

SEASONAL VARIATIONS IN THE DEGRADATION OF A NITRIFICATION INHIBITOR, DICYANDIAMIDE (DCD), IN A MANAWATU GRAZED PASTURE SOIL

Dong-Gill Kim*, Thilak Palmada, Peter Berben, Donna Giltrap, Surinder Saggar

*Global Change Processes Group, Landcare Research, Palmerston North 4442, New Zealand
Email:kimd@landcareresearch.co.nz; donggillkim@gmail.com*

Abstract

Nitrification inhibitor dicyandiamide (DCD) slows N turnover by retarding the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-), providing more chance for plant uptake of NH_4^+ . While studies evaluating the efficacy of DCD in reducing N_2O emissions have been widely conducted, the characteristics of DCD degradation and its longevity in soil are not well known. The objectives of this study were to examine seasonal variations in the degradation of DCD and to determine the major control factors for the variation. The study was conducted on a Manawatu grazed pasture soil. In non-grazing plots, two different DCD treatment levels (10 and 20 kg ha^{-1}) and a 10- kg ha^{-1} DCD treatment level with two different types of N (urine and synthetic fertilizer) were tested. In cow grazing plots, 10- kg ha^{-1} DCD was applied in March, April, and October. Soil microclimate was measured at the site. Preliminary results show that the half-life of DCD was affected by neither the rate of DCD application nor the type of N input. The half-life of DCD varied with seasonal variation in soil moisture (7–12 days, longer in wetter condition). The preliminary results suggest that to maximise the effectiveness of DCD, different DCD application rates and frequency may be used in different seasons.

Introduction

Nitrification inhibitors (NI) such as dicyandiamide (DCD), nitropyrin, and 3,4 dimethyl pyrazole phosphate (DMPP) slow the activity of *Nitrosomonas*, the genus of nitrifying bacteria responsible for the oxidation of NH_4^+ to NO_3^- , which helps retain N in the NH_4^+ form longer in soil, providing more chance for plants to uptake NH_4^+ (e.g., Abbasi and Adams, 2000; Di et al., 2007). Thus NI can inhibit nitrous oxide (N_2O) emissions both from nitrification and from denitrification of NO_3^- . It was found that NI reduces N_2O emissions by 30–80% (e.g., Abbasi and Adams, 2000; Di et al., 2007; Zaman et al., 2009; Saggar et al., 2009; Akiyama et al., 2010). N_2O contributes to greenhouse effect (Wang et al., 1976) with a global warming potential 298 times greater than of carbon dioxide (CO_2) in a 100-year time horizon (Forster et al., 2007). Of total anthropogenic N_2O emissions (5.7 Tg $\text{N}_2\text{O-N yr}^{-1}$), agricultural soils provide 3.5 Tg $\text{N}_2\text{O-N yr}^{-1}$ (IPCC, 2006). Therefore, it has been suggested that NI use can be a potent mitigation option for GHG emissions in agricultural lands (e.g., Bolan et al., 2004; Klein and Ledgard, 2005; Akiyama et al., 2010).

While studies evaluating the efficacy of DCD in reducing N_2O emissions have been widely conducted, the characteristics of DCD degradation and its longevity in soil are not well known. In an incubation experiment, the half-life of DCD was 6–15 d at 25 °C and the degradation rate was different in different types of soils (Singh et al., 2008). Through analyzing published data from incubation experiments it was found that the half-life of DCD was affected by soil temperature and the half-life is over 72 d at less than 10 °C (Kelliher et

al., 2008). It was also found that DCD might be affected by sorption onto organic matter (Sahrawat et al., 1987) and soil pH (Zhang et al., 2004). Further studies are needed to improve our understanding of the characteristics of DCD degradation.

The objectives of this study were to examine seasonal variations in the degradation of DCD and to determine the major control factors for the variation. In this study, we had three hypotheses:

1. DCD degradation rates in soil treated with different types of nitrogen (urine or synthetic nitrogen fertilizer) are not different.
2. DCD degradation rates in soil treated with different amount of DCD (10 kg or 20 kg ha⁻¹) are not different.
3. DCD degradation rate in soil is not different in different seasons.

