Agriculture, Ecosystems and Environment 186 (2014) 201–204

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Short communication

Effect of temperature on dicyandiamide (DCD) longevity in pastoral soils under field conditions

F.M. Kelliher[a,b,*], C. van Koten[a], M.J. Kear[c], M.S. Sprosen[c], S.F. Ledgard[c], C.A.M. de Klein[d], S.A. Letica[d], J. Luo[c], G. Rys[e]

[a] AgResearch, Lincoln Research Centre, Private Bag 4749, Christchurch 8140, New Zealand
[b] Lincoln University, Faculty of Agriculture and Life Sciences, P.O. Box 84, Lincoln 7647, New Zealand
[c] AgResearch, Ruakura Research Centre, Private Bag 3123, Hamilton 3240, New Zealand
[d] AgResearch, Invermay Agricultural Centre, Private Bag 50034, Mosgiel 9053, New Zealand
[e] Ministry for Primary Industries, P.O. Box 2526, Wellington 6140, New Zealand

ARTICLE INFO

Article history:
Received 26 August 2013
Received in revised form 21 January 2014
Accepted 27 January 2014
Available online 15 March 2014

Keywords:
Nitrification inhibitor
Dicyandiamide
Temperature
Degradation
Soil
Pasture

ABSTRACT

Data were analysed from five trials begun in autumn at a field site and a relationship between time for concentration of the nitrification inhibitor dicyandiamide (DCD) in soil to halve ($t_{½}$, days) and the mean soil temperature (T, °C) was developed: $t_{½} = 54–1.8\,T$. For example, when T was 8 and 16 °C, $t_{½}$ was 39 ± 6 and 25 ± 3 days (±95% confidence limit), respectively. Previously, under laboratory conditions at equivalent temperatures, the corresponding values of $t_{½}$ were 86 ± 31 and 44 ± 24 days. Thus, the proportional responses of $t_{½}$ to increasing T from 8 to 16 °C were similar, but under field conditions $t_{½}$ was about half that under laboratory conditions.

1. Introduction

Dicyandiamide (DCD) is a nitrification inhibitor, itself susceptible to biodegradation (Ulpiani, 1906; Hauser and Haselwandter, 1990). Based on published data from incubation of soil samples to which DCD had been applied, Kelliher et al. (2008) developed a relationship between time for DCD concentration to halve ($t_{½}$) and the mean soil temperature (T), accounting for 85% of the variability. Under field conditions, additional factors might be influential. For example, if rainfall was sufficient to induce some of the applied DCD to leach beyond the sampled depth (Shepherd et al., 2012), reduced concentration in soil samples might be erroneously attributed to biodegradation and $t_{½}$ under-estimated. In this study, field-trial data were analysed to test the hypothesis that the relationship between $t_{½}$ and T will be the same under laboratory and field conditions.

2. Materials and methods

The field trials were undertaken at Tokanui Dairy Research Farm, located 7 km south of Te Awamutu, New Zealand (38.0°S, 175.3°E, 50 m asl). The soil's name is Otorohanga silt loam, a Typic Orthic Allophanic soil according to the New Zealand classification system (Hewitt, 2010). Five trials (Table 1) were conducted during autumn, one beginning 29/5/09, two beginning 22/4/10 and two beginning 12/4/11. A trial began with DCD application (10 kg ha^{-1}) to six plots, each 5 m by 0.5 m and surrounded by a 0.5 m-wide buffer. Except for one trial beginning 22/4/10, when DCD was applied alone, dairy cattle urine was also applied at an equivalent nitrogen (N) application rate of 700 kg N ha^{-1} (~10 l m^{-2}).

For each trial, following DCD application, soil in the plots was sampled weekly for the first month and at two week intervals for the second and third months. For the first trial, there were two additional sets of samples taken at monthly intervals. Soil samples were collected from the 0–0.1, 0.1–0.2 and 0.2–0.4 m depth layers. Measurements of soil bulk density and carbon content by a combustion method averaged 700 kg m^{-3} and 9.3% for 0–0.1 m, 680 kg m^{-3} and 6.7% for 0.1–0.2 m and 650 kg m^{-3} and 3.5% for 0.2–0.4 m. Following water extraction (1:2.5 soil to water ratio), DCD concentration in each soil sample was measured by high performance liquid chromatography (Shimazu Corporation, Kyoto,

* Corresponding author at: AgResearch, Lincoln Research Centre, Private Bag 4749, Christchurch 8140, New Zealand. Tel.: +64 3 321 8785.
E-mail address: frank.kelliher@agresearch.co.nz (F.M. Kelliher).

