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Temperature and rainfall effects on dicyandiamide (DCD) longevity in soils under field conditions

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Executive Summary

Nitrification inhibitors have the potential to reduce nitrogen (N) loss from soils and increase N use efficiency. As the name suggests, nitrification inhibitors work by inhibiting the transformation of N via the nitrification pathway which results in prolonged ammonium retention in soils. Dicyandiamide (DCD) is an effective nitrification inhibitor to reduce N losses from soils, but DCD is susceptible to loss via biodegradation by the soil's microbial community and leaching, downwards movement through soils that can be induced by rainfall. The purpose of this project is to develop calculation methods to estimate the effects of temperature and rainfall on DCD longevity in pastoral soils under field conditions.

In an Appendix, we analyse field trial data to develop a relationship between time for DCD concentration in soil to halve after application to the surface at 10 kg/ha ($t_{½}$) and the mean temperature (T). By linear regression, the relationship may be written $t_{½}$ (days) = 54 - 1.8 * T (°C). To illustrate, when T was 8 and 16°C, $t_{½}$ was 39 ± 6 and 25 ± 3 d (± 95% confidence limit), respectively. This regression equation will be the first calculation method developed to quantify the effect of temperature on DCD longevity in soils under field conditions.

The relationship between $t_{½}$ and T was based on data when nearly all of the applied DCD was located in the uppermost 0.1 m depth of soil. If rainfall is sufficient, DCD can move downwards through soils. In soils, microbial biomass and the activity that degrades DCD should be related to the quantity of organic matter or carbon (C). Thus, for a given value of T, $t_{½}$ should be related to the soil's C content. In soils, the C content decreases with depth, so $t_{½}$ should increase with increasing depth. This leads us to ask if rainfall is sufficient to move DCD in soils deeper than 0.1 m and T is unaffected, do we need to adjust an estimate of $t_{½}$?

To answer this question, we developed a second, refined calculation method to estimate DCD degradation rate by accounting for T as shown above as well as two additional, relevant variables. This involved a model, Burn's equation, to estimate the downwards movement of DCD in response to rainfall, also connecting rainfall and DCD losses by leaching. Next, we used an exponential function to quantify the vertical distribution of C content in soils and account for a postulated relation between C content and the DCD $t_{½}$ (slower DCD degradation rate). We validated our calculation methods to estimate DCD degradation rate by analysing data from a field trial at Ruakura where 10 kg DCD/ha was applied on 1 May to 0.65-m-deep lysimeters, and DCD leaching, rainfall and soil temperature measured continuously over the following six months. During May – October, there was 862 mm of rain and an estimated 284 mm of evaporation. The total, estimated DCD loss by leaching was 2.3 kg /ha, comparable to 2.8 kg /ha that had been measured. Accounting for T, according to our first calculation method, we estimated DCD loss by degradation had been 12.6 kg /ha. Combining, we estimated the sum of DCD losses by leaching and degradation was 14.9 kg /ha (= 2.3 + 12.6), 49% more DCD than had been applied. Alternatively, accounting for T, rainfall (inducing downwards movement of DCD) and the vertical distribution of soil C content according to our refined method, we estimated DCD loss by degradation had been 9.2 kg /ha. On this basis, we estimated the sum of DCD losses by leaching and degradation was 11.5 kg /ha (= 2.3 + 9.2), only 15% more DCD that had been applied.

As stated, we can use Burn's equation to estimate the quantities of rainfall required to induce different fractions of applied DCD to move below different depths in soils. For example, when monthly evaporation is 30 mm and monthly rainfall is 40 mm, we calculate only 2% of the applied DCD will move beyond a depth of 0.1 m. For the same evaporation and rainfall of 60, 120 and 180 mm, the percentages will be 26, 64 and 77%, respectively. Generally, except for the West Coast of the South Island, June will be the month with the greatest rainfall in

New Zealand. On these bases, by analysing long-term rainfall data from six representative sites across New Zealand and using the statistics obtained from a rainfall generator, we developed another calculation method to estimate the chance that rainfall during June will exceed threshold values of 60, 120 and 180 mm. This calculation method can be modified to estimate the chance that rainfall during any month (at any location in New Zealand) will exceed any stipulated quantity. Thus, a suite of calculation methods has been developed to enable determination of the effects of temperature and rainfall on DCD longevity in pastoral soils under field conditions.

Introduction

Nitrification inhibitors have the potential to reduce nitrogen (N) loss from soils and increase N use efficiency. As the name suggests, nitrification inhibitors work by inhibiting the transformation of N via the nitrification pathway which results in prolonged ammonium retention in soils. Dicyandiamide (DCD) is a nitrification inhibitor, itself susceptible to biodegradation by the soil's microbial community (Ulpiani, 1906; Hauser and Haselwandter, 1990). The purpose of this project is to develop calculation methods to estimate the effects of temperature and rainfall on DCD longevity in pastoral soils under field conditions.

Effect of temperature on DCD longevity in soils

In an Appendix, we analyse field trial data to develop a relationship between time for DCD concentration in soil to halve after application to the surface at 10 kg/ha ($t_{½}$) and the mean soil temperature (T): $t_{½}$ (days) = 54 - 1.8 * T (°C). For example, when T was 8 and 16°C, $t_{½}$ was 39 ± 6 and 25 ± 3 d (± 95% confidence limit), respectively.

The relationship between $t_{½}$ and T was based on data when nearly all of the applied DCD was located in the uppermost 0.1 m depth of soil (Table A1). If rainfall is sufficient, DCD can move downwards through soils. For example, three months after DCD that had been applied to the soil surface of a Horotiu silt loam beneath pasture at Ruakura, including 312 mm of rainfall, DCD was (first) detected in drainage water from 0.65-m-deep lysimeters according to Shepherd et al., (2012). This leads us to ask if rainfall is sufficient to move DCD in soils deeper than 0.1 m and if T is unaffected, do we need to adjust an estimate of $t_{½}$?

