kg N ha^{-1} in June 2010 to 12.79 kg N ha^{-1} in March 2009; NH_4ClNO_3 without DCD treatment ranged from 0.51 kg N ha^{-1} in June 2010 to 8.79 kg N ha^{-1} in March 2009, and; in the NH_4ClNO_3 with DCD treatment cumulative N_2O emissions ranged from 0.47 kg N ha^{-1} in June 2010 to 6.70 kg N ha^{-1} in March 2009.

Cumulative N_2 emissions over 20 days in the $CSNO_3$ without DCD treatment ranged from 3.27 kg N ha^{-1} in March 2011 to 42.38 kg N ha^{-1} in March 2009; $CSNO_3$ with DCD treatment ranged from 3.43 kg N ha^{-1} in June 2010 to 21.77 kg N ha^{-1} in March 2009; NH_4ClNO_3 without DCD treatment ranged from 3.03 kg N ha^{-1} in June 2010 to 34.92 kg N ha^{-1} in March 2009, and; in the NH_4ClNO_3 with DCD treatment cumulative N_2 emissions ranged from 1.32 kg N ha^{-1} in March 2011 to 18.19 kg N ha^{-1} in July 2009.

3.4.1 Effect of CS on the cumulative emissions of N_2O and N_2

On each of the seven application times the presence of CS significantly increased cumulative N_2O emissions (when compared to the NH_4Cl control) on all occasions (March 2009, $P < 0.001$; July 2009, $P < 0.001$; October 2009, $P < 0.01$; March 2010,

$P < 0.001$; June 2010, $P < 0.001$; October 2010, $P < 0.05$; March 2011, $P < 0.001$). This increase ranged from a factor of between 1.27 and 6.93.

The presence of CS significantly increased cumulative N_2 emissions on only two occasions: in March 2009 ($P < 0.05$) and in March 2011 ($P < 0.01$).

When CS was applied, the N_2O mole fraction ($N_2O/(N_2O + N_2)$) increased on all occasions. The N_2O mole fraction averaged over the seven measurement periods, was significantly higher ($P < 0.001$) for $CSNO_3$ at 0.34 (±0.03 standard error) compared to NH_4ClNO_3 at 0.24 (±0.03 standard error). The average N_2O mole fraction was lower (0.19) in June 2010, under relatively dry conditions, than at other times (average 0.34).

3.4.2 Effect of DCD on the cumulative emissions of N_2O and N_2

When data was averaged over the $CSNO_3$ and NH_4ClNO_3 treatments there was an overall DCD effect on two occasions, where the application of DCD was shown to decrease cumulative N_2O emission in March 2010 ($P < 0.001$) and October 2010 ($P < 0.05$) (results not shown). When the DCD effect on $CSNO_3$ was examined there was a significant decrease ($P < 0.01$) in cumulative N_2O emissions in March 2009 from 17.28 to 12.79 $\mathrm{kg\,N\,ha^{-1}}$. However, DCD did not significantly decrease N_2O emissions in $CSNO_3$ at any other time. There was a significant decrease ($P < 0.05$) in cumulative N_2O emissions from NH_4ClNO_3 in March 2011 from 1.18 to 0.70 $\mathrm{kg\,N\,ha^{-1}}$, but DCD did not significantly decrease N_2O emissions at any other time.

Across all treatments there was a decrease in N_2 cumulative emissions in March 2009 ($P < 0.001$), July 2009 ($P < 0.01$), and October 2010 ($P < 0.05$). There was a significant decrease ($P < 0.001$) in N_2 emissions from $CSNO_3$ in March 2009, where the cumulative N_2 emission decreased from 42.38 to 21.77 $\mathrm{kg\,N\,ha^{-1}}$. DCD did not significantly decrease N_2 emission in $CSNO_3$ on any other occasion. There was a significant decrease in N_2 emissions from NH_4ClNO_3 in March 2009 and March 2011 from 34.92 to 14.54 $\mathrm{kg\,N\,ha^{-1}}$ and from 2.47 to 1.32 $\mathrm{kg\,N\,ha^{-1}}$, respectively; DCD did not significantly decrease N_2 emissions in NH_4ClNO_3 at any other time.

DCD significantly increased the N_2O mole fraction ($N_2O/N_2O + N_2$) in March 2009, but had no significant effect at other times.

