



TITLE The effect of precipitation and application rate on dicyandiamide persistence and efficiency in two Irish grassland soils

AUTHORS Cahalan, E., Minet, E., Ernfors, M., Müller, C., Devaney, D., Forrester, P. J. and Richards, K. G.

This article is provided by the author(s) and Teagasc T-Stór in accordance with publisher policies.

Please cite the published version.

The correct citation is available in the T-Stór record for this article.

NOTICE: This is the accepted version of the following article: Cahalan, E., Minet, E., Ernfors, M., Müller, C., Devaney, D., Forrester, P. J. and Richards, K. G. (2015), The effect of precipitation and application rate on dicyandiamide persistence and efficiency in two Irish grassland soils. *Soil Use and Management*, 31: 367–374, which has been published in final form at <http://dx.doi.org/10.1111/sum>.

This item is made available to you under the Creative Commons Attribution-Non commercial-No Derivatives 3.0 License.



The effect of precipitation and application rate on DCD persistence and efficiency in two Irish grassland soils

Cahalan, E.^{1, 2}, Minet, E.¹, Ernfors, M.^{1, 3}, Müller, C.^{2, 4}, Devaney, D.⁵ Forrester, P.J.¹ and Richards, K. G.^{1*}

1 = Teagasc, Johnstown Castle, Environmental Research Centre, Co. Wexford, Ireland.

2 = School of Biology and Environmental Science, University College Dublin, Belfield, Dublin 4, Ireland.

3 = Department of Biosystems and Technology, Swedish University of Agricultural Sciences, PO Box 104, SE 23053, Alnarp, Sweden.

4 = Department of Plant Ecology, Justus-Liebig University Giessen, Heinrich-Buff-Ring 26, 35392 Giessen, Germany.

5 = Environmental Agency, South East Regional Office, Kings Meadow House, Kings Meadow Road, Reading, Berkshire, RG1 8DQ United Kingdom.

***Corresponding Author:** Richards, K. G (karl.richards@teagasc.ie)

Running Title: DCD Recovery

Abstract

The nitrification inhibitor dicyandiamide (DCD) has had variable success in reducing nitrate (NO_3^-) leaching and nitrous oxide (N_2O) emissions from soils receiving nitrogen (N) fertilisers. Factors such as soil type, temperature and moisture have been linked to the variable efficacy of DCD. Since DCD is water soluble it can be leached from the rooting zone where it is intended to inhibit nitrification. Intact soil columns (15 cm diameter by 35 cm long) were taken from luvisc gleysol and haplic cambisol grassland sites and placed in growth chambers. DCD was applied at 15 or 30 kg DCD ha^{-1} , with high or low precipitation. Leaching of DCD, mineral N and the residual soil DCD concentrations were determined over eight weeks. High precipitation increased DCD in leachate and decreased recovery in soil. A soil x DCD rate interaction was detected for the DCD unaccounted (proxy for degraded DCD). In the cambisol degradation of DCD was high (circa 81%) and unaffected by DCD rate. In contrast DCD degradation in the gleysol was lower and differentially affected by rate, 67 and 46% for the 15 and 30 kg ha^{-1} treatments, respectively. Differences in DCD degradation rates between soils may be related to differences in organic matter content and associated microbiological activity. Variable degradation rates of DCD in soil, unrelated to temperature or moisture, may contribute to varying DCD efficacy. Soil properties should be considered when tailoring DCD strategies for improving nitrogen use efficiency and crop yields, through the reduction of reactive nitrogen loss.

Keywords: nitrification inhibitor, nitrate, dicyandiamide, nitrogen use efficiency, leaching, grassland soils

Introduction

Application of dicyandiamide (DCD) has been reported to reduce nitrate (NO_3^-) leaching from urine treated grassland lysimeters by 10 to 76 % (Di & Cameron, 2004; Dennis et al., 2012; Zaman & Blennerhassett, 2010) and nitrous oxide (N_2O) emissions by 25 to 70% (Di & Cameron, 2007; Smith et al., 2008, Zaman & Blennerhassett, 2010). This is due to reduced nitrification rates and thus a reduced quantity of NO_3^- -N in the soil profile which is available for leaching or denitrification. We would therefore view DCD as a possible mitigation strategy to improve N efficiency in Irish soils over the autumn and winter period, either during extended grazing or slurry spreading.

Although substantial improvements in N recovery through the use of DCD have been observed (Di & Cameron, 2004; Smith et al., 2008; Singh et al., 2009), the range of improvements varies significantly. Some studies have shown relatively small yield and/or environmental benefits of using DCD (Misselbrook et al., 1996; Pain et al., 1994; Monaghan et al., 2009; Cahalan et al., 2014). This raises the question of why DCD is more effective in some studies than in others.

DCD degradation in soil is affected by soil temperature, soil moisture and clay content (Hallinger et al., 1990). Soil texture and carbon content have also been shown to affect DCD efficacy (McCarty & Bremner, 1989). DCD is subject to microbial decay in soils, where it can be rapidly metabolised provided that certain species of bacteria are present (Hallinger et al., 1990; Schwarzer et al., 1991; Estermaier et al., 1992). Degradation of DCD has been reported to be correlated with soil temperature, with half-life ranging from 6-15 days at 25°C (Kelliher et al., 2008). Rajbanshi et al., (1992) found that a temperature increase of 10°C doubled the degradation rate of DCD in soil, suggesting that a metabolic rather than chemical process degrades DCD.