In soils, microbial biomass and the activity that degrades DCD should be related to the quantity of organic matter or carbon (C). Thus, for a given value of T, $t_{½}$ should be related to the soil's C content. For example, biodegradation rate and $t_{½}$ of some biocides in soils has been proportional to the C content (Veeh et al., 1996, McDowell et al., 1997). This suggests DCD degradation rate and $t_{½}$ should be proportional to the C content. In soils, the C content decreases with depth, so $t_{½}$ should increase with increasing depth. The nitrification rate was negligible or slow in subsoil samples collected at depths 0.4 – 0.6 m and incubated following dairy cattle urine application for 100 days at 12 °C, compared with that in topsoil samples collected at depths 0 – 0.2 m, and DCD application significantly reduced these rates (Di et al., 2010). In soils, the relationship between depth (z, expressed as a positive downwards direction) and C content can be described by an exponential function according to Cook and Kelliher (2006) as:

$$C(z) = C_0 e^{-z/z^*} \qquad (1)$$

where C_0 is C at the soil surface where z = 0, e = 2.718 and z* is a length scale which determines how much C content decreases as z increases. Using this relationship, we can refine the process for estimating $t_{½}$ by accounting T as well as C(z), assuming a proportional relationship between C and $t_{½}$. Firstly, we require soil sample data to determine C(z) by equation (1). For the field trials that determined $t_{½}$, DCD was applied to Otorohanga silt loam soil at Tokanui Dairy Research Farm. During the trials, soil samples were collected from the 0 - 0.1, 0.1 – 0.2 and 0.2 – 0.4 m depth layers and C content measured by a combustion method averaged 9.3, 6.7 and 3.5%, respectively. To re-iterate, this information will be used with equation (1) to quantify the relationship between the soil's C content and z to estimate C content across depth intervals from the surface downwards. Taking z to be a midpoint of the sampled depth interval, the data were best fitted to equation (1) when z* was 0.3 m and C_0 was 10.5%, yielding C(z) for the Tokanui Dairy Research Farm. The C estimate for the uppermost 0.1 m depth of soil was 8.9% when z was 0.05 m. This estimate can be normalised by division by 8.9%, meaning it becomes transformed to a value of one (= 8.9%/8.9%). On this basis, normalised estimates will be 1 for 0 - 0.1 m, 0.717 for 0.1 - 0.2 m (i.e., 71.7% of the value for 0 – 0.1 m) and accordingly throughout the soil profile to the deepest depth interval.

We have postulated the DCD degradation rate and $t_{½}$ should be proportional to T and soil C content, and for the Tokanui Dairy Research Farm, we have developed estimates of C content across 0.1 m depth intervals down through the soil. An implicit assumption of this refined method for estimating DCD $t_{½}$ will be that T does not change with depth in the soil, keeping in mind that T will be a mean value over periods of many days (this assumption has been tested, but these data will not be shown). To illustrate the refined method by calculations, when rainfall is insufficient to move DCD in soils deeper than 0.1 m, the estimate of $t_{½}$ based on T will be multiplied by 1. Alternatively, when rainfall is sufficient to move all of the applied DCD to the depth interval 0.1 – 0.2 m, the estimate of $t_{½}$ based on T will be multiplied by 0.717 (the normalised estimate of C when z is 0.15 m), so reduced by 28.3%. To proceed further, we need a method to determine the effect of rainfall on DCD movement through soils.

Rainfall and DCD movement through soils

If rainfall is sufficient, DCD applied to the surface will move downwards through a soil. Burn's equation is attractive for estimating DCD movement through soils because it is simple and it has been shown to yield accurate predictions in many instances (e.g., Magesan et al., 1999). Burn's equation may be written

$$F_z = e^{-z\theta/(R - E)} \qquad (2)$$

where F_z will be the fraction (of DCD) that moves below depth z (mm) in a soil, θ the soil's volumetric water content ($m^3\ m^{-3}$) at field capacity (obtained approximately two days after thorough wetting by rainfall or irrigation when the drainage rate should have become minimal), R the rainfall (mm) and E the evaporation (mm).

Accounting for temperature and rainfall effects on DCD longevity in soils

We have now developed methods to estimate the effects of temperature and rainfall on DCD longevity in pastoral soils under field conditions. According to the first method, when the applied DCD is located in the uppermost 0.1 m depth of soil, $t_{½}$ (days) = 54 - 1.8 * T (°C). If rainfall is sufficient to move DCD in soils deeper than 0.1 m, determined by equation (2), we will need to refine our first method's estimate of $t_{½}$ according to the normalised estimated of C(z) determined by equation (1).

For our first method, we assume DCD has been applied to the surface and it is located in the uppermost 0.1 m depth of soil. As described in the Appendix, $t_{½}$ was determined following Kelliher et al. (2008) by fitting a first-order exponential function to time (t) courses of DCD concentration in a soil (C) during field trials. The equation was written as $C[t] = C_0e^{-kt}$ where C_0 is C when t was zero (the day DCD had been applied) and $\{Ln[2]/k\} = t_{½}$. Thus calculated from $t_{½}$, term k indicates the DCD degradation rate according to units of day^{-1}. This transformation allows us to use T to determine the DCD loss by degradation in a soil. Calculations can be done on a monthly basis. By denoting the quantity of DCD in soil at the beginning of a month as C_0, we can calculate the monthly DCD loss by degradation according to $[C_0 - C_0e^{-kt}]$ where t is the number of days in the month.

To illustrate our first method, we will analyse data reported by Shepherd et al. (2012). On 1 May 2008, at Ruakura, they applied 10 kg DCD/ha to the surface of Horotiu pastoral soil contained in 0.65-m-deep lysimeters. Horotiu soil is similar to the Otorohanga soil at Tokanui Dairy Research Farm (Mark Shepherd, personal communication). To estimate DCD degradation rate by monthly calculations, we require monthly values of T. We calculated T from measurements made at depth 0.1 m in soil beneath grass mown regularly at the Ruakura weather station. The measurements were made at 3 second intervals for one minute prior to each hour, averaged and recorded by a data logger. This will be called an hourly measurement protocol and we consider the corresponding monthly values of T to be "true" means as required for the calculations. Alternatively, by our calculations, we have learnt that the monthly values of T reported by Shepherd et. al. (2012) used a different measurement protocol. Their measurements were made at 9 am each day (local time, including days with standard time and days with daylight savings time). Thus, to estimate T, Shepherd et al. (2012) assumed a 9 am local time measurement was equal to a daily mean. We tested this assumption by comparing six pairs of monthly T values for May, June, July, August, September and October 2008 calculated from hourly mean and once-daily measurements. On average, T calculated from once-daily measurements was less than T calculated from hourly mean measurements by 1.4 °C (± 0.2 °C, standard deviation). Though undetermined, during November – April, T calculated from once-daily measurements should also be different to T calculated from hourly mean measurements. For $t_{½}$ (days) = 54 - 1.8 * T (°C), if T was under-estimated by 1.4 °C, $t_{½}$ would be over-estimated by 3 days. In future, to avoid this unnecessary bias error, T should be calculated from hourly mean measurements.