3.5 Source of N_2O

Following the procedure of Arah (1997) the fraction (d_D) of the N_2O flux which was derived from the $^{15}NO_3$ pool and the ^{15}N atom fraction (a_D) of that pool were calculated. Values of a_D indicate the enrichment of the ^{15}N labelled denitrifying pool and its change over time is indicative of the rate of nitrification. Calculations of d_D and a_D can only be performed when the nitrate pool is labelled and when there is a detectable N_2O flux. Therefore only values obtained from the $^{14}CS^{15}NO_3$ and $^{14}NH_4Cl^{15}NO_3$ treatments are presented. As the N_2O peak emission pattern was different for each application event, N_2O a_D values when the N_2O flux was above 2 ppmv, and N_2O d_D values are given at times of maximum peak N_2O emissions. Values of a_D are presented in Table 3 for $^{14}CS^{15}NO_3$ and $^{14}NH_4Cl^{15}NO_3$ with and without DCD.

N_2O a_D values at the first sampling time after application (after approximately 2 h) was 0.50, which was the same as the theoretical enrichment of 0.50 atom fraction ^{15}N (50 atom % ^{15}N). At all application times a_D values for $CSNO_3$ were higher than a_D for NH_4ClNO_3, indicating that the rate of nitrification was slower for $CSNO_3$ than for NH_4ClNO_3 (March 2009, $P < 0.001$; July 2009, $P < 0.01$; October 2009, $P < 0.01$; March 2010, $P < 0.001$; June 2010, $P < 0.01$; October 2010, NS; March 2011, $P < 0.001$). Examining the change in N_2O a_D with time it was apparent that the presence of CS caused a delay in nitrification (Fig. 5). The application of DCD significantly increased the values of a_D in $CSNO_3$ on five occasions compared to the $CSNO_3$ without DCD treatment (March 2009, $P < 0.001$; March 2010, $P < 0.05$; June 2010, $P < 0.001$; October 2010, $P < 0.05$; March 2011, $P < 0.01$). The application of DCD also significantly increased the values of a_D in NH_4ClNO_3 on the same five occasions compared to the NH_4ClNO_3 without DCD treatment (March 2009, $P < 0.001$; March 2010, $P < 0.001$; June 2010, $P < 0.001$; October 2010, $P < 0.05$; March 2011,

$P < 0.01$). DCD did not have a significant effect on N_2O a_D in either the $CSNO_3$ and NH_4ClNO_3 treatments in July and October 2009. Enrichment of N_2O from the $^{15}NH_4$ labelled treatments increased with time (Fig. 6) suggesting that ^{15}N-labelled ammonium was oxidized through the nitrification process, enriching the NO_3 pool, from which $^{15}N_2O$ was evolved.

N_2O d_D is the fraction of the emitted N_2O which is derived from the ^{15}N labelled denitrifying nitrate pool, with a N_2O d_D value of unity (1.00) indicating that 100 % of the N_2O emitted is from the nitrate pool. Values of N_2O d_D (Table 4) for $CSNO_3$ with and without DCD were not significantly different from unity; therefore the source of the N_2O emitted from the $CSNO_3$ treatments was the nitrate pool. Values of N_2O d_D for NH_4ClNO_3 were significantly lower than unity in March 2009, March 2010, June 2010 and March 2011 with values of 0.96, 0.90, 0.65, and 0.87 being measured, indicating that 4 %, 10 %, 35 % and 13 %, respectively of the N_2O emitted was derived from a natural abundance nitrate pool. DCD did not significantly change N_2O d_D in either the $CSNO_3$ or NH_4ClNO_3 treatments.

4 Discussion

4.1 N_2O and N_2 cumulative emissions

N_2O and N_2 cumulative emissions were expressed as a percentage of the applied N (ammonium-N and nitrate-N). In our study, over the seven treatment dates, between 0.4–8.7 % of the applied N (NH_4^+ and NO_3^-) was lost as N_2O and between 2.1–23.2 % was lost as N_2 in the $CSNO_3$ treatment. When NH_4ClNO_3 was applied between 0.3–4.8 % was lost as N_2O and 1.7–20.4 % was lost as N_2. Lowest emissions were measured when soil moisture was low. The current IPCC default N_2O emission factor is 1 % of the applied N, regardless of N source (organic-N or fertiliser-N) (IPCC, 2006). The current study did not include unfertilized control plots, therefore emission factors could not be calculated, however the average percentage N_2O and N_2 losses expressed in terms of N applied indicate that N gas losses are large, with increased losses in the presence of CS. The total cumulative emission of N_2O-N plus N_2-N, averaged over the seven measurement periods, expressed as a percentage of the available N applied was 15.9 % for $CSNO_3$ without DCD, 12.4 % for $CSNO_3$ with DCD, 12.4 % for NH_4ClNO_3 with DCD, and 8.7 % for NH_4ClNO_3 without DCD.

