Developing revised emission factors for nitrous oxide emissions from agricultural pasture treated with nitrification inhibitors

Final Report

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Executive Summary

We conduct a literature review and develop three methods to describe how anthropogenic nitrous oxide (N_2O) emissions from pastoral agriculture soils can be reduced using nitrification inhibitors. Most nitrification inhibitors have not been assessed for their effectiveness in reducing N_2O emissions from grazed pasture systems. Further, it is essential that application of the nitrification inhibitor to New Zealand soils is sustainable with no deleterious environmental consequences. Dicyandiamide (DCD) (chemically written as $C_2H_4N_4$) has been studied for more than 80 years (for example, McGuinn 1924) and subject to many tests with no reported environmental side effects. Suter et al. (2006) determined that DCD and DMPP (3, 4-dimethylpirazol phosphate) were the available nitrification inhibitors most suited for use in pastoral systems. In New Zealand, Suter et al. reported DMPP is only available as a coated ammonium nitrate fertiliser. They concluded that this form of DMPP delivery would greatly limit its efficacy with respect to urine excreta patches in soils beneath grazed pasture and also make the inhibitor's use cost prohibitive. We thus focus on DCD.

The rate of DCD degradation in soils depended strongly on temperature (i.e., slower degradation rate in cooler soils). For DCD decomposition in soils, based on the peer reviewed literature including a New Zealand study, we fitted an exponential function with soil temperature as the independent variable and accounted for 91 % of the variance. We expressed DCD decomposition as the time taken for its concentration in soils to decline to half the initial (application) value, called the half life, $t_{½}$. Based on average soil temperature during New Zealand field trials involving DCD application and longterm average soil temperatures throughout New Zealand, DCD application should be most effective if restricted to May – September when soil temperature < 12 °C (for example, when soil temperature was 4, 8 and 12 °C, our function predicted $t_{½}$ was 109, 73 and 49 days, respectively). A suitable DCD application rate was 10 kg/ha and two applications each year were one following grazing in autumn and another following grazing in late winter.

Based on the New Zealand peer-reviewed literature, in conjunction with dairy cattle urine application during autumn to Lismore and Templeton soils located at Lincoln, DCD application corresponded with a 74 ± 4% (average ± standard deviation, n = 5) reduction in nitrate leaching ($Frac_{LEACH}$). Based on the peer reviewed literature and dairy cattle urine application, we recommend that DCD application be considered to correspond with a 74% reduction in $Frac_{LEACH}$.

Based on the New Zealand peer-reviewed literature, in conjunction with dairy cattle urine application during autumn to the Lismore, Templeton and Horotiu soils as well as a pumice soil located at Taupo, DCD application corresponded with a 67 ± 6% reduction in the direct N_2O emissions factor ($EF_{3(PRP)}$). For a dairy cattle grazing trial on Pukemutu soil, DCD application corresponded with a percentage reduction in $EF_{3(PRP)}$ that was statistically indistinguishable from the peer-reviewed literature average. Based on these data, we recommend that DCD application be considered to correspond with a 67% reduction in $EF_{3(PRP)}$.

To put these DCD application responses into perspective, sensitivity calculations may be done according to the New Zealand's N_2O emissions inventory. For New Zealand, this

inventory is largely determined by the direct emissions factor for excreta nitrogen (N) deposited onto soils during grazing, $EF_{3(PRP)}$. Iindirect emissions are included in the inventory and these depend on indirect emission factors (a composite value of 0.025 will be used here for illustration) and the fraction of deposited N that leaches beyond the soil, $Frac_{LEACH}$. The New Zealand specific value for $Frac_{LEACH}$ is 0.07. Consequently, 93 % of N deposited onto soils determine the direct emissions according to the fractional value of $EF_{3(PRP)}$. The New Zealand specific value for $EF_{3(PRP)}$ is 0.01. Hence, for excreta deposited onto soils during grazing, a 67% reduction in $EF_{3(PRP)}$ and no change in $Frac_{LEACH}$ corresponded with a 56 % reduction in (total) N_2O emissions follows DCD application. In contrast, no change in $EF_{3(PRP)}$ and a 74% reduction in $Frac_{LEACH}$ corresponded with only a 7 % reduction in N_2O emissions following DCD application. For no change in $EF_{3(PRP)}$ and a 48% reduction in $Frac_{LEACH}$, a 5 % reduction in N_2O emissions corresponded with DCD application. The N_2O inventory's response to DCD application was thus much more sensitive to changes in $EF_{3(PRP)}$ than $Frac_{LEACH}$. Computationally, the relatively consistent response of $EF_{3(PRP)}$ to DCD application was more important than the more variable response of $Frac_{LEACH}$.