In 2008 at Ruakura, for May, June and July, T calculated from hourly mean measurements averaged 10.3 °C (Table 1). By our first method, the corresponding monthly DCD losses by degradation were 4.7, 2.6 and 1.9 kg/ha, totalling 9.2 kg/ha or 92% of the quantity of DCD applied to the soil on 1 May 2008. By analysing the data reported by Shepherd et al. (2012), for May – October, we determined monthly DCD losses by leaching had been 0, 0, 0.6, 2.1, 0 and 0.1 kg/ha, respectively, for a 6-month total of 2.8 kg/ha. As 10 kg DCD/ha was applied, this information indicated that by our first method, we had over-estimated the DCD loss by degradation. Moreover, by our first method, the monthly DCD losses by degradation for August, September and October were 1.6, 1.2 and 0.7 kg/ha. Thus, for the May - October, the total estimated loss was 12.7 kg/ha, exceeding the application rate, and confirming we had over-estimated the DCD loss by degradation by our first method.

If rainfall is sufficient to move DCD through soils deeper than 0.1 m, determined by equation (2), we can refine our first method's estimate of DCD loss by degradation using the normalised estimates of C(z) determined by equation (1). To use equation (2), we need to determine an appropriate value of θ. Term θ reflects a soil's volumetric water content at field capacity. For the Horotiu soil, θ will be 0.4 m^3/m^3 (Mark Shepherd, personal communication). We also need to estimate monthly E and we will follow Scotter and Heng (2003). Following Shepherd et al. (2012), monthly rainfall (R) comes from measurements made at the Ruakura weather station. Using these data in equation (2), six calculations will be done for consecutive 0.1 m intervals in the soil to depth 0.6 m and another to depth 0.65 m. These calculations will estimate DCD loss by leaching beyond depth 0.65 m and determine the vertical distribution of DCD. The vertical distribution of DCD will determine the "sub-quantities" of DCD in each 0.1 m deep layer of soil which will be subjected to loss by degradation according to T and refined (reduced) using the normalised estimates of C(z) determined by equation (1).

For May – July 2008, monthly rainfall was 82, 161 and 207 mm, respectively, and by our refined method, the corresponding monthly DCD losses by degradation were 4.1, 1.5 and 1.0 kg/ha, totalling 6.6 kg/ha and 28% less than that estimated for this period by our first method. The difference between our two methods of estimating DCD loss by degradation is substantial, and research seems warranted to test the hypothesis for our refined method that depth in soil affects the DCD degradation rate. For August – October 2008, monthly rainfall was 181, 71 and 160 mm, respectively, and by our refined method, the corresponding monthly DCD losses by degradation were 0.9, 1.2 and 0.5 kg/ha, totalling 2.6 kg/ha and 24% less than that estimated for this period by our first method. Thus, for May – October 2008, by our refined method, the DCD losses by degradation was 9.2 kg/ha.

For May – October 2008, by equation (2), we estimated the monthly DCD losses by leaching to be 0, 0.8, 1.0, 0.5, 0 and 0 kg/ha, respectively, totalling 2.3 kg/ha. Combining, for May – October 2008, by our refined method, the DCD losses by degradation (9.2 kg/ha) and leaching (2.3 kg/ha) totalled 11.5 kg/ha. This loss estimate is only 15% more than the quantity of DCD applied to the soil on 1 May 2008. However, for May – October 2008, the monthly DCD losses by leaching measured by the lysimeters were different to our estimates and the measurements were 0, 0, 0.6, 2.1, 0 and 0.1 kg/ha, respectively, totalling 2.8 kg/ha. Thus, using equation (2), the total DCD loss by leaching had under-estimated the measurements by 22%. Moreover, using equation (2), we estimated that 243 mm of rain during May and June had induced DCD loss by leaching of 0.8 kg/ha during June. Alternatively, the measurements indicated 450 mm of rain during May – July had been needed to induce DCD loss by leaching of 0.6 kg/ha during July. Thus, while this case study suggested equation (2) produced a reasonable estimate of DCD leaching over 6 months, monthly estimates may be less reliable.

We have determined that rainfall affected the longevity of DCD in Horotiu pastoral soil contained in 0.65-m-deep lysimeters at Ruakura, keeping in mind that Horotiu soil is similar to Otorohanga soil at Tokanui Dairy Research Farm. In the case study, rainfall had been sufficient for surface-applied DCD to move downwards in the soil. Rainfall can be related to the soil by the pore volume. This expresses a soil's pore space as a depth, the product of porosity and depth of soil. A soil's porosity depends on the bulk and particle densities. For Horotiu soil in the lysimeters, the porosity was 0.60 m^3/m^3 according to Shepherd et al. (2012). Thus, for the 650-mm-deep lysimeters at Ruakura, a pore volume would be 390 mm (= 0.60 m^3/m^3 * 650 mm). During the field trials at Tokanui Farm, soil samples were collected from the 0 - 0.1, 0.1 – 0.2 and 0.2 – 0.4 m depth layers and the bulk density averaged 700, 680 and 650 kg/m^3, respectively, and 677 kg/m^3 overall. For Otorohanga soil, the particle density is 2,210 kg/m^3 according to Singleton (1991). Combining these data, the calculated porosity and the pore volume will be 0.69 m^3/m^3 (= 1 – [677/2210]) and 449 mm, respectively. Thus, the calculated pore volume for Otorohanga soil is within 15% of that for the Horotiu soil, supporting the suggestion that the two soils are similar. By equation (2), we estimated that 243 mm of rain during May and June had induced DCD loss by leaching beyond a depth of 0.65 m that was equal to 0.8 kg/ha during June. We can calculate that 243 mm of rain would be equivalent to 62% of a pore volume for the Horotiu soil (100 * [243/390]). Alternatively, the lysimeter measurements indicated 450 mm of rain during May – July had been needed to induce DCD loss by leaching of 0.6 kg/ha during July or 115% of a pore volume for the Horotiu soil (100 * [450/390]). It is also noteworthy that Shepherd et al. (2012) reported rainfall equivalent to one-half of a pore volume (= 195 mm) had been required for DCD to be detected for the first time in drainage water from the lysimeters. In summary, we have estimated that rainfall equivalent to 50 – 115% of a pore volume (195 – 450 mm) was needed to induce DCD loss by leaching beyond a depth of 0.65 m in the Horotiu and Otorohanga soils.