The simultaneous application of cattle slurry and NO_3^- induced a large increase in cumulative N_2O emissions compared to those measured from NH_4Cl combined with NO_3^-, with increases of between 1.27 and 6.93 fold being measured. This increase indicates that the easily mineralisable carbon components in cattle slurry promoted N_2O emissions derived from NO_3^-. Lampe et al. (2006) found that the application of slurry and mineral fertiliser increased N_2O emissions by between 30 to 150 % compared to emissions from CAN alone following the application in spring to a grassland soil. This effect has been reported in a number of other studies (Stevens and Laughlin, 2001a; Stevens and Laughlin, 2002; Dittert et al., 2005; Velthof and Oenema, 1993).

The use of the ^{15}N tracer technique allowed the simultaneous measurement of N_2O and N_2, and hence the N_2O mole fraction ($N_2O/(N_2O + N_2)$) to be calculated. The application of CS and NO_3^- significantly increased N_2 emissions in March 2009 and March 2011. CS did not have an effect on N_2 emission at any other time. Previous studies have reported a range of N_2O mole fractions: Mathieu et al. (2006) reported a range of 0.15–0.94 measured from undisturbed soil cores following the application of ^{15}N-nitrate after 24 h; Stevens and Laughlin (2001a) measured an average N_2O mole fraction of 0.31 for $NH_4HCO_3NO_3$ and 0.66 for $CSNO_3$. Despite the high variability of reported values for N_2O mole fractions, the current study showed that an increase in the N_2O mole fraction occurred on each of the seven occasions when CS was applied with nitrate to grassland soils, compared to NH_4ClNO_3. This increase in N_2O mole fraction was due to the increase in N_2O emissions in the presence of CS. Averaged across the seven application dates the mole fraction was 0.34 for $CSNO_3$ compared to 0.24 for NH_4ClNO_3. The average N_2O mole fraction was lower (0.19) in June 2010, under

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relatively dry conditions, than at other times (average 0.34), indicating a lower N_2O mole fraction under conditions more conducive to nitrification.

4.2 N_2O a_D and N_2O d_D

As the occurrence of nitrification can be inferred from the rate of dilution of the labelled nitrate pool, N_2O a_D results have demonstrated that the rate of nitrification in $CSNO_3$ was slower than in NH_4ClNO_3, with a delay in the on-set of nitrification occurring in the $CSNO_3$ treatments. The application of a readily available organic carbon source to the soil stimulates microbial respiration and causes a subsequent decrease in oxygen concentration in the soil pore space (Tiedje, 1988). Stevens and Laughlin (2001a) also found that the application of CS increased soil respiration, thus creating conditions where NO_3 would be used as the terminal-electron acceptor instead of O_2.

In the current study, although nitrification often occurred it only made a significant contribution (35 %) to the N_2O flux in June 2010. At this time there was zero rainfall indicating that the dry soil conditions favoured nitrification. CS d_D values were not different from unity, hence all N_2O came from the denitrifying nitrate pool, as the metabolism of the carbon source in the slurry enhanced anaerobic conditions. When CS was not present the N_2O d_D values for NH_4ClNO_3 treatments were lower than those for $CSNO_3$ providing further evidence that nitrification rates were more rapid in the NH_4ClNO_3 treatments.

4.3 Effect of DCD

The N_2O a_D values in both $CSNO_3$ and NH_4ClNO_3 treatments were significantly higher with than without DCD on five occasions; therefore DCD appeared to be effective in inhibiting the nitrification process. DCD did not affect the N_2O a_D values in both $CSNO_3$ and NH_4ClNO_3 treatments in July 2009 or October 2009. Cumulative rainfall over five days post application was 30.0 mm and 33.0 mm for July and October 2009, respectively. This suggested that either anaerobic conditions inhibited nitrification or that DCD moved down the soil profile post application during this heavy rainfall, and therefore was not acting as a nitrification inhibitor on these occasions. Zerulla et al. (2001) highlighted that a shortcoming of using DCD was that it is susceptible to losses through leaching due to its high water solubility. Monaghan et al. (2009) showed that between 2 and 16 % of the DCD applied annually could be lost in drainage water.

Overall DCD significantly lowered ($P < 0.01$) both N_2O and N_2 fluxes in March 2009 and October 2009, but only N_2 fluxes in July 2009. It had no significant effect on cumulative emissions at other times. Although this study has found DCD to be an effective nitrification inhibitor by examining the changes in N_2O a_D, its effectiveness was not always translated into a reduction in N_2O emissions, when an ammonium-N (as mineral N or CS) and nitrate-N fertiliser source were applied together. DCD did not alter the fraction of the emitted N_2O which was derived from the denitrifying nitrate pool at any time in either the $CSNO_3$ or the NH_4ClNO_3 treatments. As the source of N_2O was found to be predominantly from the nitrate pool, the benefit in inhibiting NH_4^+-N oxidation by DCD, was too small to be seen against the large nitrate pool already present. Other studies have shown that DCD was effective in reducing N_2O emissions from ammonium based fertilisers (Dobbie and Smith, 2003; Skiba et al., 1993) and cattle slurries (Hatch et al., 2005; Merino et al., 2002). Skiba et al. (1993) found that N_2O was produced predominantly produced by nitrification when soils were dry and DCD reduced emissions by at least 40 %. A recent study conducted at two grassland sites in Ireland found DCD to be highly effective, reducing N_2O emissions from CS by up to 82 % (Cahalan et al., 2012). The effect of DCD in lowering N_2O emissions is limited in the presence of a nitrate source, when denitrification is the main source of N_2O.