There has been one field trial, conducted at Lincoln, quantifying the effects of repeated applications of DCD to grazed pasture. The recently-published, peer-reviewed paper about this trial (Moir et al. 2007) focussed herbage production. Based on seasonal measurements over four years, on average, application of DCD corresponded with a 21 % increase of dry matter production on whole paddock and annual bases. The increase ranged from 17 % in an inter-urine area during year two to 36 % for an area that received urine in year 3. For the N_2O emissions inventory, dry matter intake of grazing animals is determined by calculating the energy requirements for maintenance and production of milk, meat and wool. Intake is based on annually-updated information (weight, determining the maintenance requirement, and production data). Because animal production rate is effectively determined in real time by the inventory, dry matter intake could correctly capture a positve effect of DCD on pasture herbage production.

Our first emissions calculation method, called method 1, is an aggregated N_2O emissions inventory comparable to current calculations reported by government. The effects of nitrification inhibitors are calculated using 'annualised' revisions of emissions factors $EF_{3(PRP)}$ and EF_1 and term $Frac_{LEACH}$. For the other two methods, separate calculations are done for October – April when nitrification inhibitors should not be used and May – September when nitrification inhibitors should be used because they will then be more effective. For method 2, the nitrogen applied to soils as excreta from grazing animals remains an aggregation of urine and dung, so calculations for October – April are the same as for method 1. For May – September, method 2 uses a second set of revised values for $EF_{3(PRP)}$ and EF_1 and $Frac_{LEACH}$. Method 3 includes this disaggregation plus the excreta are also disaggregated into urine and dung, so a third set of revised values for $EF_{3(PRP)}$, EF_1, and $Frac_{LEACH}$ are used for each of the two periods. There is sparse date for these emission factors. However, disaggregation of excreta into urine and dung is strongly supported by a scientific argument. For cattle urine, on average, based on New Zealand field trials, $EF_{3(PRP)}$ was 5 and 100 times larger than that of cattle and sheep dung, respectively. This comparison mostly reflects the lower N content of dung. Further, sheep dung is also relatively dry and N_2O emissions increase significantly under anaerobic (wet) conditions.

As case studies, we determined changes in emissions between 1990 and 2004 and 2010 with DCD applied to all land grazed by dairy cattle. Using method 1, with DCD, the increase of

emissions was 3.0 Gg by 2004 and 5.3 Gg by 2010. Compared to the emissions increases in the absence of DCD, DCD mitigation (the reduced change of emissions) was 4.7 Gg in 2004 and 5.3 Gg in 2010. According to method 2, the corresponding DCD mitigation was significantly greater at 7.7 Gg in 2004 and 8.8 Gg in 2010. Finally, according to method 3, all emissions were reduced each year by around 50 % (for example, from 31.2 to 18.5 Gg in 1990) and the corresponding DCD mitigation was 6.5 Gg in 2004 and 7.4 Gg in 2010. We conclude that method 2 is most strongly supported by research that has been conducted in New Zealand, recognising only sparse data are available for emissions from excreta disaggregated into urine and dung components. However, the research gaps deserves attention because Method 3 provides the most realistic portrayal of N_2O emissions from pastoral agriculture soils.

1. Background

The agriculture sector produces around 50% of the total greenhouse gas emissions from New Zealand. One-third of New Zealand's agricultural emissions are nitrous oxide (N_2O) from soils. In 2004, N_2O emissions were 24% greater than those in 1990 (Ministry for the Environment 2006). Kelliher and Clark (2004) estimated that the excess of current, national, annual N_2O emissions above the 1990 level could be largely attributed to a concurrent increase in the quantity of urine excreted onto agricultural soils by grazing dairy cattle.

N_2O emissions enter the atmosphere:
(a) directly from soils:
- urine and dung excreted by sheep and cattle during grazing
- nitrogen fertiliser application and the biological fixation of nitrogen from the atmosphere
(b) indirectly from soils as a result of ammonia volatilisation and nitrate leaching.

In soils, nitrogen conversion rate into N_2O can be reduced by the application of chemical compounds called nitrification inhibitors. One such compound is dicyandiamide (DCD). Research, conducted recently in New Zealand, showed that strategic application of a nitrification inhibitor to pasture, following simulated urine excretion by grazing dairy cattle, significantly reduced direct and indirect N_2O emissions over extensive periods[1].