Increasing soil temperature with increasing moisture contents has also shown to linearly reduce the half-life of DCD in soil (Singh et al., 2008). Bock et al., (1981) suggested that DCD may be lost by leaching, as DCD is relatively soluble in water (23g L^{-1} at 13°C) and is therefore at risk of being separated from ammonium-N.

Leaching of DCD has been observed to be related to soil type and precipitation, with higher DCD leaching occurring under higher precipitation on free draining soils. Teske & Matzel (1988) found that in a sandy soil 50 - 80% of DCD could be leached as a result of irrigation. Menneer et al., (2008) found that 58% of applied DCD was leached over a period of 192 days from free-draining soil lysimeters kept under field conditions. Shepherd et al., (2012) found that both precipitation and soil type significantly affected DCD leaching, with 12-45% of applied DCD leached during the experiment. Thus there are a number of important factors controlling DCD concentration and efficacy in soils. This contributes to the uncertainty involved in determining the effectiveness of DCD applications to different agricultural soils.

Grasslands in Ireland, receive 800 - 1200 mm precipitation per year (Met Eireann, 2010). Temperate soils are thus subjected to high levels of leaching pressure. Autumn field conditions in Ireland usually consist of high precipitation coupled with relatively high soil temperatures ($12\text{-}14^{\circ}\text{C}$), which are conditions conducive for leaching to occur.

The use of DCD is a recognised measure to mitigate both NO_3^- leaching and N_2O emissions. However, under high levels of precipitation (such as in Ireland), where reductions in soil NO_3^- concentrations are required, DCD has greater susceptibility to leaching from the soil profile. The efficacy of DCD has been shown to be greater at

drier soil moisture contents (Hallinger et al., 1990). We investigated the effect of simulated precipitation and DCD application rate on two contrasting temperate grassland soils under controlled conditions with the objective of establishing whether DCD degradation is potentially affected by soil factors that might explain the varying effects of DCD on yield and environmental parameters, which have been reported in the literature.

Materials and Methods

Intact soil columns were taken from two contrasting soils and placed in a growth chamber where environmental parameters such as temperature and moisture could be manipulated to coincide with Irish autumn conditions, a period when DCD usage would be potentially of greatest benefit.

Soil Column Preparation

Soil columns were in Ireland. The world reference base classifications for the soils collected from two contrasting grassland sites were a luvic gleysol (gleysol) at Johnstown Castle (52°18'N; 6° 30'W) and a haplic cambisol (cambisol) at Moorepark (52°17'N; 8°23'W) (for soil properties see, Table 1). Although similar in texture at the surface, the gleysol demonstrates a clay content increase with depth whereas for the cambisol the clay content decreased with depth (Kramers et al., 2009). Both soils were selected as they were part of a larger experiment investigating the efficacy of DCD in reducing reactive nitrogen losses from dairy farming. Historically the soils were both intensively managed but to minimize variability had received no slurry or

fertiliser and were ungrazed for two years prior to cores being collected. Both soils had similar mineral N concentrations before the experiment began. Intact soil columns were used so that simulated precipitation would percolate downwards through the soil profile. The soil columns were collected in cylindrical PVC drainage pipes with an internal diameter of 152 mm and length of 350 mm. Grass on top of the soil columns was cut to 3 mm high, to minimise the influence of herbage growth on the experiment, as both sites may have differed in herbage production, potentially increasing the variability of the results. A steel cutting ring was placed over the PVC pipes to extract the soil columns. The cutting ring was gradually pushed into the ground using a mechanical excavator and then soil was removed gradually from the base of the cutting ring as the pipe was lowered into the soil. The bottom 5 cm of soil from the soil columns was then removed and fine gravel was added in its place to aid drainage. Heated petrolatum was poured down the space between the soil columns and the edge of the PVC pipe, to prevent edge flow effects (Cameron et al., 1992). The base of each soil column was sealed using a stop-end cap, with a 5mm wide drainage outlet pipe. Leachate was accumulated in 1L polyethylene collection flasks, which were placed under each soil column. Each soil column was saturated before the initiation of the experiment and then left to drain for 48 hours until a drained upper limit of water content was reached.

Experimental Design

Each soil column was randomly assigned to a $2 \times 3 \times 2$ (soil \times DCD rate \times precipitation) factorial arrangement, within an environmental control chamber, with four replicates per treatment. Each column was randomly assigned into a block of four replicates. Environmental conditions within the chamber were set to a typical Irish

autumn regime of 12°C during the day, 8°C at night and a constant humidity (85%) (Met Eireann, 2010). Daylight was set to 12 hours each day (typical for autumn) and the soil columns were placed in the growth chamber for two weeks before treatments were applied to allow for acclimation of the soil. During this period each soil column was kept watered to offset any potential evaporation losses. There were two precipitation treatments used in this experiment, low (30 year average) and high (twice the 30 year average). The total volume of simulated rainfall was the equivalent of 179 mm and 358 mm for the low and high precipitation treatments, respectively. Precipitation was manually applied using a polypropylene syringe fitted with a spray nozzle attachment at all times. On the sixth day of each week 20 mm (low precipitation) or 40 mm (high precipitation) of water was applied to simulate precipitation events, which are typical daily figures for high rainfall days in Ireland. Water was applied in 4 splits over a 24 hour period to ensure excessive volumes of water were not applied at once as this would not occur naturally and could lead to surface ponding (Sigua et al., 1993). Maintenance precipitation of 2 mm was applied every two days to maintain soil moisture status and offset any potential losses through evaporation.