0167-8809/$ – see front matter
http://dx.doi.org/10.1016/j.agee.2014.01.026

Table 1
DCD half-lives ($t_{½}$), estimated by regression analysis from the data of five field trials as shown in Fig. 1, and percentages of the DCD in sampled soil layers with depths of 0–0.1, 0.1–0.2 and 0.2–0.4 m.

Trial	Year	Treatment	$t_{½}$ [ds][a]	R–$t_{½}$ [Rs–$t_{½}$][b]	DCD in soil layer		
					0–0.1 m	0.1–0.2 m	0.2–0.4 m
			days	mm	%	%	%
1	2009	DCD + urine	42 [41]	136 [136]	15	63	22
2	2010	DCD + urine	35 [28]	106 [43]	86	12	2
2	2010	DCD + urine	35 [42]	106 [152]	46	33	21
3	2010	DCD alone	23 [21]	35 [33]	86	11	3
4	2011	DCD + urine	20 [22]	93 [102]	66	30	3
5	2011	DCD + urine	18 [15]	90 [90]	76	23	1

[a] ds, days after DCD application when the soil was sampled.
[b] R–$t_{½}$, rainfall during the $t_{½}$ period; Rs–$t_{½}$, rainfall from DCD application until the soil was sampled.

Japan), including a Bio-Rad Aminex® organic acid column HPX-87H (300 mm × 7.80 mm I.D.) and using a method based on that of Schwarzer and Haselwandter (1996). Each sample's DCD concentration was calculated on an oven-dry weight basis, having been corrected for bulk density, water content and efficiency of the water extraction process (Welten et al., 2012).

During the trials, at a depth of 0.1 m, T was measured at 3 s intervals for one minute prior to each hour, averaged and recorded by a data logger. Rainfall totals were also recorded on an hourly basis. Following Kelliher et al. (2008), a first-order exponential degradation model was fitted (using Genstat 13) to time (t) courses of DCD concentration in the soil (C): $C[t] = C_0e^{-kt}$ where C_0 was C when time was zero, the day DCD had been applied, k was a decay coefficient and $\{\mathrm{Ln}[2]/k\} = t_{½}$. By fitting this model to $C[t]$ data, for the time series from each trial, we determined mean estimates of C_0 and $t_{½}$, as well as standard errors (SE) and 95% confidence limits. For robustness, we stipulated the upper limit of a C_0 estimate needed to be at least 90% of the DCD application rate.

Anticipating the results, for the $t_{½}$ periods, the proportions of DCD found in each sampled layer were subjected to corroborative DCD leaching calculations using Burn's equation following Magesan et al. (1999). The calculations required rainfall, evaporation and drainage rates. Evaporation rates were estimated following Scotter and Heng (2003). Drainage rates were estimated on the basis of surplus rainfall, the difference between rainfall and evaporation and the soil's storage capacity, set by the field capacity ($0.4\,m^3\,m^{-3}$, Mark Shepherd, personal communication). The calculations required a soil water content parameter that was also set to $0.4\,m^3\,m^{-3}$ (data not shown; separate calculations using this approach reasonably reproduced the DCD leaching measurements reported by Shepherd et al., 2012).

3. Results

Rainfall during the $t_{½}$ periods varied widely from 35 to 136 mm (Table 1). However, except for the period of maximum rainfall, by sampling, DCD was mostly located in the uppermost 0.1 m deep sample at the end of the $t_{½}$ period. This result was corroborated by DCD leaching calculations.

After DCD application to the plots, with and without dairy cattle urine, time series analyses of DCD concentration in the soil samples indicated these data could be fitted to a first-order exponential degradation model (Fig. 1). In 2009, the estimates of C_0 and $t_{½}$ were 12 ± 2 kg DCD ha^{-1} (±95% confidence limit) and 42 ± 6 days (DCD + urine, trial 1). In 2010, the corresponding estimates were 11 ± 2 kg DCD ha^{-1} and 23 ± 6 days for DCD alone (trial 2) and 11 ± 2 kg DCD ha^{-1} and 35 ± 14 days for DCD + urine (trial 3). In 2011, for two trials conducted with DCD + urine in different sets