Currently, New Zealand's greenhouse gas inventory does not capture and report decreased N_2O emissions as a result of nitrification inhibitor application. However, it is feasible to make the required changes. Most significantly, for areas treated by nitrification inhibitors, activity inputs would be needed seasonally at the farm scale. These include the treated area, timing and location, and the stocking and production rates because they determine excretion rate. These activity inputs and the N_2O emissions factors (EFs) will need to be scientifically defensible and robust because international, expert teams regularly review inventory methods. Further, these changes will automatically propagate into reporting under the United Nations Framework Convention on Climate Change (UNFCCC). New Zealand's N_2O emissions inventory is determined using methods provided by the Intergovernmental Panel on Climate Change (IPCC) and adopted by the Conference of Parties to the UNFCCC.

Three New Zealand-specific emission factors are used in the N_2O emissions inventory: EF_1 for fertiliser, $EF_{3(PRP)}$ for excreta (urine and dung) from grazing animals and $Frac_{LEACH}$ for leaching.

[1] See, in particular: Clough, T.J., Di, H.J., Cameron, K.C., Sherlock, R.R., Metherell, A., and Clark, H. (2006). Effect of using eco-n^{tm} nitrification inhibitor technology in dairy farming on New Zealand's agricultural greenhouse gas (GHG) inventory, and methodology for its incorporation at a national level. Report prepared for the Ministry of Agriculture and Forestry by Centre for Soil and Environmental Quality, Lincoln University.

2. Purpose

This report has two main purposes. Firstly, we review national and international literature on the effectiveness of nitrification inhibitors in reducing direct and indirect N_2O emissions from grazing animal urine and dung excreta, nitrogen fertiliser and soils. Afterwards, we develop and use three revised methods to describe how anthropogenic emissions of N_2O are reduced below that which would have occurred in the absence of the use of the nitrification inhibitors. The revisions included other aspects that are described in the next section.

3. Objectives

The project comprised two parts. Objectives specified in the contract for the Part I are:

- Review national and international literature on the effectiveness of nitrification inhibitors in reducing direct and indirect N_2O emissions from grazing animal urine and dung excreta, nitrogen fertiliser and soils. Assess the relevance of the literature and the scientific rigour applied in the work.

- Develop criteria through which non-peer-reviewed literature will be assessed. Non-peer reviewed literature will then be assessed according to the criteria and, where appropriate, findings incorporated in the report.

- Develop revised emission factors for EF_1, $EF_{3(PRP)}$, and $Frac_{LEACH}$ or any other emissions factors that might be modified, under a range of scenarios building on and refining the method of Clough *et al.* (2006), including:
  - Rate and application of nitrification inhibitors (per hectare);
  - The formulations, methods and circumstances (including timing) through which nitrification inhibitors are applied that may affect annual emission factors
  - Number of hectares applied with nitrification inhibitors and the soil's drainage class that can strongly affect $EF_{3(PRP)}$;
  - The stocking and production rates that determine nitrogen excretion rate
  - Historical time series from date of first use of nitrification inhibitors,
  - Any other factors that might be relevant in assessing the level of emission reduction due to nitrification inhibitors

- The derivation of these factors will:
  - Quantify the level of uncertainty associated with each emission factor and its associated nitrification efficacy factor (fractional reduction in emission factor attributable to the use of the inhibitor) and the reasons for this uncertainties;
  - Compare uncertainties with general uncertainties from nitrous oxide emissions from the agricultural sector; and

- Be consistent with the principles of Inter-governmental Panel on Climate Change (IPCC) Good Practice Guidance in that the data are transparent, accurate, complete and consistent[2].

- Compare the revised factors with:
- IPCC default emissions factors;
- New Zealand Specific emission factors
- Emissions factors developed by other countries.

- Complete the Ministry for the Environment checklist for inventory change approval.

The objectives specified in the contract for the Part II are:

- Describe how anthropogenic emissions of N_2O are reduced below that which would have occurred in the absence of the use of the nitrification inhibitors.

- Compare the likely reduction in emissions with those calculated elsewhere, if available, for Clean Development Mechanisms (CDM) and Joint Implementation (JI) agreements involving nitrification inhibitors.

To our knowledge, comparable CDM or JI agreements involving nitrification inhibitors were not available for comparison. Consequently, this objective will not be considered further in the report.

- Estimate future use of nitrification inhibitors and limitations to their use, and impact on emissions until the end of Commitment Period 1 to enable an estimate of future liabilities associated with N_2O emissions.