List of experimental treatments

- (1) 0 DCD, low precipitation
- (2) 15 kg DCD ha⁻¹, low precipitation
- (3) 30 kg DCD ha⁻¹, low precipitation
- (4) 0 DCD, high precipitation
- (5) 15 kg DCD ha⁻¹, high precipitation
- (6) 30 kg DCD ha⁻¹, high precipitation

Treatments 1 - 6 were applied to both the Johnstown Castle (gleysol) and Moorepark (cambisol) soil columns and all treatments received $(\text{NH}_4)_2\text{SO}_4$ applied at a rate of 60 kg N ha⁻¹. The N rate was chosen to reflect the average inorganic N application rate associated with landspreading cattle slurry on grassland in Ireland. Cattle slurry can be spread onto grassland fields in Ireland up until 15th October each year. The DCD rate of 15 kg ha⁻¹ was chosen as this was the recommended rate used in New Zealand where DCD was found to be effective.

DCD was mixed with deionised water before application. Soil columns not receiving DCD had an equivalent volume (50 ml) of water applied. The DCD and N treatments were combined and applied to each of the corresponding soil columns in a solution using a polypropylene syringe with a cone shaped nozzle attachment. Leachate was taken from the collection jar at the base of each soil column on the seventh day of each week (24h after precipitation event) for eight weeks and stored at 4°C until analysis commenced.

Sampling and Chemical Analysis

The total drainage volume was recorded from each core after each precipitation event. Three sub-samples were transferred to 50 ml centrifuge tubes. The 1L polyethylene containers were emptied, cleaned and replaced under each corresponding core for the following precipitation event. Samples requiring DCD analysis were filtered through a 0.45 µm membrane filter to remove most physical contaminants prior to analysis.

When the leaching period of the experiment was complete, each core was destructively sampled ten weeks post treatment application. Soil samples were taken at 0-10, 10-20, and 20-30 cm layers. Each soil layer was extracted using 2M KCl to determine DCD, NO_3^- -N and NH_4^+ -N contents. Leachate and soil extract NO_3^- -N and NH_4^+ -N concentrations were analysed colorimetrically (HMSO, 1982; Kopp & McKee, 1983) using a KONE Aquakem Analyser (600A Module, Labmedics Analytical Solutions). DCD was analysed by reverse-phase HPLC analysis (Waters Alliance 2695) and UV-visible detection (Turowski & Deshmukh, 2004) at 215 nm with a photodiode array detector (Waters 996). Method detection limits (mg L^{-1}), of each analyte were as follows - DCD 0.005; NO_3^- -N 0.25; and NH_4^+ -N 0.09. The DCD extraction efficiency using KCl was 95.6% for the gleysol and 95.3% for the cambisol. This was tested by adding a known quantity of DCD to a test soil and analysing the extracted material.

Calculations and Statistics

Concentrations of DCD and N were converted from mg L^{-1} to kg ha^{-1} by multiplying soil column drainage volume and leachate concentration and then using soil column surface area, to scale up to a per hectare basis. Treatment effects on the response variables measured using the GLIMMIX procedure of SAS 9.3 (© 2002-2010, SAS Institute Inc., Cary, NC, USA). Mean separation was by Tukey's mean comparison test. The control (no DCD) treatment was excluded from the analysis as it contained no DCD.

Results

Cumulative drainage from each treatment

Between 56 – 100 % of applied precipitation (179 mm and 358 mm for the low and high precipitation treatments, respectively) was recovered from each core 24 h after each precipitation event was completed.

DCD recovery in leachate

The concentration of DCD in leachate ranged from 6 to 21% of DCD applied in the gleysol and 6 to 18% of DCD applied in the cambisol (Figure 1). There was a highly significant effect ($P < 0.001$) of precipitation on the percentage of DCD recovered in leachate (Table 2). Recovery of DCD was significantly greater in the high precipitation treatments (18%), compared with low precipitation treatments where 7% of applied DCD was recovered in leachate (Table 3), when averaged over soil and DCD rate.

Soil DCD recovery

Recovery of DCD in soil varied from 3 to 57 % (Figure 1). There was a significant interaction between soil and DCD rate and a significant effect of precipitation on the recovery of DCD in soil at the end of the experiment (Table 2). The percentage of DCD recovered from the gleysol at the high DCD rate (43%) was greater than that from the low DCD rate (19%) (Table 3). However, for the cambisol the percentage of applied DCD was unaffected by DCD application rate. Recovery of DCD was greatly

affected by the soil type, with the cambisol retaining significantly smaller DCD concentrations than the gleysol (Table 3). Precipitation was important for the percentage of applied DCD recovered in the soil at the end of the experiment. Significantly more DCD (26%) was recovered from soil under low precipitation compared with high precipitation, from which 12% of DCD was recovered.