Estimating the chance of rainfall sufficient to induce DCD movement through soils

We have determined that, if sufficient, rainfall can induce DCD losses by leaching. We have postulated rainfall can also affect the longevity of DCD in soils by inducing downwards movement to depths beyond 0.1 m where there is less organic matter, microbial biomass and a slower degradation rate. Using equation (2), we can estimate the fraction of the applied DCD that moves below a depth of 0.1 m. For the Horotiu and Otorohanga soils, θ will be 0.4 m^3/m^3 and we will set monthly evaporation E to 30 mm, a minimum value that will be obtained in winter during June, July and August. Thus, for the fraction to exceed zero, the monthly rainfall must exceed 30 mm. When R is 40 mm, we calculate only 2% (fraction = 0.02) of the applied DCD will move beyond a depth of 0.1 m. For R of 60, 120 and 180 mm, the percentages will be 26, 64 and 77%, respectively. Generally, except for the West Coast of the South Island, June will be the month with the greatest rainfall in New Zealand. On these bases, calculations will be developed to estimate the chance that rainfall during June exceeds the threshold values of 60, 120 and 180 mm. Moreover, we will develop a general calculation method that could be used to estimate the chance of rainfall during any month (at any location in New Zealand) exceeding any quantity.

To estimate the chance of rainfall during June exceeding threshold values, we will develop a daily rainfall generator. Following Scotter et al. (2000), we recognise that weather systems tend to produce rainfall over several days. Thus, rainy and dry days tend to be clumped together, and this needs to be taken into account. On this basis, we begin by asking whether or not a day has rain. The question will be answered using a random number generator and comparing this number with one of two probabilities. One probability applies if the preceding day is dry, P(W/D), and the other if it is rainy, P(W/W). We will determine P(W/D) as

$$P(W/D) = bf \qquad (3)$$

where b is an empirical parameter and 0.75 generally works well in New Zealand according to Scotter et al. (2000) and f is the average fraction of rainy days during a month. We then determine P(W/W) as

$$P(W/W) = 1 - b + bf \qquad (4)$$

If the day is dry, we are finished. For rainy days, we then ask how much rain fell (x). We will determine x using a Weibull-type function that delivers the cumulative probability of x (F) that Scotter et al. (2000) showed may be solved as

$$x = [(x_m - 1)/1.19][-Ln(1 - F)]^{1.33} + 1 \qquad (5)$$

where x_m is mean x for the month and Ln denotes the natural (base e, 2.718) logarithm.

For the daily rainfall generator, long-term records must be compiled and analysed to estimate term x_m, a ratio of mean rainfall (mm) and the mean number of days when rainfall exceeded 1 mm, the latter to be the estimate of term f. Sites must be selected for data analysis, recognising the need to compile a representative range of information. The sites will be selected from dairying regions because DCD has generally been applied to soils used for this purpose. This includes Waikato, Taranaki, Otago and Southland regions. A substantial proportion of dairy products also come from the Canterbury region, but as will be shown, a representative range of rainfall data can be compiled with data from six sites located in the other four regions. For context, though problematic, mean annual rainfall for the six sites ranged from 691 - 2055 mm, while mean rainfall during June was 61, 103, 126, 155, 176 and 200 mm at Invermay, Invercargill airport, Ruakura, New Plymouth airport, Whatawhata and Stratford Demonstration Farm, respectively (Table 2).

The rainfall generator will be used to calculate values of x during June at a site. To illustrate, calculations will be explained for Ruakura. Re-iterating, for June at Ruakura, mean values of rainfall and number of rainy days were 126 mm and 13 days, respectively. Term f in equations (3) and (4) will be 0.43 (= 13 days/30 days) and term x_m in equation (5) will be 9.7 mm/d (= 126 mm/13 days). Using these values and equations (3) – (5), including the random number generator, 30 calculations of x will be done and summed to obtain a monthly value of rainfall for June for Ruakura. These calculations will be repeated 100 times to obtain a randomly-generated set of (100) monthly rainfall values. To estimate the chance that rainfall during June would exceed different values, the calculated set will be sorted in order from the least rainfall to the greatest. The least rainfall will be the one percentile value up to the greatest rainfall which will be the one hundredth percentile value. The percentile values can then be interpreted to estimate the chance that rainfall during June would exceed a given value. For example, 126 mm was the 64th percentile value, indicating a 36% chance that rainfall (during June at Ruakura) will exceed 126 mm, the mean value (Figure 1). If the probability distribution for rainfall had been a symmetrical, bell-shaped curve, often called normal, the chance would have been 50% for the mean. There should be no upper limit of monthly rainfall, so the probability distribution should be asymmetrical, according to the Weibull-type function that delivers the cumulative probability of x in equation (5). The calculations also allow us to estimate chances that rainfall during June at Ruakura will exceed 60, 120 and 180 mm and these were 89, 41 and 10%, respectively.