Materials and methods

Site description

Field experiments were set up on a Tokomaru silt loam soil managed for grazing dairy cows (3 cows ha⁻¹) at Massey University Research Dairy Farm 4, Palmerston North, New Zealand (40° 23' S, 175° 36' E) in 2010. The soil is classified as an Argillic-fragic Perch-gley Palllic Soil (Hewitt, 1998) or Typic Fragiaqualf (Soil Survey Staff, 1998), and derived from deep deposits of loess-brown river sediments. The Tokomaru silt loam soil consists of a weakly to moderately developed brown silt loam A-Horizon, a weakly developed grey strongly mottled, clay loam B-Horizon, and a highly compacted, weakly developed pale gray, silt loam fragipan C-Horizon that acts as a natural barrier to drainage (Hewitt, 1998). Average rainfall (1970–2000) at this site is about 965 mm, which is fairly evenly distributed throughout the year, with driest months being January–March. The mean annual sunshine is ~1900 h (Saggar et al., 2007). The mean annual air temperature is 12.8°C, and the coldest and warmest months are July (6.8°C) and January (18.1°C) (Saggar et al., 2007).

Experimental design

Two different experimental sites were set up on the farm: a non-grazing site and a cow-grazing site. In the non-grazing site, a fence was installed a month period to treatments and two different experiments were conducted: 1) application of 10 and 20 kg DCD ha⁻¹ with no N input in six replicated plots (2.5 × 2.5 m) on three occasions (25 August, 5 October, 2 November 2010); and 2) application of 10 kg DCD ha⁻¹ with cow urine (700 kg N ha⁻¹) and synthetic N fertilizer (25 kg N ha⁻¹) in six replicated plots (2.5 × 2.5 m) on 27 April 2010. In the cow-grazing site, DCD was applied (10 kg DCD ha⁻¹) in nine replicated plots (600–1000 m²) on three occasions (2 March, 23 April, 4 October 2010).

Soil sampling and DCD analysis

Ten intact soil cores (diameter 25 mm) were collected in each plot with a soil auger in soil depth 0–10 and 10–20cm. Soil sampling was conducted initially every 3 days for a week following DCD applications and then weekly or bi-weekly later. Collected soils were transferred to a laboratory and processed within 3 hours. Extraction of DCD in soil was conducted by shaking 10 g of moist soil in 20 ml of deionised water for 1 hr on an end-over-end shaker in the laboratory. The extract was then centrifuged (9000 rpm for 3 min.) and the supernatant filtered through No. 42 Whatman filter paper. A 5 ml sample of the extract was then acidified with the addition of 0.2 ml of 0.66 M H₂SO₄ and allowed to stand for at least 30 minutes before centrifuging (4500 rpm for 10 min) to remove precipitated material. The

concentration of DCD in the acidified supernatant was determined using a cation-H guard column (30 × 4.6 mm) with a 0.025M H₂SO₄ mobile phase at a flow rate of 0.6 ml/min and a 210 nm UV detector on a Waters 2695 high pressure liquid chromatography (Waters, Milford, MA, USA)(Schwarzer and Haselwandter, 1996).

Soil microclimate

On-site instrumentation was used to collect half-hourly averaged values of soil temperature (at 5 cm, a thermistor probe, CS107, Campbell Scientific, USA), soil moisture (at 5 cm, time domain reflectometry probes, CS615, Campbell Scientific, USA), air temperature and precipitation values throughout the study period.