Unaccounted DCD

Determination of the percentage of DCD that was not accounted for at the end of the experiment ranged from 35 to 87% and resulted in the detection of three significant interactions (Table 2). The interaction between soil x DCD rate was significant, Table 3 outlines how the percentage of unaccounted DCD was greater for the cambisol and was unaffected by DCD application rate. The unaccounted DCD pool was smaller for the gleysol irrespective of DCD rate. However the percentage of DCD which was unaccounted for was significantly less at the 30 kg ha⁻¹ DCD rate. Although a soil × precipitation interaction was detected (P = 0.03), a significantly greater percentage of DCD was not accounted for in the cambisol compared with the gleysol. This unaccounted for DCD pool was not affected differentially according to Tukey's mean comparison test (Table 3). The DCD rate × precipitation effect was also significant. The percentage of DCD which was unaccounted for was not differentially affected by DCD rate but, as already stated, under the high precipitation regime a smaller percentage of DCD was unaccounted for at the 30 compared with the 15 kg ha⁻¹ rate.

Mineral N leaching

Two significant interactions were detected for cumulative NO_3^- -N leached, these were soil x DCD rate and soil x precipitation (Table 2). Mean NO_3^- -N leached varied from 5.2 kg ha^{-1} (cambisol low precipitation at 15 kg DCD rate) to 44.4 kg ha^{-1} (gleysol low precipitation at 0 DCD) over the eight week rainfall period (Table 4). Cumulative NO_3^- -N leaching from the cambisol at low precipitation was 6.4 kg ha^{-1} which was significantly less than from the cambisol (18.6 kg ha^{-1}) and both gleysol treatments (23.1 and 22.3 kg ha^{-1}), where NO_3^- leaching was unaffected by precipitation regime (Table 4). There was significantly more NO_3^- -N leaching from the gleysol at the 0 DCD rate (37.7 kg ha^{-1}) compared with the DCD treatments (Table 4). While NO_3^- leaching rates were smaller for the cambisol than the gleysol control, DCD application did not reduce NO_3^- leaching in the former soil. There was no significant effect of DCD application rate on NO_3^- leaching from the cambisol.

Cumulative NH_4^+ -N leaching ranged from 0.03 to 2.02 kg ha^{-1} on the cambisol low precipitation 15 kg DCD rate and gleysol high precipitation 30 kg DCD, respectively. Although losses were small, a significant interaction between soil and precipitation for NH_4^+ leaching was detected. Cumulative NH_4^+ -N leaching was significantly greater in the gleysol high precipitation (1.76 kg ha^{-1}) compared to the gleysol low precipitation (0.54 kg ha^{-1}) and to both cambisol treatments (0.04 and 0.17 kg ha^{-1} for low and high precipitation, respectively).

Discussion

DCD leaching & recovery

A large percentage of this DCD that was unaccounted for in leachate or soil was most likely degraded to its end products of NH_3 , CO_2 and H_2O (Amberger, 1989). It has been reported that DCD can adsorb to organic matter (OM) or clay particles within the soil (Singh et al., 2008). The DCD extraction efficiencies using KCl for both soils were >95% and thus DCD adsorption is likely to be a minor issue in relation to the observed recoveries. DCD has been observed to degrade over time and at 12°C DCD has been found to degrade completely after 12 weeks in some soils (Amberger, 1989). This could explain why there were high rates of DCD degradation in the cambisol. The degradation rates of DCD in both the soils differed significantly, although both soils were incubated at the same temperature and had similar DCD leaching levels. In a meta-analysis, Kelliher et al. (2008) identified a negative relationship between DCD half-life and temperature. Using this relationship the predicted half-life of DCD in the current study was 73 days. However, over the duration of the study (63 days) degradation rates approaching 90% were observed in one soil. Both soils were incubated at the same temperature, thus controlling for the temperature effect on degradation rate which suggests that other factors are at play in driving differential DCD degradation rates across soils. DCD has been reported to degrade faster at high soil organic matter contents (Amberger & Vilsmeier, 1979; Puttana et al., 1991). Although both soils in this experiment were high in OM, the gleysol had a 30% smaller OM content than the cambisol, which could have contributed to the larger degradation rates in the cambisol, due to greater biological activity (Fontaine et al., 2003). Our results are consistent with reports that DCD degradation is influenced by soil chemical and microbial properties in addition to temperature, although this hypothesis requires further testing in an experiment outside the scope of this study.

Ernfors et al., (2013) also reported significant differences in DCD degradation rates in 3 soils incubated at 15°C and these soils had contrasting chemical and microbial properties.

The results indicate that there is a negative relationship between the percentage of applied DCD retained in soil and precipitation. These findings are in agreement with Shepherd et al., (2012) who reported DCD leaching levels of 12 to 46% which increased with increasing precipitation. In addition Shepherd et al., (2014) observed that drainage volume influenced DCD efficacy with a 7% decrease in efficacy per 100mm of extra drainage. However, DCD retention can also be affected by soil (Singh et al., 2008). Corre & Zwart (1995) found that only 7% of the DCD applied to a peat soil was leached to groundwater. In our study no significant effect of soil on DCD leaching was observed. This is consistent with Shepherd et al., (2012) who observed that soil effects on DCD leaching were directly related to drainage volume, although we did not observe any significant effect of soil on drainage volume in our study.