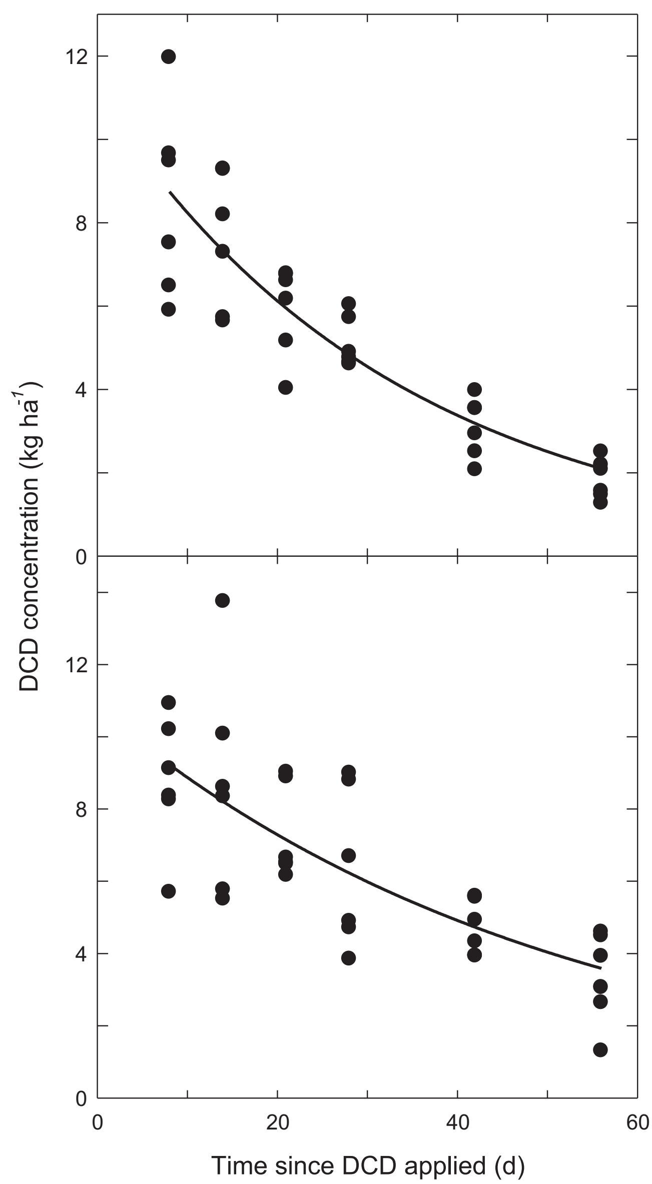

Fig. 1. Time courses of dicyandiamide (DCD) concentration in soil samples (0–0.4 m depth) after application to plots at Tokanui Farm on 22 April 2010. For the upper panel, 10 kg DCD ha^{-1} was applied to six plots; for the lower panel, application included a mixture of 10 kg DCD ha^{-1} and 700 kg N ha^{-1} as dairy cattle urine to six other plots.

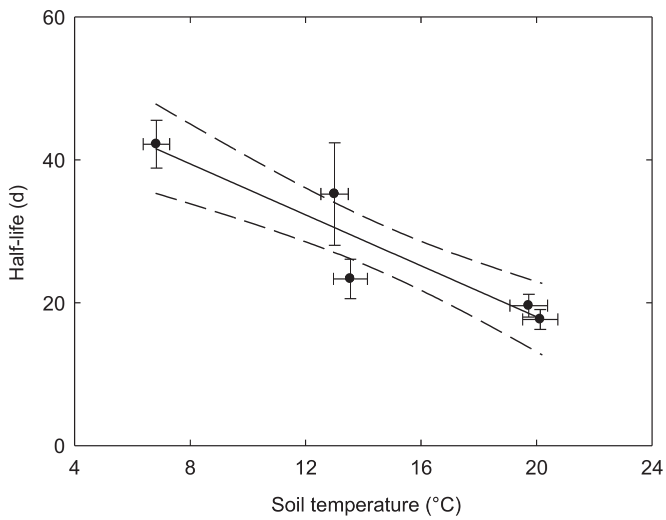

Fig. 2. Relationship between the half-life ($t_{½}$, days) of dicyandiamide (DCD) in soil during five field trials begun in autumn at Tokanui Farm and corresponding values of mean soil temperature (T, °C; 0.1 m depth). Over the period denoted $t_{½}$, the mean DCD concentration declined to half its application rate of 10 kg ha^{-1}. Linear regression analysis yielded $t_{½}$ = 54–1.8 T, and, on average, $t_{½}$ could be estimated with a standard error (SE) of 5 days, equivalent to 20% of the mean $t_{½}$. For 95% confidence, the estimated SEs were doubled as shown by the dashed curves.

of plots, the corresponding estimates were 9 ± 2 kg DCD ha^{-1} and 20 ± 4 days (trial 4) and 10 ± 2 kg DCD ha^{-1} and 18 ± 2 days (trial 5).