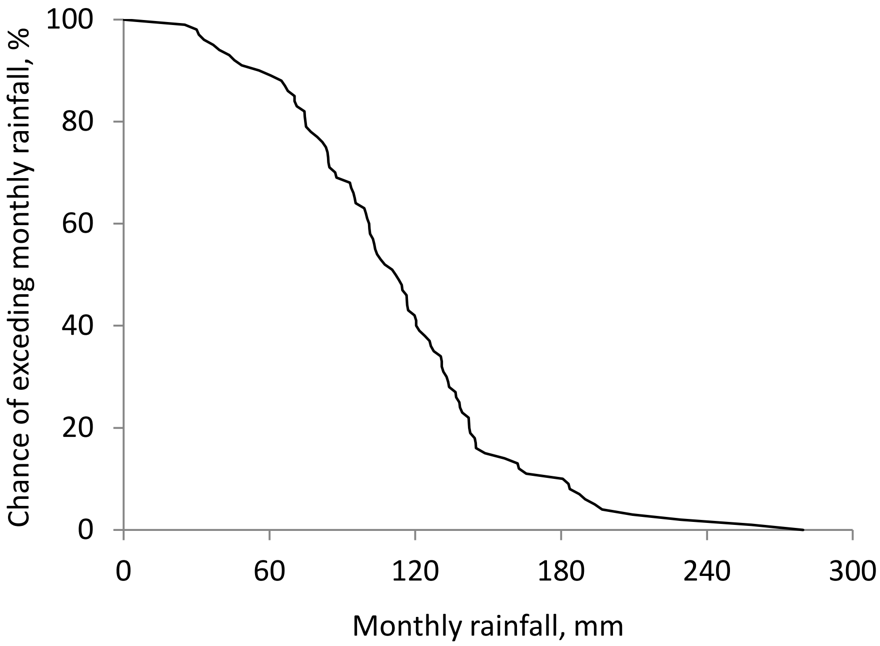

Figure 1 Relation between 100 simulations of rainfall during June at Ruakura using a rainfall generator and the chance of exceeding monthly rainfall. The latter was determined by sorting rainfall from smallest (1 percentile value = 25 mm) to largest (100 percentile value = 280 mm).

For Invermay, the chance that rainfall during June exceeds 60 mm was 46%, but the corresponding percentage averaged 93 ± 3% (± standard deviation) for the five other sites (Figure 2). This suggests rainfall during June should exceed 60 mm across most of New Zealand. For the Horotiu and Otorohanga soils, assuming monthly evaporation had been 30 mm in June, we estimated 60 mm of rain should induce 26% of DCD applied to the surface to move beyond a depth of 0.1 m. Assuming these soils and 60 mm of rain during June are representative, when DCD is applied to well-drained pastoral soils on 1 June, we estimate 26% should be located deeper than 0.1 m by the end of the month. By increasing the rainfall threshold to 120 mm, this percentage increases from 26 to 64%. For data from the six sites, the relationship between mean rainfall in June and chance of monthly rainfall exceeding 120 mm was proportional. By linear regression with the mean rainfall during June, the chance of rainfall exceeding 120 mm could be estimated with a standard error of 4%. Increasing the rainfall threshold to 180 mm, we estimate 77% of DCD applied to the surface should be located deeper than 0.1 m by the end of the month. For mean rainfall during June > 100 mm, our data also portrayed a proportional relationship. By linear region, the chance of rainfall exceeding 180 mm could be estimated with a standard error of 3%. Slopes of the two regressions estimating the chances that rainfall during June would exceed 120 and 180 mm (0.60 ± 0.03 and 0.60 ± 0.03, respectively) were not significantly different. Thus, for June, a regression slope around 0.6 may apply for thresholds > 180 mm.

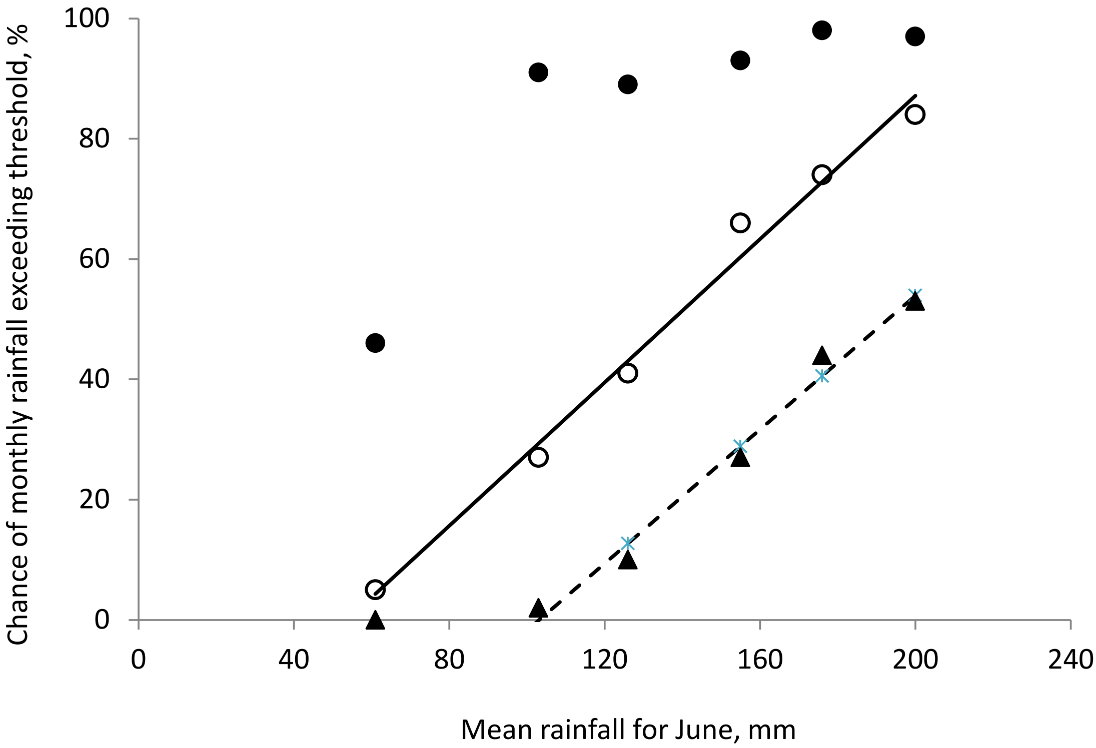

Figure 2 Relationship between the mean rainfall for June at six sites across New Zealand and the chance that rainfall during June will exceed threshold values of 60 mm (solid circles), 120 mm (open circles) and 180 mm (solid triangles). By linear regression with mean rainfall for June as shown by a line, the chance that rainfall during June will exceed 120 and 180 mm could be estimated with standard errors of 4 (solid line, slope = 0.60 ± 0.03, intercept = -32.03 ± 4.66) and 3% (dashed line for the five data points with rainfall during June > 100 mm, slope = 0.56 ± 0.04, intercept = -57.46 ± 6.16), respectively.