Mineral N leaching

In the 0 DCD control treatments, there was significantly more NO_3^- leaching from the gleysol than in the cambisol, suggesting a higher N mineralisation potential in this soil (Hoekstra et al., 2011). DCD was found to significantly reduce nitrate leaching in the gleysol by 64 and 55% for the 15 and 30 kg DCD ha^{-1} application rates, respectively. These reductions in leaching are in line with other findings (Dennis et al., 2012; Singh et al., 2009). The lack of an effect of DCD on NO_3^- leaching from the cambisol is

thought to be due to the rapid DCD degradation rates observed in this soil. In a field study on the same cambisol, O'Connor et al. (2012) observed that DCD had almost no effect on soil mineral N content which the authors attributed to DCD leaching. Our study highlights that the higher rates of DCD degradation on this cambisol is a more likely reason for the lack of nitrification inhibition observed in both studies.

DCD did not affect NH_4^+ -N level in leachate (Table 2), as has been reported previously (Singh et al., 2009). Loads of NH_4^+ leached were small in this experiment. Significantly greater rates of NH_4^+ leached from the gleysol at the high precipitation level compared to the low precipitation and from the cambisol at both precipitation levels. This could be due to 1. macropore leaching (Kramers et al., 2009) or 2. a higher rate of N mineralisation within the gleysol, or 3. greater inhibition of nitrification in the gleysol, which resulted in a greater pool of NH_4^+ -N available for leaching or a combination of all of these factors. Increasing the DCD rate from 15 kg ha^{-1} up to 30 kg ha^{-1} did not impact on the cumulated NO_3^- -N and NH_4^+ -N concentrations in the drainage water from either soil, suggesting that at moderate rates of N application (60 kg N ha^{-1}), increasing the DCD application rate over 15 kg DCD ha^{-1} is not beneficial.

Our study highlights the point that the efficacy of DCD and associated agronomic and or environmental benefits are likely to be soil specific and therefore requires optimal DCD application rates and strategies to be tailored by soil. The similar DCD leaching observed between soils is more than likely due to the similar total leachate drainage volumes which Shepherd et al., (2012 & 2014) found was strongly associated with DCD leaching. The main difference between the two soils that influenced DCD

efficacy was the significant difference in unaccounted for DCD which is expected to be a useful proxy for DCD degradation.

Conclusion

The efficacy of DCD in reducing nitrate leaching is soil dependent. Soil type was found to significantly affect total DCD recovery from soil and leachate, which varied from 31 to 65 % in the gleysol to 13 to 23% on the cambisol. Leaching of DCD was similar between the two soils and was not associated with DCD effects on nitrate leaching. The low DCD recovery on the cambisol was associated with no significant effect of DCD use on nitrate leaching on this soil. Our results suggest that increasing the rate of DCD above 15 kg ha⁻¹ does not increase the efficacy of DCD on nitrate leaching in either of the soils tested. Greater precipitation had a negative impact on DCD retention in both soils, which has implications for using DCD in countries such as Ireland. Soil properties are important factors to be considered when tailoring DCD management strategies for reduction of reactive nitrogen loss to the environment, improving nitrogen use efficiency and crop yields.

Acknowledgements

The authors would like to thank P.J. O'Connor for soil column collection, Nicholas Cavan for DCD recovery and all the laboratory/field staff at Teagasc Johnstown Castle and Moorepark with their assistance on this project. To Jim Grant for his statistical advice. This research was financially supported under the National Development Plan, through the Research Stimulus Fund, administered by the Department of Agriculture, Food and the Marine under grants 07519 and 07545.

References

- Amberger, A. & Vilsmeier, K. 1979. Inhibition of the nitrification of liquid manure nitrogen by dicyandiamide. *Journal of Agronomy & Crop Science* **148**, 239–246.
- Amberger, A. 1989. Research on dicyandiamide as a nitrification inhibitor and future outlook. *Communications in Soil Science and Plant Analysis* **20**, 1933-1955.
- Bock, B. R., Lawrence, J. E. & Williams, H. M. 1981. Relative mobility of dicyandiamide, ammonium and urea by mass flow in soils. In: *Proceedings of the Technical Workshop on Dicyandiamide* (eds R.D.Hauck & H.Behnke), SKW Trostberg, Germany, pp 25–37,
- Cahalan, E., Ernfors, M., Müller, C., Devaney, D., Laughlin, R. J., Watson, C. J., Hennessy, D., Khalil, M. I., McGeough, K. L. & Richards, K. G. 2014. The effect of the nitrification inhibitor dicyandiamide (DCD) on nitrous oxide and methane emissions after cattle slurry application to Irish grassland. *Agriculture, Ecosystems and Environment*, **199**, 339-349.
- Cameron, K. C., Smith, N. P., McLay, C. D. A., Fraser, P. M., McPherson, R. J., Harrison, D. F. & Harbottle, P. 1992. Lysimeters without edge flow: An improved design and sampling procedure. *Soil Science Society of America Journal*, **56**, 1625-1628.
- Corre, W. J. & Zwart, K. B. 1995. Effects of DCD addition to slurry on nitrate leaching in sandy soils. *Netherlands Journal of Agricultural Science* **43**, 195-204.
- Dane, J. H. & Clarke Topp, G. 2002. Methods of Soil Analysis - Part 4 Physical Methods. *Chapter 6 - Miscible Solute Transport*. Madison, Wisconsin, USA, Soil Science Society of America.
- Dennis, S.J., Cameron, K.C., Di, H.J., Moir J.L., Staples, V., Sills, P. & Richards K.G. 2012. Reducing nitrate losses from grazed grassland in Ireland using a nitrification inhibitor (DCD). *Biology and the Environment* **1**, 79-89.