- Recommend how the revised factors should be monitored, including the long-term effectiveness of nitrification inhibitors as a nitrification inhibitor

- The production rate and number of animals (based on farm records) grazing on pastures treated and not treated with nitrification inhibitors and the soil's drainage class (based on treated area soil inspections)

- The rate of nitrification inhibitors applied, in terms of total treated hectares (based on certified applicator GPS records) and dosage in kilograms of nitrification inhibitors per hectare (also based on certified applicator records)

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[2] Definitions of these terms by the UNFCCC are:
Accuracy: Estimates should be accurate in the sense that there is no systematically over or under bias in emissions or removals as far as can be judged, and that uncertainties are reduced as far as practicable.
Transparency: means that assumptions and methodologies used for an inventory should be clearly explained to facilitate replication and assessment of the inventory by users of the reported information.
Consistency: an inventory should be internally consistent in all its elements with inventories of other years. An inventory is consistent if the same methodologies are used for the base and all subsequent years and if consistent data sets are used to estimate emissions or removals from sources or sinks.
Completeness: an inventory covers all sources and sinks ,as well as gases, included in the IPCC Guidelines as well as other existing relevant source/sink categories which are specific to individual Annex I Parties. Completeness also means full geographic coverage of sources and sinks of an Annex 1 Party.

- The relative effectiveness of nitrification inhibitor products available

Most nitrification inhibitors have not been assessed for their effectiveness in reducing N_2O emissions from grazed pasture systems. This fact rendered much of the international literature irrelevant to the project. Further, it is essential that application of the nitrification inhibitor to New Zealand soils is sustainable including no deleterious environmental consequences. Dicyandiamide (DCD) (chemically written as $C_2H_4N_4$) has been studied for more than 80 years (for example, McGuinn 1924) and it has been subject to many tests with no reported environmental side effects (Suter et al. 2006). Suter et al. (2006) determined that DCD and DMPP were the available nitrification inhibitors most suited for use in pastoral systems. The reader is also directed to a review done in New Zealand by Edmeades (2004). In New Zealand, Suter et al. reported DMPP is only available as a coated ammonium nitrate fertiliser. They concluded that this form of DMPP delivery would greatly limit its efficacy with respect to urine excreta patches in soils beneath grazed pasture and also make the inhibitor's use cost prohibitive. Research trials using DCD have recently been conducted in New Zealand's pastoral agricultural system. In agreement with Suter et al. (2006), we focus on DCD. Consequently, this objective will not be considered further in the report.

- any other factors that may be relevant to national N_2O emissions related to nitrification inhibitors

- provide a draft report of Part II

4. Nitrous oxide emissions inventory for agricultural soils

For agricultural soils, the nitrous oxide (N_2O) emissions inventory begins by determining a nitrogen (N) application rate. An emissions factor is then applied to account for the fraction of applied N that is emitted into the atmosphere. This is known as the direct emissions component of the inventory. Indirect emissions account for N_2O that comes from the fraction of applied N that leaches through the soil, $Frac_{LEACH}$, with the New Zealand specific value equal to 0.07. The sum of direct and indirect N_2O emissions yields total N_2O emissions. Direct emissions comprise about 70 % of total N_2O emissions.

To illustrate the computation of direct N_2O emissions (F_{N2O}) in a given year, we write a simplified equation comprised of average quantities

$$F_{N2O} = \{[a_n\ d\ (1/c)\ p_n\ x_N] + f\}\ EF$$

where a_n is the number of grazing, farmed animals, d is the animal's energy requirement (MJ per animal per year, MJ is one million joules), c is feed (hereafter, pasture) energy content (MJ per kg dry matter), p_n is pasture nitrogen (N) content, x_N is the fraction of N intake (N intake is equal to the product of a_n, d, (1/c) and p_N) that is excreted as urine and dung onto soils, f is the mass quantity of N fertiliser applied to soils (according to sales records compiled annually by FertResearch, Hilton Furness, personal communication) and EF is an emissions factor (mass of nitrous oxide emitted per mass of N deposited on the soil). To use the equation, the units of F_{N2O} must be converted from mass of N per year to mass of N_2O per year by multiplication by 1.57 (ratio of the molecular weights = 44/28). The equation shows

that the N loading rate onto soils includes urine and dung excreta deposited during grazing and fertiliser application.

The primary data for a_n comes from a survey sent by the Ministry of Agriculture and Forestry to around 40,000 farms annually that yields close to a 90 % response. During the year, a_n depends on a monthly population model developed by H. Clark to account for births, deaths and slaughter. Variable *d* is also determined monthly by the Australian feeding standards for grazing ruminants (CSIRO 1990), including industry-supplied animal weight and production data (e.g. milk production, fecundity rates, weights of animals at slaughter, etc.), according to Clark et al. (2003). Weight data are used to account for the maintenance component of variable *d*. Values for *c* vary monthly ranging from 9.6 – 12.6 MJ kg^{-1}, however the average value over each year is assumed constant. For this report, p_N was 3.7 % for dairy cattle and 3.0 % for beef cattle, sheep and deer. Also for this report, we assumed that DCD application did not change the variables a_n, d, c and p_N. Scenarios according to changes in these variables following DCD application were reported earlier by Clough et al. (2006, 2007). For this report, values of x_N for urine and dung were computed monthly according to the difference between N intake and N that went into product (such as milk and wool) and weight gain.