5 Conclusions

The current study used the ^{15}N tracer technique to simultaneously measure N_2O and N_2 emissions from cattle slurry in the presence of fertiliser NO_3. N_2O emissions were predominantly from denitrification of the NO_3 pool. N_2O emissions from CS in the presence of NO_3 fertiliser were very high (0.4–8.7 % of applied N) over a 20 day period, under mild moist conditions in Northern Ireland. Emissions were significantly larger from the CS treatment compared to the NH_4Cl treatment, supplying the same rate of N as in the slurry. This was probably due to the easily mineralisable C components in the CS promoting N_2O emissions from the added fertiliser NO_3 pool. This study supports the view that organic fertilisers should not be applied at the same time as nitrate based fertilisers, as significant increases in N_2O emissions occur. The average N_2O mole fraction ($N_2O/(N_2O + N_2)$) over all seven application dates was 0.34 for $CSNO_3$ compared to 0.24 for the NH_4ClNO_3 treatment, indicating the dominance of N_2 emissions.

The rate of nitrification in $CSNO_3$ was slower than in NH_4ClNO_3 and DCD effectively inhibited nitrification in both treatments. However, the effect of DCD in lowering N_2O emissions is limited in the presence of a NO_3 fertiliser, when denitrification is the main source of N_2O. To obtain the maximum cost-benefit of DCD in lowering N_2O emissions, under mild moist conditions, its application should be restricted to ammonium based organic or synthetic fertilisers.

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Table 1. Properties and application rates of the cattle slurries.

	Raw CS properties												Amended CS properties			
	NH_4^+-N	Acetic acid	Ethanol	*i*-butyric acid	*i*-valeric acid	Lactic acid	*n*-butyric acid	*n*-valeric acid	Propanol	Propionic acid	Total VFAs	Dumas C	pH	Dry matter	NH_4^+-N rate	NO_3^--N rate
Application Date	$mg\,kg^{-1}$	$g\,l^{-1}$	$g\,l^{-1}$	$g\,l^{-1}$	$g\,l^{-1}$	$g\,l^{-1}$	$g\,l^{-1}$	$g\,l^{-1}$	$g\,l^{-1}$	$g\,l^{-1}$	$g\,l^{-1}$	$g\,kg^{-1}$ dry matter		%	$kg\,N\,ha^{-1}$	$kg\,N\,ha^{-1}$
March 2009	2845	5.54	0.00	0.16	0.30	0.00	0.14	0.00	0.00	1.66	7.80	409.9	7.88	5.00	135.1	65
June 2009	2001	7.98	0.00	0.26	0.38	0.00	0.88	0.14	0.00	2.72	12.36	430.2	7.88	5.00	82.7	65
October 2009	1545	5.74	0.00	0.18	0.34	0.00	0.36	0.00	0.00	1.70	8.32	370.2	7.40	3.79	103.4	65
March 2010	1960	3.99	0.00	0.07	0.17	0.00	0.16	0.00	0.00	0.51	4.90	415.8	8.27	5.02	140.6	65
June 2010	1671	4.28	0.00	0.12	0.20	0.00	0.46	0.00	0.00	1.06	6.12	421.3	7.14	5.39	114.7	65
October 2010	1068	2.14	0.10	0.00	0.14	0.00	0.08	0.00	0.00	0.08	2.54	393.7	7.52	3.16	80.0	65
March 2011	2485	5.18	0.00	0.16	0.30	0.00	0.50	0.06	0.00	1.42	7.62	424.9	7.43	5.00	73.9	65

Table 2. Cumulative fluxes of N_2O and N_2 evolved over 20 days after treatment application for $CSNO_3$ and NH_4ClNO_3 with and without DCD.