- Di, H. J. & Cameron, K. C. 2004. Treating grazed pasture soil with a nitrification inhibitor, eco-N™, to decrease nitrate leaching in a deep sandy soil under spray irrigation - a lysimeter study. *New Zealand Journal of Agricultural Research* **47**, 351-361.
- Di, H. J., Cameron, K. C. & Sherlock, R. R. 2007. Comparison of the effectiveness of a nitrification inhibitor, dicyandiamide, in reducing nitrous oxide emissions in four different soils under different climatic and management conditions. *Soil Use and Management* **23**, 1-9.
- Ernfors, M., Brennan, F. P., Richards, K. G., McGeough, K. G., Griffiths, B. S., Laughlin, R. J., Watson, C. J., Philippot, L., Grant, J., Minet, E. P., Moynihan, E., & Müller, C. 2014. The nitrification inhibitor dicyandiamide increases mineralization-immobilisation turnover in slurry-amended grassland soil. *The Journal of Agricultural Science* **152**, 137-149.
- Estermaier, L. M., Sieber, A. H., Lottspeich, F. L., Matern, D. H. M. & Hartmann, G. R. 1992. Biochemical degradation of cyanamide and dicyandiamide. *Angewandte Chemie International Edition in English* **31**, 620-622.
- Fontaine, S., Mariotti, A. & Abbadie, L. 2003. The priming effect of organic matter: A question of microbial competition? *Soil Biology & Biochemistry* **35**, 837-843
- Hallinger, S., H. Goldbach, P. Wallnofer, & A. Amberger. 1990. Studies of the biodeterioration of the nitrification inhibitor dicyandiamide ("Didin"). *Verband Deutscher Landwirtschaftlicher Untersuchungs und Forschungsanstalten Reihe Kongressberichte* **32**, 665-670.
- HMSO. 1982. Ammonia in Waters, In S. C. o. Analysts, ed. Methods for the Examination of Water and Associated Materials (Blue Book). HMSO, London.
- Hoekstra, N.J., Lalor, S., Richards, K.G., O'Hea, N., Dungait, J., Schulte, R.P.O & Schmidt, O. 2011. The fate of slurry N fractions in herbage and soil during two growing seasons following application. *Plant and Soil* **342**, 83-96.

- Kelliher, F. M., Clough, T. J., Clark, H., Rys, G. & Sedcole, J. R. 2008. The temperature dependence of dicyandiamide (DCD) degradation in soils: A data synthesis. *Soil Biology and Biochemistry* **40**, 1878-1882.
- Kopp, J.F. & McKee, G. D. 1983. Phosphorus, all forms. Method 365.2 (Colorimetric, Ascorbic Acid, Single Reagent) Methods for chemical analysis of water and wastes. EPA 600/4-79/020. U.S. Environmental Protection Agency, Cincinnati, OH.
- Kramers, G., Richards, K.G. & Holden, N.M. 2009. Using image analysis to determine the effect of soil type and initial moisture conditions on preferential flow in three Irish grassland soils. *Geoderma* **153**, 362–371.
- McCarty, G. W. & Bremner, J. M. 1989. Laboratory Evaluation of Dicyandiamide as a Soil Nitrification Inhibitor. *Communications in Soil Science and Plant Analysis* **20**, 2049-2065.
- Menneer, J. C., Ledgard, S. & Sprosen, M. 2008. Soil N process inhibitors alter nitrogen leaching dynamics in a pumice soil. *Australian Journal of Soil Research* **46**, 323-331.
- Met Eireann (2010). Climate - 30 Year Averages – Rosslare [Internet]. Available at: <http://www.met.ie/climate/rosslare.asp>; accessed 11/05/13.
- Misselbrook, T.H., Laws, J.A. & Pain, B.F. 1996. Surface application and shallow injection of cattle slurry on grassland: nitrogen losses, herbage yields and nitrogen recoveries. *Grass and Forage Science* **51**, 270-277.
- Monaghan, R. M., Smith, L. C. & Ledgard, S. F. 2009. The effectiveness of a granular formulation of dicyandiamide (DCD) in limiting nitrate leaching from a grazed dairy pasture. *New Zealand Journal of Agricultural Research* **52**, 145-159.
- O'Connor, P.J., Hennessy, D., Brophy, C., O'Donovan, M. & Lynch M.B. 2012. The effect of the nitrification inhibitor dicyandiamide (DCD) on herbage production when applied at different times and rates in the autumn and winter. *Agriculture, Ecosystems and Environment* **152**, 79– 89