Statistical analysis

The normality of the distribution of the data was analyzed using the Shapiro-Wilk normality test (Shapiro and Wilk, 1965). One-way analysis of variance (ANOVA) was used to evaluate the differences in means of half-life of DCD and soil microclimate variables. When the standard assumptions of normality were violated, non-parametric Kruskal-Wallis one-way ANOVA on ranks (Kruskal and Wallis, 1952) was used. Dunn's test was used for all pairwise comparisons following Kruskal-Wallis one-way ANOVA on ranks. Differences were considered significant at the $P < 0.05$ level. To determine the relationship between weather and soil microclimate and half-life of DCD, correlation analysis using the GLM procedure of SAS software (SAS Institute, 2009) was applied. The NONLIN procedure of SAS software (SAS Institute, 2009) was used to derive the best fit of N half-life of DCD models for the relationship between weather and soil microclimate variables and half-life of DCD. These statistical analyses were conducted using SAS ver. 9.2 (SAS Institute, Cary, NC, USA and SigmaPlot ver. 11.0 (Systat Software Inc., San Jose, CA, USA).

Results and discussion

1. Effect of the amount of N input on half-life of DCD

In the first treatment on 25 August 2010, initial concentrations in 10 kg DCD treatment (0–10 cm soil depth) was 6.6 ± 0.6 kg DCD ha⁻¹ and 20 kg DCD treatment was 10.7 ± 2.0 kg DCD ha⁻¹, and they were significantly different ($P = 0.041$). Half-lives of DCD for 10 kg and 20 kg DCD treatments (0–10 cm soil depth) were 10.0 ± 0.9 d and 10.1 ± 1.2 d, respectively, and these values are not significantly different ($P = 0.941$) (Table 1).

In the second treatment on 5 October 2010, initial concentrations in 10 kg DCD treatment (0–10 cm soil depth) was 4.5 ± 1.1 kg DCD ha⁻¹ and 20 kg DCD treatment was 8.9 ± 1.0 kg DCD ha⁻¹, and they were significantly different ($P = 0.005$). Half-life of DCD for 10 kg and 20 kg DCD treatments (0–10 cm soil depth) were 9.1 ± 1.2 d and 10.0 ± 0.2 d, respectively, and they are not significantly different ($P = 0.437$) (Table 1).

Table 1 Half-life of DCD (d, mean ± SE) in soil (0–10 cm soil depth). Two different amount of DCD (10 and 20 kg ha⁻¹) were applied with no N treatment in August and October 2010.

Application date (day/month/year)	25/08/2010	05/10/2010
Treatment	Half-life of DCD (d, mean ± SE)	
DCD 10kg ha ⁻¹ (n=6)	$10.0 \pm 0.9^{a\#}$	9.1 ± 1.2^a
DCD 20kg ha ⁻¹ (n=6)	10.1 ± 1.2^a	10.0 ± 0.2^a

[#]Identical letters in a column indicate values that are not significantly different

2. The effect of type of N input on half-life of DCD

In the first treatment on March 2010, there was no significant difference in the half-life of DCD (0–10-cm soil depth) relating to different N treatments (control, synthetic fertilizer and urine) ($P = 0.732$) (Table 2; Fig. 1). In the second treatment on June 2010, there was no significant difference in the half-life of DCD in 0–10-cm soil depth between different N treatments (control and synthetic fertilizer) ($P = 0.520$) (Table 2). Also, during these periods, there was no significant difference between the effects of the different types of N treatments (control and synthetic N fertilizer) on the half-life of DCD in the 10–20-cm soil horizon ($P = 0.974$) (Table 2). The half-life of DCD at at 10-20cm depth was significantly longer than at 0-10cm depth in the control plot ($P = 0.008$) (Table 2).

Table 2 Half-life of DCD (d, mean \pm SE) in soil (0–10 and 10–20-cm soil depth) treated with synthetic fertilizer (25 kg N ha⁻¹) and urine (700 kg N ha⁻¹) and control.