Recommendations

- **Under field conditions when DCD is located in the uppermost 0.1 m depth of soils, the time for DCD concentration in soil to halve from an application rate of 10 kg/ha ($t_{½}$) can be estimated from the mean soil temperature (T) as $t_{½}$ (days) = 54 - 1.8 * T (°C).**

By our regression analysis, when T is 8 and 16°C, $t_{½}$ will be 39 ± 6 and 25 ± 3 d (± 95% confidence limit), respectively. Since the research for this report was undertaken, Welten et al. (2013) published a paper including data portraying a saturating relationship between initial DCD concentration in soil samples (mg DCD/kg soil) and $t_{½}$ (days) when incubated at 20°C. The data in their Figure 6 suggested saturation level of the DCD concentration was ~14 kg/ha if bulk density was 700 kg/m^3 and all of the DCD was located in the uppermost 0.1 depth. Thus, for DCD application rate < 14 kg/ha, $t_{½}$ will increase as DCD application rate increases and this relation should be proportional.

- **Based on a test against field trial data, we would recommend Burn's equation to estimate the downwards movement of DCD through soils and think DCD should degrade slower with increasing depth in soils because carbon concentration and microbial activity decrease with increasing depth in soils.**

- **A refined calculation method to estimate DCD degradation rate would be recommended when, following DCD application, rainfall is sufficient to induce DCD movement beyond 0.1 m depth in soils. Based on our calculations for well-drained soils, a monthly rainfall threshold for this decision should be ~120 mm.**

When monthly rainfall and evaporation were 120 and 30 mm, respectively, we estimated 64% of DCD applied to the surface of a well-drained soil should move beyond a depth of 0.1 m. Alternatively, when monthly rainfall was reduced to 60 mm and evaporation remained 30 mm, the percentage reduced to 26%. June should be the wettest month and by analysing long-term rainfall statistics, we developed a calculation method to estimate the chance (%) of rainfall exceeding 120 mm as [0.60 * mean rainfall during June] – 32. The chance ranged from 5% at Invermay (mean rainfall during June = 61 mm) to 41% at Ruakura (126 mm) and 84% at Stratford Demonstration Farm (200 mm).

- **Further research is warranted to test our hypothesis that DCD should degrade slower with increasing depth in soils because there is less carbon and microbial activity there.**

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Table 1 Monthly rainfall (R) and evaporation (E) and monthly mean soil temperature (T) at Ruakura after 10 kg DCD/ha was applied to the soil surface of a Horotiu silt loam in 0.65-m-deep lysimeters on 1 May 2008. The R and E data were used to estimate the fraction of DCD that leached beyond a depth of 0.1 m (F_z with z denoting depth) using Burn's equation. The T data were used to estimate DCD loss by degradation. A refined estimate of DCD loss by degradation was also based on T as well as F_z calculated at 0.1 m intervals to a depth of 0.65 m and the relationship between soil carbon content (C) and z (C(z)). The monthly DCD leaching losses measured using the lysimeters were determined from data reported by Shepherd et al. (2012), and no further losses were measured after 31 October 2008.

Month	R	E	R – E	F_z, z = 0.1 m	T	DCD loss by degradation accounting for T	DCD loss by degradation accounting for T, F_z, and C(z)	DCD loss by leaching according to Burn's equation	DCD loss by leaching according to lysimeters
	mm	mm	mm		°C	kg/ha	kg/ha	kg/ha	kg/ha
May	82	40	42	0.39	11.3	4.7	4.1	0.0	0.0
June	161	30	131	0.74	10.3	2.6	1.5	0.8	0.0
July	207	32	175	0.80	9.3	1.9	1.0	1.0	0.6
August	181	43	138	0.75	10.4	1.5	0.9	0.5	2.1
September	71	58	13	0.05	12.9	1.2	1.2	0.0	0.0
October	160	81	79	0.60	15.1	0.7	0.5	0.0	0.1
Sum	862	284	578			12.6	9.2	2.3	2.8

Table 2 Rainfall characteristics of six sites used to develop a relationship between mean rainfall during June and chance of the monthly rainfall exceeding threshold values. For equations (2) and (3), parameter f was the mean number of rainy days in June divided by 30, the number of days in June, while parameter x_m was the mean rain in June divided the mean number of rainy days in June.

Site	Latitude, longtitude, altitude above sea level	Years of rainfall record	Mean annual rain	Mean rain during June	Mean number of rainy days in June
Ruakura	37.8°S, 175.3°E, 40 m	1905 – 1980 (75)	1201	126	13
Whatawhata	37.8°S, 175.1°E, 104 m	1952 – 1980 (28)	1635	176	15
Stratford Demonstration Farm	39.3°S, 174.3°E, 311 m	1961 – 2002 (41)	2055	200	14
New Plymouth airport	39.0°S, 174.2°E, 27 m	1944 – 1980 (36)	1529	155	14
Invermay	45.8°S, 170.3°E, 24 m	1943 – 1977 (34)	691	61	9
Invercargill airport	46.4°S, 168.3°E, 0 m	1939 – 1980 (41)	1037	103	15

Appendix – Manuscript submitted for publication on 6 May 2013

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

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Abstract

We analysed data from five trials at a field site and developed the following 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): $t½ = 54 - 1.8 * T$. For example, when T was 8 and 16°C, $t_{½}$ was 39 ± 6 and 25 ± 3 days (± 95% confidence limit), respectively. Earlier, under laboratory conditions at equivalent temperatures, we found $t_{½}$ was 86 ± 31 and 44 ± 24 d (n = 16). Thus, 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.

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. Here we analyse field-trial data to test the hypothesis that the relationship between $t_{½}$ and T will be the same under laboratory and field conditions.