- Pain, B. F., Misselbrook, T. H. & Rees, Y. J. 1994. Effects of nitrification inhibitor and acid addition to cattle slurry on nitrogen losses and herbage yields. *Grass and Forage Science* **49**, 209-215.
- Puttana, K., Gowda, N.M.N. & Rao, E.V. S. P. 1999. Effect of concentration, temperature, moisture, limiting and organic matter on the efficacy of the nitrification inhibitors benzotriazole, o-nitrophenol, m-nitroaniline and dicyandiamide. *Nutrient Cycling in Agrosystems* **54**, 251-257.
- Rajbanshi, S. S., Benckiser, G. & Ottow, J. C. G. 1992. Effects of concentration, incubation temperature, and repeated applications on degradation kinetics of dicyandiamide (DCD) in model experiments with a silt loam soil. *Biology and Fertility of Soils* **13**, 61-64.
- Renaud, F. G., Brown, C. D., Fryer, C. J. & Walker, A. 2004. A lysimeter experiment to investigate temporal changes in the availability of pesticide residues for leaching. *Environmental Pollution* **131**, 81-91.
- Schwarzer, C., & Haselwandter, K. 1991. Enzymatic degradation of the nitrification inhibitor dicyandiamide by a soil bacterium. *Soil Biology and Biochemistry* **23**, 309-310.
- Shepherd, M., Wyatt, J. & Welten B. 2012. Effect of soil type and rainfall on dicyandiamide concentrations in drainage from lysimeters. *Soil Research* **50**, 67-75.
- Shepherd, M., Welten B., Wyatt J. & Balvert S. 2014. Precipitation but not soil texture alters effectiveness of dicyandiamide to decrease nitrate leaching from dairy cow urine. *Soil Use and Management* **30**, 361–371.
- Sigua, G. C., Isensee, A. R. & Sadeghi, A. M. 1993. Influence of rainfall intensity and crop residue on leaching of atrazine through intact no-till soil cores. *Soil Science* **156**, 225-232.
- Singh, J., Saggarr, S., Giltrap, D. L. & Bolan, N. S. 2008. Decomposition of dicyandiamide (DCD) in three contrasting soils and its effect on nitrous oxide emission, soil respiratory activity, and microbial biomass - an incubation study. *Australian Journal of Soil Research* **46**, 517-525.

- Singh, J., Saggar, S. & Bolan, N. S. 2009. Influence of dicyandiamide on nitrogen transformation and losses in cow-urine-amended soil cores from grazed pasture. *Animal Production Science* **49**, 253-261.
- Smith, L. C., de Klein, C. A. M. & Catto, W. D. 2008. Effect of dicyandiamide applied in a granular form on nitrous oxide emissions from a grazed dairy pasture in Southland, New Zealand. *New Zealand Journal of Agricultural Research* **51**, 387-396.
- Teske, W. & Matzel, W. 1987. Die Beeinflussung der nitrifikationshemmenden Wirkung von Dicyandiamid durch Abbau und Verlagerung im Boden. *Arch. Acker-Pflanzenbau Bodenkd* **32**, 241-246.
- Turowski, M. & Deshmukh, B. 2004. Direct chromatographic method for determination of hydrogen cyanamide and dicyandiamide in aqueous solutions. *Analytical Letters* **9**, 1981-1989.
- Zaman M. & Blennerhassett J.D. 2010. Effects of the different rates of urease and nitrification inhibitors on gaseous emissions of ammonia and nitrous oxide, nitrate leaching and pasture production from urine patches in an intensive grazed pasture system. *Agriculture, Ecosystems and Environment* **136**, 236–246

List of Tables

Table 1 Soil physical and chemical properties (0-7.5cm)

Table 2 – Results of statistical tests to evaluate the effect of soil, DCD rate, and precipitation regime on DCD recovery (%) in leachate, soil, or unaccounted and cumulative drainage (mm), nitrate and ammonium leaching (kg N ha^{-1}).

Table 3 The effect of soil by DCD rate, precipitation, soil by precipitation and DCD rate by precipitation on the recovery (%) of DCD in soil, leachate and unaccounted at the end of the experiment.

Table 4 The effect of soil by precipitation and soil by DCD rate on drainage volume (mm) and the cumulative load of nitrate leached (kg N ha^{-1}).

List of Figures

Figure 1a (High Precipitation) & b (Low Precipitation) - Total DCD recoveries, as a percentage, remaining in the soil, leachate and unaccounted. Treatment labels refer to soil (gleysol/cambisol) and DCD application rate (0/15/30 kg ha⁻¹).

Table 1

		Johnstown Castle (JC)	Moorepark (MP)
Property	Unit		
Location	-	52°18'N; 6°30'W	52°17'N; 8°23'W
Soil Type	-	(Luvic gleysol)	(Haplic cambisol)
Parent Material	-	Glacial Deposits	Sandstone
Sand	%	61	54
Silt	%	24	34
Clay	%	15	12
Bulk Density	g cm ⁻³	1.38	1.01
pH	-	6.3	5.7
Loss on ignition	%	7.7	10.0
TN	%	0.27	0.42
TC	%	3.1	4.2
C:N ratio	-	11.3	10.0
Olsen's P	mg L ⁻¹	18	29.7

- 1 Table 2 – Results of three-way ANOVA tests to evaluate the effect of soil, DCD rate, and precipitation regime on DCD recovery (%) in leachate,
 2 soil, or unaccounted and cumulative drainage (mm), nitrate and ammonium leaching (kg N ha⁻¹).

Source of variation	Recovery of DCD (%)			Drainage (mm)	Cumulative N leaching (kg N ha ⁻¹)	
	Leachate	Soil	Unaccounted		Nitrate-N	Ammonium-N
Soil	n.s.	***	***	***	***	***
DCD rate	n.s.	**	**	n.s.	***	n.s.
Precipitation	***	**	n.s.	***	***	***
Soil x DCD	n.s.	**	**	n.s.	*	n.s.
Soil x Precipitation	n.s.	n.s.	*	*	*	**
DCD rate x Precipitation	n.s.	n.s.	**	n.s.	n.s.	n.s.
Soil x DCD rate x Precipitation	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

* Significant P<0.05

** Significant P<0.01

*** Significant P<0.001

n.s., non-significant P>0.05

3

4 Table 3 The effect of soil by DCD rate, precipitation, soil by precipitation and DCD
 5 rate by precipitation on the recovery (%) of DCD in soil, leachate and unaccounted at
 6 the end of the experiment.