Application date (day/month/year)	27/04/2010	22/06/2010	
Treatment	Half-life (0–10-cm depth)	Half-life (0–10-m depth)	Half-life (10–20-cm depth)
Control + DCD (n=6)	14.5 \pm 1.5 ^{a#}	11.6 \pm 1.0 ^b	25.9 \pm 4.2 ^c
N fertilizer + DCD (n=6)	13.7 \pm 0.70 ^a	14.0 \pm 2.5 ^b	24.9 \pm 5.7 ^c
Urine + DCD (n=6)	11.3 \pm 2.4 ^a	ND	ND

ND: no data

[#]Identical letters in a column indicate values that are not significantly different

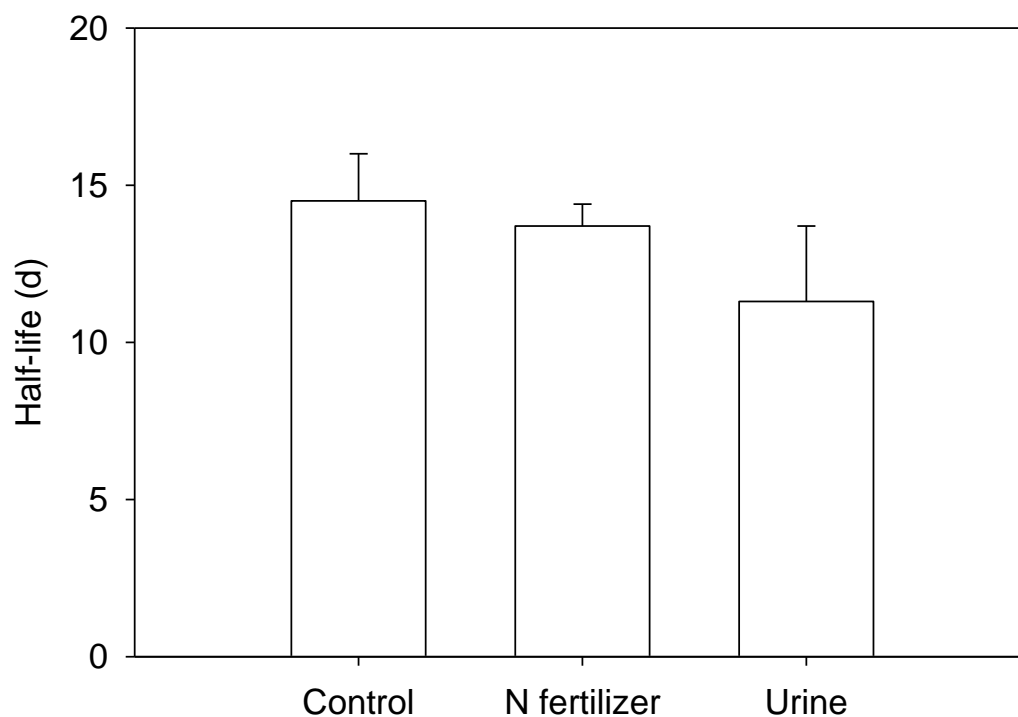


Fig. 1 Type of N input (fertilizer or urine) had no significant effect on half-life of DCD in soil (0–10 cm) for the April application.

3. Seasonal variation of half-life of DCD in the cow-grazing site

The half-life of DCD (0–10-cm soil depth) applied on cow-grazing plots in early October, early March, and late April was 7.2 ± 0.8 d, 9.8 ± 0.6 d and 12.4 ± 2.5 d, respectively (Table 3), and it has a significant positive correlation with soil moisture (0–10-cm soil depth) ($P = 0.01$) (Fig. 2).

Table 3 Half-life of DCD (d, mean \pm SE) in soil (0–10-cm soil depth) in the cow-grazing site (n=9). Three different applications of DCD (each 10 kg ha^{-1}) were applied in March, April, and October 2010. Soil moisture and temperature is the mean of values recorded at 30-minute intervals (0–10-cm soil depth) in each period and rainfall is the cumulative value recorded in each period.