The field trials were done 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 was an Otorohanga silt loam, a Typic Hapludand according to the USA classification system. Five trials (Table A1) 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) 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 (~10 litres/m^2). Afterwards, 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 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 concentrations were measured by high performance liquid chromatography (Shimazu Corporation, Kyoto, Japan), including a Bio-Rad Aminex® organic acid column HPX-87H (300 × 7.80 mm I.D.) and using a method based on that of Schwarzer and Haselwandter (1996). Soil DCD concentrations, corrected for bulk density, water content and the efficiency of DCD extraction, were calculated on an oven-dry weight basis. During the trials, T was measured at 0.1 m soil depth at 3 second 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 function was fitted for each trial (using Genstat 13) to time (t) courses of DCD concentration in the soil (C): $C[t] = C_0e^{-kt}$ where $\{Ln[2]/k\} = t_{½}$, yielding mean estimates of C_0 (C when time was zero, the day DCD had been applied) and $t_{½}$, as well as standard errors and 95% confidence limits. Data from two trials and fitted functions are shown in Figure A1 as examples. For 2009, estimates of C_0 and $t_{½}$ were 12 ± 1 kg DCD/ha (± SE) and 42 ± 3 days (DCD + urine, trial 1); for 2010, 11 ± 1 kg DCD/ha and 23 ± 3 days (DCD alone, trial 2) and 11 ± 1 kg DCD/ha and 35 ± 7 days (DCD + urine, trial 3); and for 2011, 9 ± 1 kg DCD/ha and 20 ± 2 days (DCD + urine, trial 4) and 10 ± 1 kg DCD/ha and 18 ± 1 days (DCD + urine, trial 5).

For the $t_{½}$ periods, the rainfall and proportions of DCD found in each soil depth layer were also determined (Table A1). The proportions were corroborated by DCD leaching calculations using Burn's equation following Magesan et al. (1999). The calculations required evaporation and drainage rates. The former was estimated following Scotter and Heng (2003). Drainage was 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)). Rainfall during $t_{½}$ periods varied widely from 35 to 136 mm, resulting in different vertical distributions of DCD (Table A1). However, the 0.2 – 0.4 m layer generally contained a small proportion of DCD and by our calculations it seems unlikely a substantial proportion leached beyond 0.4 m depth, indicating little or no apparent effect of rainfall on $t_{½}$.

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: $t_{½} = 54 - 1.8 * T$ (Figure A2). The regression was performed using a bootstrapping technique to account for the standard errors associated with (mean) T.

Following the methods used at the Tokanui Farm trials, including equivalent DCD and urine N applications, additional data were available from a field trial that began on 22/5/09 at Telford Farm, located 1000 km to the south (46.3 °S, 169.7 °E, 30 masl). The soil was a Tokomairiro silt loam, which is a Fragiochrept according to the USA classification system. Analysis of the Telford Farm trial's data yielded an estimated C_0 of 8 ± 1 kg DCD/ha, $t_{½}$ of 41 ± 12 days and T of 5.3 ± 0.4 °C. During the $t_{½}$ period, rain fell on 14 days and totalled 39 mm. By extrapolation, using the Tokanui Farm regression, when T is 5.3 °C, $t_{½}$ will be 44 ± 7 days. This estimate agrees well with the $t_{½}$ value estimated for Telford Farm.

Under laboratory conditions, we found no effect of DCD application rate (estimated for the soil samples to have been 5 – 32 kg DCD/ha) on $t_{½}$ and when T was 8 and 16°C, $t_{½}$ was 86 ± 31 and 44 ± 24 d (n = 16, Kelliher et al., 2008, samples were collected from the 0 – 0.1 m depth layer (n = 6, Rajbanshi et al., 1992) and 0 – 0.2 m (n = 4, Di and Cameron, 2004), but sampling depth was not reported for the remaining data). 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.

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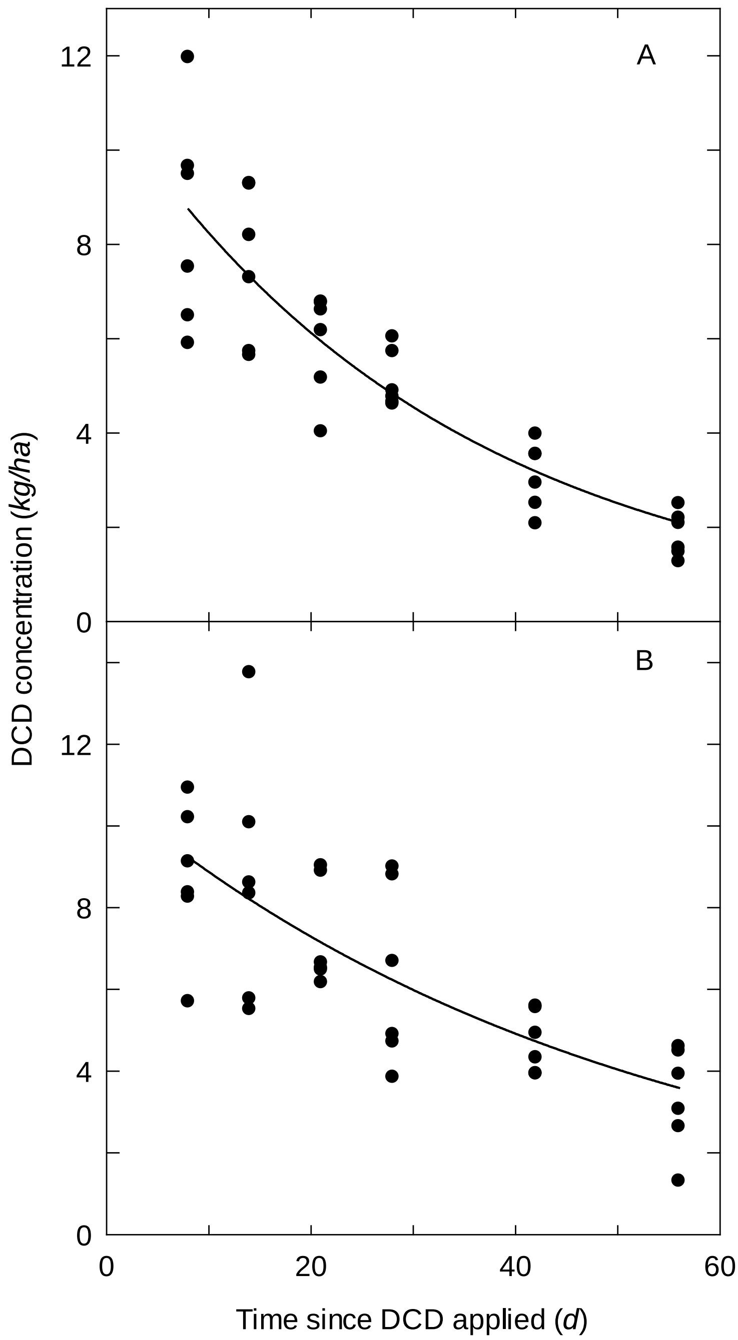