Recovery of DCD in soil		
	DCD rate (kg ha ⁻¹)	Soil recovery of DCD (%)
<i>Soil x DCD rate interaction</i>		
Cambisol	15	6c†
Cambisol	30	8bc
Gleysol	15	19b
Gleysol	30	43a
<i>Precipitation</i>		
	Low	26a
	High	12b
Recovery of DCD in leachate		
	Precipitation	Leachate recovery of DCD (%)
	Low	7b
	High	18a
Unaccounted for DCD		
	DCD rate (kg ha ⁻¹)	Unaccounted for DCD (%)
<i>Soil x DCD rate interaction</i>		
Cambisol	15	82a
Cambisol	30	81a
Gleysol	15	67b
Gleysol	30	46c
<i>Soil x Precipitation interaction</i>		
Cambisol	Low	84a
Cambisol	High	79a
Gleysol	Low	61b
Gleysol	High	52b
<i>DCD rate by precipitation(kg ha⁻¹)</i>		
15	Low	78a
15	High	71a
30	Low	69ab
30	High	58b

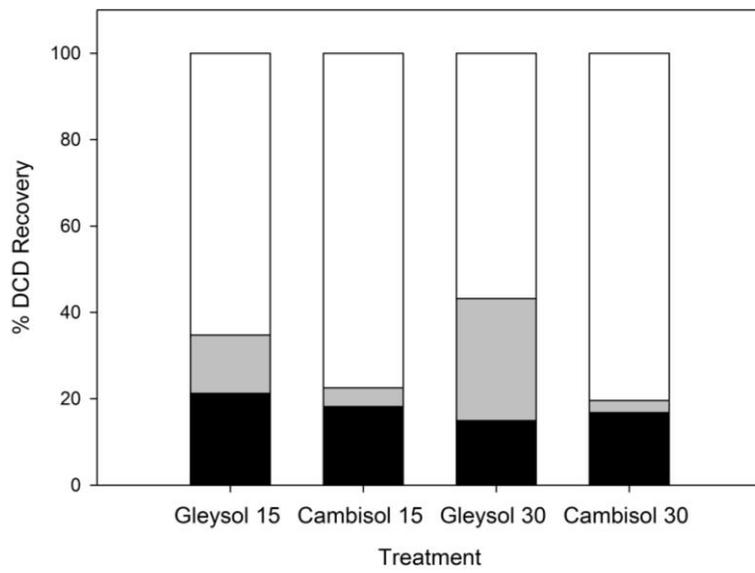
† Mean separation by Tukey's test, means followed by different letters are significantly different by Tukey's test ($p \leq 0.05$).

7

- 8 Table 4 The effect of soil by precipitation and soil by DCD rate on drainage volume
 9 (mm) and the cumulative load of nitrate leached (kg N ha^{-1}).

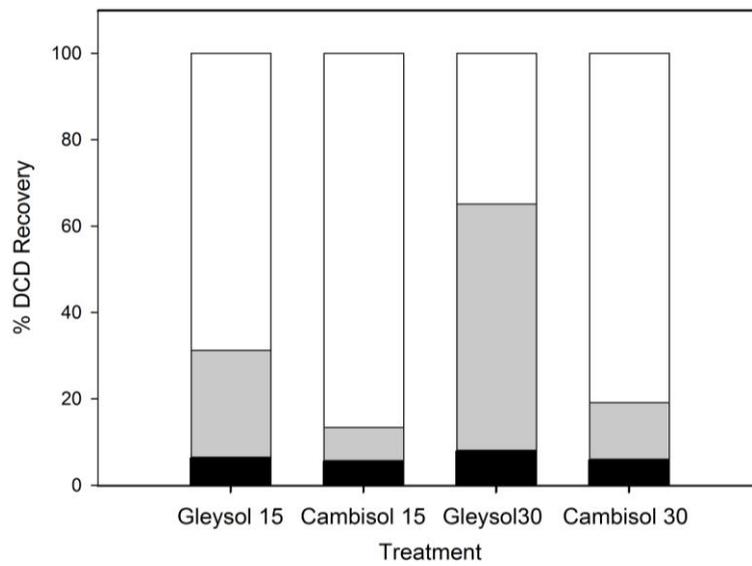
Drainage		
	Precipitation	Drainage (mm)
<i>Soil x Precipitation interaction</i>		
Cambisol	Low	129c
Cambisol	High	285a
Gleysol	Low	104d
Gleysol	High	274b
Nitrate leaching		
<i>Soil x Precipitation interaction</i>		
	Precipitation	Nitrate-N leaching (kg ha^{-1})
Cambisol	Low	6.4b
Cambisol	High	18.6a
Gleysol	Low	23.1a
Gleysol	High	22.3a
<i>Soil x DCD rate interaction</i>		
	DCD rate (kg ha^{-1})	Nitrate-N leaching (kg ha^{-1})
Cambisol	0	14.7b
Cambisol	15	11b
Cambisol	30	11.8b
Gleysol	0	37.7a
Gleysol	15	13.4b
Gleysol	30	17b

11 Figure 1a



12

13 Figure 1b



14