Application date (day/month/year)	Half-life (d, mean \pm SE)	Soil moisture (%)	Soil temperature ($^{\circ}\text{C}$)	Rainfall (mm)
02/03/2010	$7.2 \pm 0.8^{\text{a}\#}$	25.0	15.3	55.9
26/04/2010	$9.8 \pm 0.6^{\text{b}}$	27.3	11.9	140.6
07/10/2010	$12.4 \pm 2.5^{\text{c}}$	29.7	15.9	80.1

[#]Identical letters in a column indicate values that are not significantly different

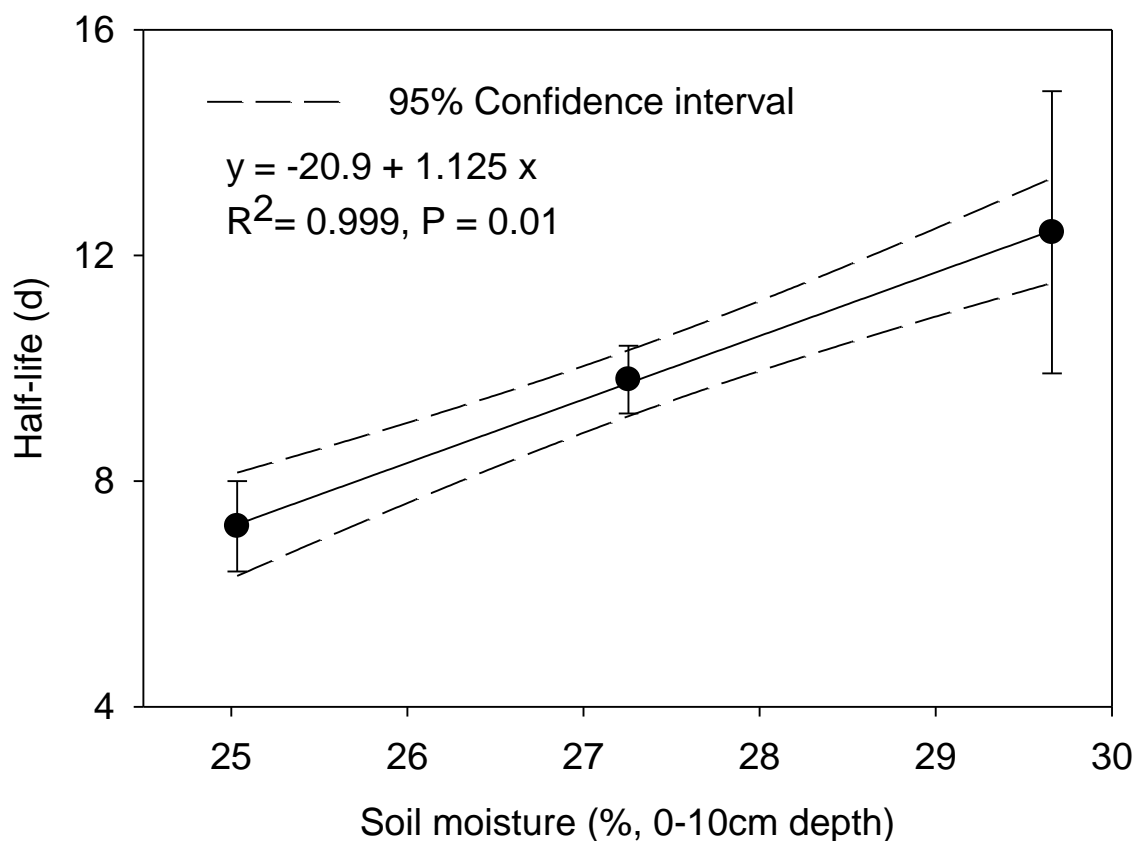


Fig. 2. Half-life of DCD has a significant positive correlation with soil moisture (0–10-cm soil depth).

Conclusions

The preliminary results of this study show that neither the rate of DCD application (10 and 20 kg ha⁻¹) nor the type of N input (synthetic fertilizer and urine) had a statistically significant impact on the half-life of DCD in a Manawatu grazed pasture soil. The half-life of DCD varied seasonally ranging from 7 days in March to 12 days in December. There was a strong correlation between soil moisture and half-life with a longer half-life observed in wetter conditions. The preliminary results suggest that to maximize the effectiveness of DCD, different DCD application rates and frequency may be used in different seasons. Besides the results provided here, further experiments have been conducted and the collected data will be analysed. Finally, conclusive results will be provided later in a peer-refereed journal.

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