Application Date	Treatment	N_2O (kg N ha^{-1})			N_2 (kg N ha^{-1})			N_2O mole fraction ($N_2O/(N_2O + N_2)$)			Rainfall 5 d post application (mm)	Average soil temperature (at 5 cm depth) over 20 d (°C)
		without DCD	with DCD	**Signif.**	without DCD	with DCD	**Signif.**	without DCD	with DCD	**Signif.**		
March 2009	$CSNO_3$	17.28	12.79	**	42.38	21.77	**	0.28	0.36	**	7.1	7.8
	NH_4ClNO_3	8.79	6.70	NS	34.92	14.54	*	0.19	0.31	**		
July 2009	$CSNO_3$	12.91	12.73	NS	34.27	19.83	NS	0.29	0.38	NS	30.0	15.3
	NH_4ClNO_3	6.12	4.43	NS	30.11	18.19	NS	0.19	0.19	NS		
October 2009	$CSNO_3$	6.09	6.54	NS	10.42	14.97	NS	0.36	0.32	NS	33.0	8.2
	NH_4ClNO_3	4.18	5.15	NS	11.10	9.67	NS	0.29	0.36	NS		
March 2010	$CSNO_3$	9.71	9.01	NS	23.91	21.52	NS	0.30	0.29	NS	19.4	5.6
	NH_4ClNO_3	4.49	3.98	NS	21.35	16.99	NS	0.16	0.19	NS		
June 2010	$CSNO_3$	0.76	0.88	NS	3.77	3.43	NS	0.17	0.21	NS	0.0	15.4
	NH_4ClNO_3	0.51	0.47	NS	3.03	3.08	NS	0.15	0.13	NS		
October 2010	$CSNO_3$	8.60	6.60	NS	13.55	8.47	NS	0.39	0.44	NS	1.0	9.3
	NH_4ClNO_3	6.52	4.26	NS	12.23	9.49	NS	0.36	0.33	NS		
March 2011	$CSNO_3$	2.98	4.85	NS	3.27	4.32	NS	0.46	0.50	NS	5.5	10.1
	NH_4ClNO_3	1.18	0.70	*	2.47	1.32	*	0.33	0.24	*		

Significance levels: *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$, NS no significant difference.

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Table 3. The fraction of the ^{15}N labelled nitrate pool (a_D) for $CSNO_3$ and NH_4ClNO_3 with and without DCD.

	March 2009	July 2009	October 2009	March 2010	June 2010	October 2010	March 2011
Time to reach minimum detectable flux (days)	10	4	3	10	3	11	11
$CSNO_3$ without DCD	0.37	0.47	0.51	0.46	0.45	0.36	0.38
$CSNO_3$ with DCD	0.47	0.48	0.48	0.50	0.49	0.44	0.44
NH_4ClNO_3 without DCD	0.25	0.40	0.42	0.36	0.43	0.33	0.30
NH_4ClNO_3 with DCD	0.45	0.43	0.44	0.47	0.48	0.39	0.39
$CSNO_3$ vs NH_4ClNO_3	<0.001	<0.01	<0.01	<0.001	<0.01	NS	<0.001
DCD effect on $CSNO_3$	<0.001	NS	NS	<0.05	<0.001	<0.05	<0.01
DCD effect on NH_4ClNO_3	<0.001	NS	NS	<0.001	<0.001	<0.05	<0.01

NS, not significant at $P<0.05$, LSD, least significant difference at $P = 0.05$.

Table 4. The fraction of N_2O derived from the labelled nitrate pool (d_D) during peak N_2O emissions for $CSNO_3$ and NH_4ClNO_3 with and without DCD.

	March 2009	July 2009	October 2009	March 2010	June 2010	October 2010	March 2011
$CSNO_3$ without DCD	0.99	1.00	0.98	0.96	0.88	0.99	0.94
$CSNO_3$ with DCD	0.99	1.00	0.96	0.96	0.89	0.99	0.96
NH_4ClNO_3 without DCD	0.96	0.97	0.95	0.90	0.65	0.98	0.87
NH_4ClNO_3 with DCD	0.98	0.93	0.96	0.88	0.65	0.97	0.76
Difference from unity							
$CSNO_3$ without DCD	NS	NS	NS	NS	NS	NS	NS
$CSNO_3$ with DCD	NS	NS	NS	NS	NS	NS	NS
NH_4ClNO_3 without DCD	<0.01	NS	NS	<0.05	<0.001	NS	<0.05
NH_4ClNO_3 with DCD	<0.05	NS	NS	<0.05	<0.001	NS	<0.05
$CSNO_3$ vs NH_4ClNO_3	<0.001	NS	NS	<0.05	<0.001	NS	<0.01
DCD effect on $CSNO_3$	NS	NS	NS	NS	NS	NS	NS
DCD effect on NH_4ClNO_3	NS	NS	NS	NS	NS	NS	NS

NS, not significant at $P < 0.05$, LSD, least significant difference at $P = 0.05$.