For each $t_{½}$ period, mean T (±SE) was estimated by applying an auto-regression and moving-average model to the mean daily T data. Then, by linearly regressing estimated mean T against $t_{½}$, a relationship was determined: $t_{½}$ = 54–1.8 T (Fig. 2). The regression was performed using a bootstrapping technique to account for the standard errors associated with (mean) T. On average, $t_{½}$ could be estimated with a 95% confidence limit of 5 days.

4. Discussion

The relationship between mean T and $t_{½}$ for Tokanui Farm was subjected to a test using data from a field trial we conducted on another pastoral farm. This trial began 22/5/09 at Telford Farm (46.3°S, 169.7°E, 30 m asl) which was located 1000 km south of Tokanui Farm. The Telford Farm's soil name is Tokomairiro silt loam, a Fragic Perch-gley Pallic soil according to the New Zealand classification system (Hewitt, 2010). Analysis of the Telford Farm trial's data yielded estimates of C_0 equal to 8 ± 1 kg DCD ha^{-1} and $t_{½}$ of 41 ± 12 days and the mean T was 5.3 ± 0.8 °C. During the $t_{½}$ period at Telford Farm, rain fell on 14 days and totalled 39 mm. By an extrapolation of the Tokanui Farm regression, when T is 5.3 °C, $t_{½}$ will be 44 ± 7 days.

Watkins et al. (2013) reported field trial data from a study where the application rate to pasture plots had been 3 kg DCD ha^{-1}. We fitted a first-order exponential degradation model to their data, the C_0 estimate was 3.6 ± 1.0 kg DCD ha^{-1}, $t_{½}$ 6 ± 3 days and the corresponding mean T 18.8 ± 1.2 °C. For the Tokanui Farm trials, the application rate to pasture plots had been 10 kg DCD ha^{-1} and by our regression, when T is 18.8 °C, $t_{½}$ will be 20 ± 4 days. According to this comparison, by increasing the DCD application rate from 3 to 10 kg DCD ha^{-1}, $t_{½}$ increased by 233%. For soil samples from a field trial site subjected to different DCD application rates, incubated in the laboratory at 20 °C and sampled at intervals, data analysis yielded an exponential relationship between C_0 and $t_{½}$ whereby increasing C_0 from 3 to 10 mg DCD kg^{-1} soil corresponded with $t_{½}$ increasing by 48% (Welten et al., 2013).

Dong-Gill et al. (2012) and Wakelin et al. (2013) also reported field trial data from studies where the application rate to pasture plots was 10 kg DCD ha^{-1}. Dong-Gill et al. (2012) sampled soils to a depth of 0.2 m, reported values of C_0 ranging from 2.4 to 6.6 kg DCD ha^{-1} and by linearly regressing mean T against $t_{½}$, a relationship was determined: $t_{½}$ = 20–0.7 T. By their regression, when T is 10 and 16 °C, $t_{½}$ will be 13 ± 2 and 9 ± 2 days, respectively. By the Tokanui Farm regression, the corresponding values of $t_{½}$ were substantially longer at 36 ± 5 and 25 ± 3 days. For Wakelin et al. (2013), we calculated C_0 was 2.5 DCD ha^{-1} by combining their reported C_0 of 3 mg DCD kg^{-1} soil, the sampled depth of 0.075 m and assuming a bulk density of 1100 kg m^{-3}, a mean from measurements made near their trial site. Their reported $t_{½}$ was 20 days and the corresponding mean T was 3 °C. By an extrapolation of the Tokanui Farm regression, when T is 3 °C, $t_{½}$ will again be substantially longer at 49 ± 8 days. For these two studies, C_0 estimates were much less than the DCD application rate and for T ranging from 3 to 16 °C, their estimates of $t_{½}$ were substantially less than those estimated by the Tokanui Farm regression.