Figure A1 Time courses of dicyandiamide (DCD) concentration in soil samples (0 - 0.4 m depth) after application to plots at Tokanui Farm on 22 April 2010. For the data portrayed in panel A, 10 kg DCD/ha was applied to six plots; for panel B, application included a mixture of 10 kg DCD/ha and 700 kg N/ha as dairy cattle urine to six other plots.

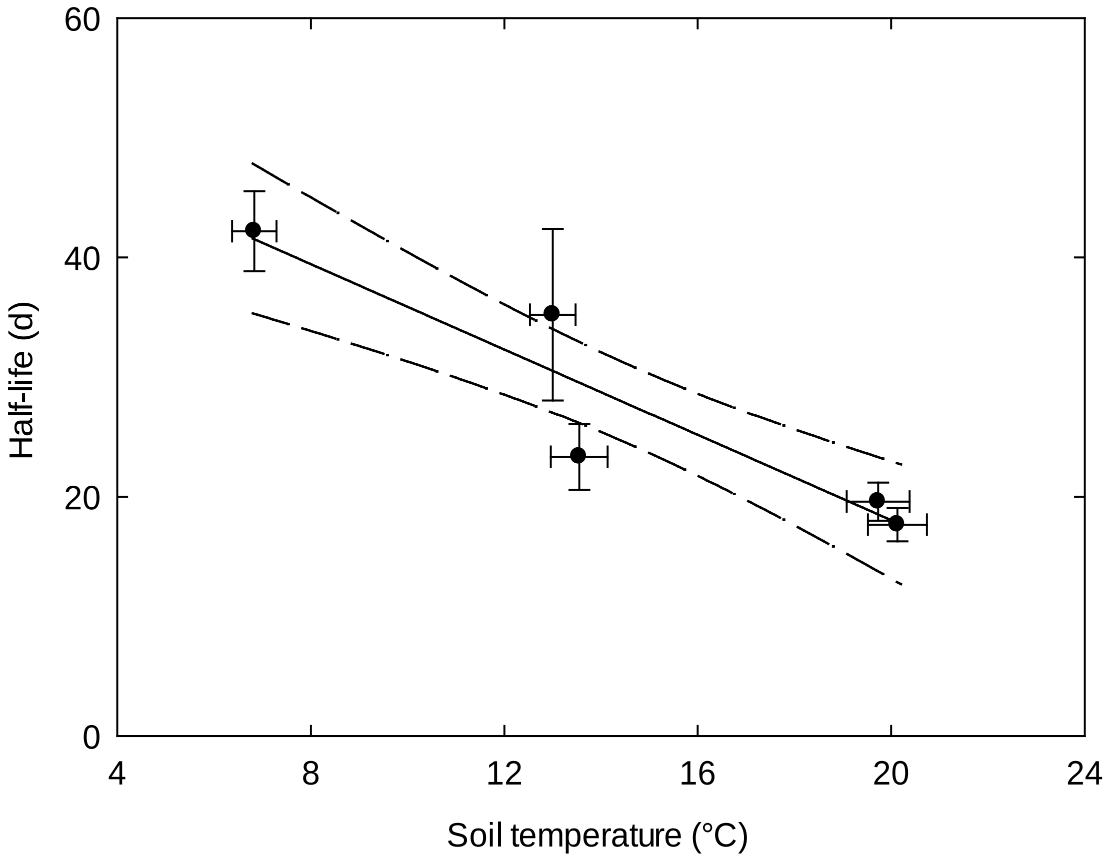

Figure A2 Relationship between the half-life ($t_{½}$, days) of dicyandiamide (DCD) in soil during five field trials at Tokanui Farm and corresponding values of mean soil temperature (T, °C; 0.1 m depth). Over the period denoted $t_{½}$, the mean DCD concentration declined to half its application rate of 10 kg/ha. 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, estimated SEs have been doubled as shown by the dashed curves.

Trial	Year	Treatment	$t_{½}$ and [day when the soil was sampled]	Rainfall during $t_{½}$ period and [Rainfall from DCD application to day when the soil was sampled]	Proportion of DCD in the 0 – 0.1 m layer	Proportion of DCD in 0.1 – 0.2 m layer	Proportion of DCD in 0.2 – 0.4 m layer
			Days	Mm	%	%	%
1	2009	DCD + urine	42 and [41]	136 and [136]	15	63	22
2	2010	DCD + urine	35 and [28]	106 and [43]	86	12	2
2	2010	DCD + urine	35 and [42]	106 and [152]	46	33	21
3	2010	DCD alone	23 and [21]	35 and [33]	86	11	3
4	2011	DCD + urine	20 and [22]	93 and [102]	66	30	3
5	2011	DCD + urine	18 and [15]	90 and [90]	76	23	1

Table A1 Year and treatments for field trials of DCD application to a pastoral soil at Tokanui Farm. The DCD half-life ($t_{½}$) was estimated for each trial by the regression shown in Figure 2. Also shown is the time when the soil was sampled as close as possible to the end of $t_{½}$ period. For trial 2, two times of sampling were closest to $t_{½}$ (7 days before and 7 days afterwards) and rainfall between these occasions was substantial; results from both sets of samples are therefore presented. Rainfall is given for each $t_{½}$ period as well as that for the period until the soil was sampled. When the soil was sampled, the proportion of DCD in each layer was determined.