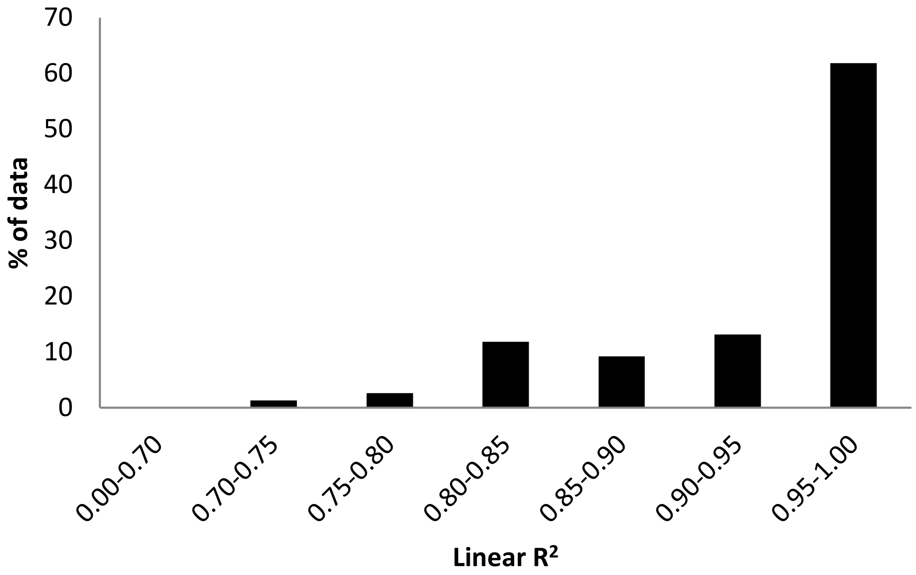

Fig. 1. Percentage of data for given ranges of co-efficient of determination (R^2) of the linear regression, $n = 76$.

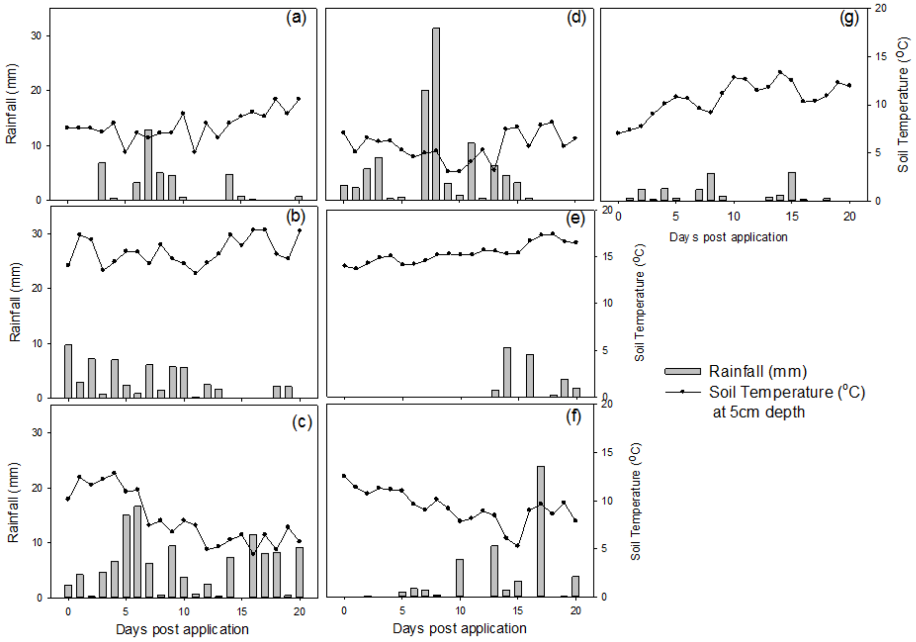

Fig. 2. Rainfall and soil temperature at 5 cm depth for 20 days post treatment application for: **(a)** March 2009, **(b)** July 2009, **(c)** October 2009, **(d)** March 2010, **(e)** June 2010, **(f)** October 2010, **(g)** March 2011.