By a meta-analysis of data from studies where soil samples had been subjected to DCD application and incubated at different temperatures, regression yielded $t_{½} = 168e^{-0.084T}$ and when T was 8 and 16 °C, $t_{½}$ was 86 ± 31 and 44 ± 24 days (Kelliher et al., 2008). Comparing these estimates with those from the Tokanui Farm regression, the proportional responses of $t_{½}$ to increasing T from 8 to 16 °C were broadly similar, but under field conditions, $t_{½}$ was about half that under laboratory conditions. Given that there was no apparent effect of rainfall on $t_{½}$ under field conditions in this study, we postulate that microbial activity in soils under field conditions, including effects from plants, had been substantially greater at a given temperature than that in soil samples incubated in laboratories.

In conclusion, after five field trials when DCD was applied to pasture plots during autumn, with and without dairy cattle urine, time series analyses of DCD concentration in the soil indicated these data could be fitted to a first-order exponential degradation model. The model yielded estimates of the DCD half-life, $t_{½}$. By linearly regressing estimated mean soil temperature during the $t_{½}$ period, T, against $t_{½}$, a statistically-significant relationship could be determined. Under the field conditions of this study, DCD degraded in soil much faster than in soil samples incubated at the same temperature. These results warrant further research in different soils under a wider range of conditions.

Acknowledgements

Funding was provided by the Ministry for Primary Industries, DairyNZ, Fonterra and the Fertiliser Association of New Zealand. The senior author is grateful to Joy Jiao, Mark Shepherd, Val Snow and Brendon Welten for valuable discussions. Natalie Watkins kindly shared her data with us.

References

Dong-Gill, K., Giltrap, D., Saggar, S., Palmeda, T., Berben, P., Drysdale, D., 2012. Fate of the nitrification inhibitor dicyandiamide (DCD) sprayed on a grazed pasture: effect of rate and time of application. Soil Res. 50, 337–347.
Hauser, M., Haselwandter, K., 1990. Degradation of dicyandiamide by soil bacteria. Soil Biol. Biochem. 22, 113–114.
Hewitt, A.E., 2010. New Zealand soil classification. In: Landcare Research Science Series No. 1, 3rd ed. Manaaki Whenua Press, Lincoln, NZ, pp. 136.
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 Biol. Biochem. 40, 1878–1882.
Magesan, G.N., Scotter, D.R., White, R.E., 1999. The utility of Burn's equation to describe solute movement through soil under various boundary and initial conditions. Eur. J. Soil Sci. 50, 649–656.
Schwarzer, C., Haselwandter, K., 1996. Enzymatic degradation of the nitrification inhibitor dicyandiamide by a soil bacterium. Soil Biol. Biochem. 23, 309–310.

Scotter, D.R., Heng, L., 2003. Estimating reference crop evaporation in New Zealand. J. Hydrol. (NZ) 42, 1–10.
Shepherd, M., Wyatt, J., Welten, B., 2012. Effect of rainfall and soil type on dicyandiamide concentration in drainage from lysimeters. Soil Res. 50, 67–75.
Ulpiani, C., 1906. Evoluzione chimica e biochimica della calico-cyanamide nel terreno agrario. Rendi. Soc. Chim. Roma 4, 30–43.
Wakelin, S.S., Clough, T.J., Gerard, E.M., O'Callaghan, M., 2013. Impact of short-interval, repeat application of dicyandiamide on soil N transformation in urine patches. Agric. Ecosyst. Environ. 167, 60–70.
Watkins, N.L., Schipper, L.A., Sparling, G.P., Thorrold, B., Balks, M., 2013. Multiple small monthly doses of dicyandiamide (DCD) did not reduce denitrification in Waikato dairy pasture. N. Z. J. Agric. Res. 56, 37–48.
Welten, B., Kear, M., Dexter, M., Judge, A., 2012. Efficiency of DCD extraction from soils. In: Currie, L.D., Christensen, C.L. (Eds.), Advanced Nutrient Management: Gains from the Past–Goals for the Future. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand, p. 5.
Welten, B.G., Ledgard, S.F., Schipper, L.A., Waller, J.E., Kear, M.J., Dexter, M.M., 2013. Effects of prolonged oral administration of dicyandiamide to dairy heifers on excretion in urine and efficacy in soil. Agric. Ecosys. Environ. 173, 28–36.