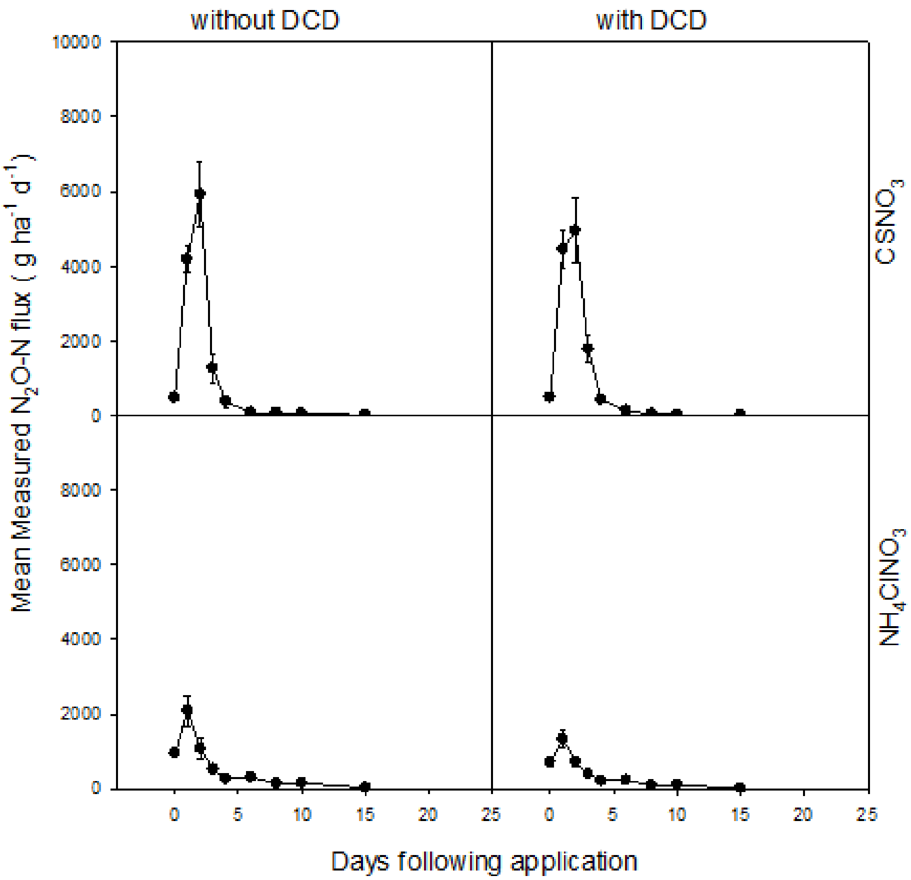

Fig. 3. Mean measured N_2O-N fluxes versus time for $CSNO_3$ and NH_4ClNO_3 with and without DCD for July 2009.

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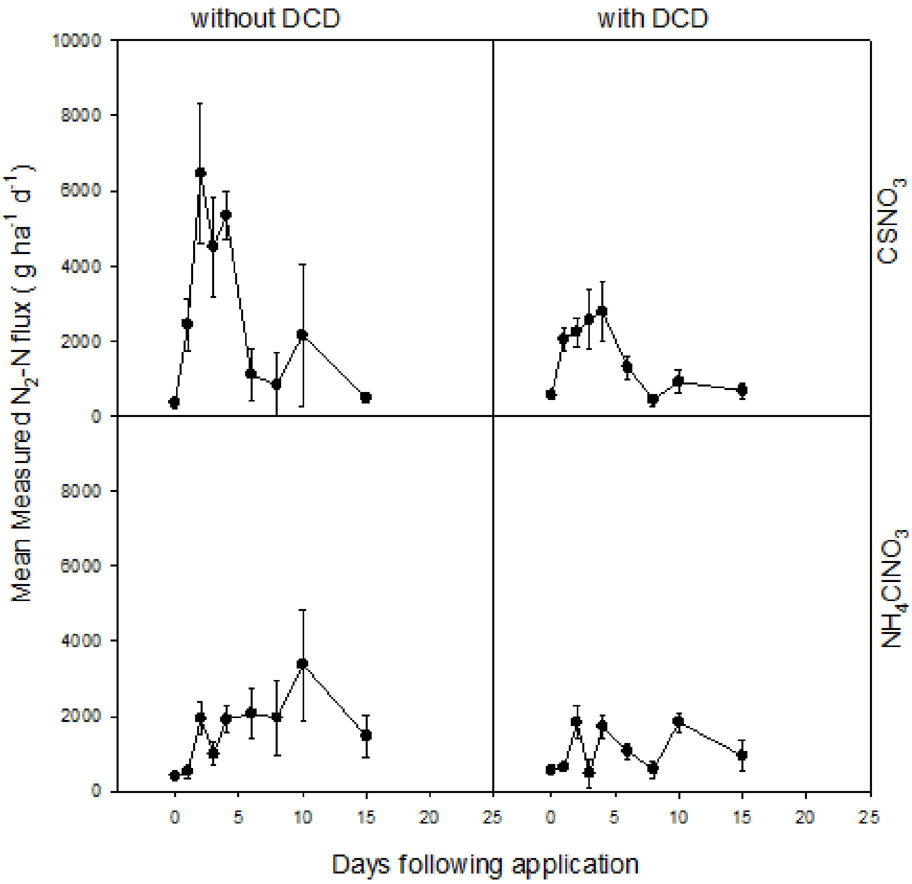

Fig. 4. Mean measured N_2-N fluxes versus time for time for $CSNO_3$ and NH_4ClNO_3 with and without DCD for July 2009.

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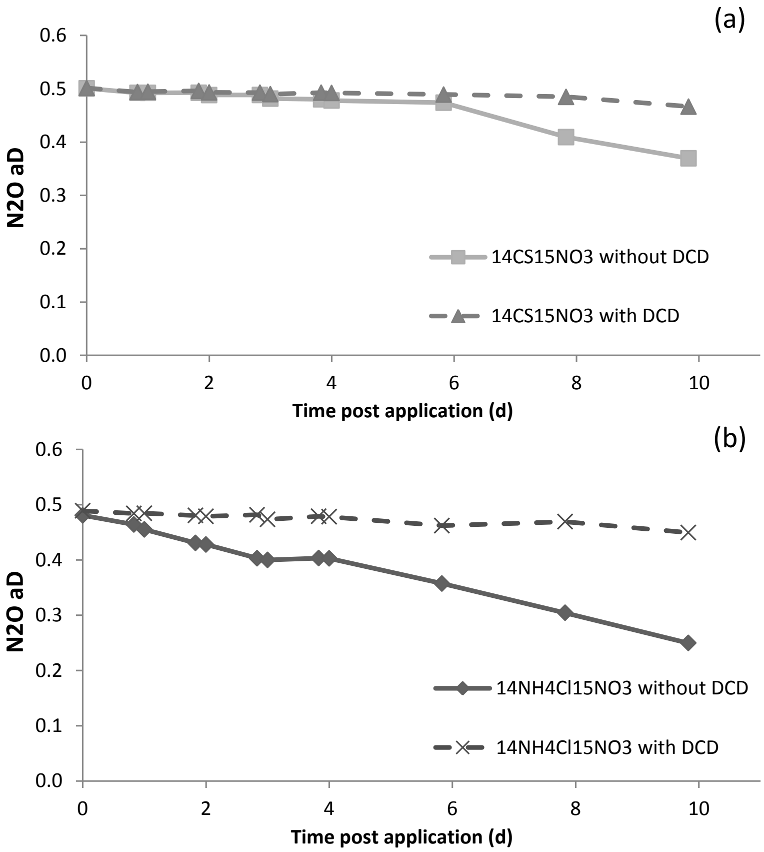

Fig. 5. Change in the ^{15}N mole fraction of the labelled nitrate pool (a_D) over time in March 2009 for $^{14}CS^{15}NO_3$ **(a)** and for $^{14}NH_4Cl^{15}NO_3$ **(b)** with and without DCD.

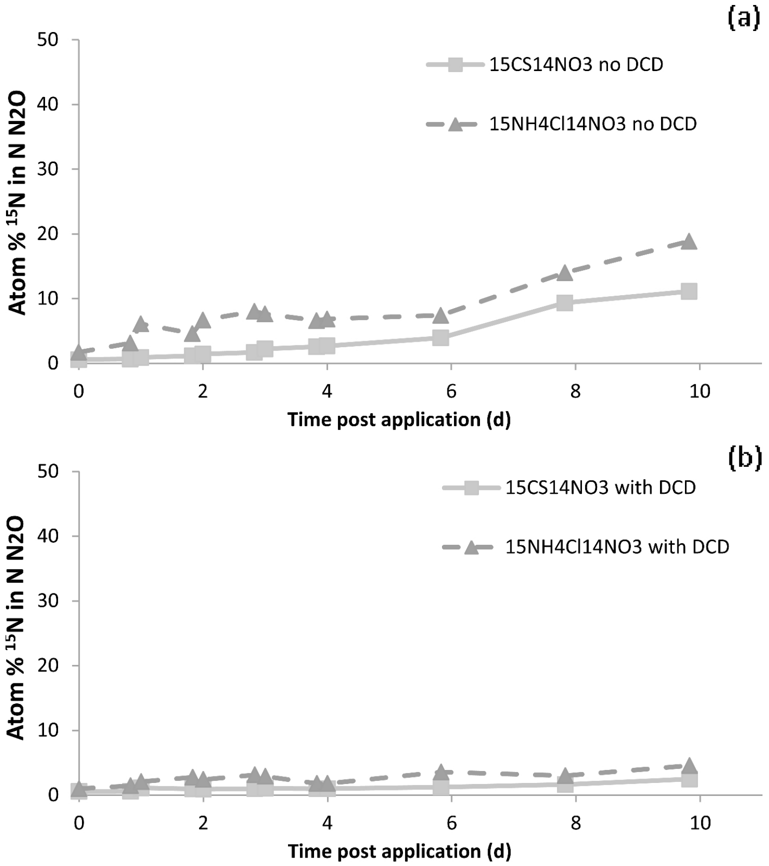

Fig. 6. Change in atom% ^{15}N in N_2O over time in March 2009 for $^{15}CS^{14}NO_3$ and $^{15}NH_4Cl^{14}NO_3$ without DCD **(a)** and with DCD **(b)**.

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