The direct EF for excreta is called $EF_{3(PRP)}$. The $EF_{3(PRP)}$ data are cumulative values of direct N_2O emissions over 5 to 10 months following an excreta application (fraction of applied nitrogen emitted to the atmosphere as nitrous oxide) based on field chamber measurements of the NzOnet field trials (Barton et al., 2000; de Klein et al., 2003, 2004; Sherlock *et al.*, 2003a,b). The data are analysed to compute a statistic known as the geometric average, a robust measure of the central tendency. As an example, for four hypothetical $EF_{3(PRP)}$ measurements, a geometric average of 0.008 may be calculated from the quantity [0.001*0.011*0.012*0.030] raised to a power of (1/4) where the four measurements are multiplied together in the square brackets and the power coefficient is equal to the inverse of the number of measurements. The arithmetic average is 0.014 or 75 % larger than the geometric average because the large value, 0.030, skewed this central tendency's estimate from the small sample. The analysis of $EF_{3(PRP)}$ data involves small samples that can exhibit tremendous variance. This reflects the conditions producing nitrous oxide in soils, mostly attributable to high nitrogen and water contents that are generally shortlived. As illustrated above, unlike the arithmetic average, the geometric average is not prone to undue contamination by (low probability) outliers that sometimes occur.

De Klein (2006) reviewed 40 different studies, including those conducted in New Zealand, and recommended to the IPCC that grazing animal excreta inputs to N_2O emissions inventories should be disaggregated into cattle and sheep excreta. For $EF_{3(PRP)}$, de Klein (2006) recommended values of 0.02 for cattle excreta and 0.01 for sheep excreta. To our knowledge, nevertheless, the IPCC default value for $EF_{3(PRP)}$ remains equal to 0.02. The New Zealand specific value for $EF_{3(PRP)}$ is equal to 0.01. For dairy cattle urine, 17 trials yielded a geometric average of 0.009 = 0.01 (Table A.1 in the Appendix). These data support the New Zealand specific value of $EF_{3(PRP)}$.

The direct EF for N fertiliser is called EF_1. For urea, applied over one year in eight equal dressings of 50 kg N/ha (during March, April, June, July, September, October, November and December 1990) to imperfectly-drained Manawatu silt loam soil beneath pasture at Palmerston North, a 365 day long study yielded EF_1 = 0.0130 (Ruz-Jerez et al. 1990). The NzOnet field trials included two measurements of EF_1 at the Hamilton site (de Klein et al.,

2004). As urea, on 23 August 2003, 50 kg N/ha was applied to adjacent freely-drained and poorly-drained soils (Horotiu and Te Kowhai, respectively) beneath pasture. The 146 day long study yielded EF_1 values of 0.0200 for the Horotiu soil and 0.0270 for the Te Kohai soil, so the geometric average EF_1 is 0.0232. Seasonal measurements of EF_1 were recently reported by Luo et al. (2007). They also applied 50 kg N/ha as urea to Te Kowhai soil beneath pasture at a site located close to that used for the NzOnet trials. Application dates, number of days when direct emissions from the urea treated areas were greater than the controls, and EF_1 values were 9 June 2003, 21 days and 0.0052, 20 August 2003, 20 days and 0.0127, 13 November 2003, 14 days and 0.004, 8 April 2004, 7 days and 0.0003, 1 July 2004, 30 days and 0.0156, 24 November 2004, 5 days and 0.001, 19 February 2005, zero days and 0.0000 and 12 July 2005, 23 days and 0.0059. The geometric average cannot be computed when there is a zero in the set of data. For Luo et al. (2007), excluding data from the 19 February 2005 application, the geometric average value of EF_1 is 0.0036.

The New Zealand specific value for EF_1 is equal to 0.01. The three trials, discussed above, yielded (geometric) average values of EF_1 equal to 0.013, 0.0232 and 0.0036. The geometric average of these three values is 0.0103. Consequently, on average, these data support the New Zealand specific value for EF_1.

Laegreid and Aasveit (2002) reviewed international data comprised of 880 measurements and concluded EF_1 averaged 0.008. Independently, and based on their international data set of 846 measurements, Bouwman et al. (2002) concluded EF_1 averaged 0.009. Based on an updated and most recent international data set of 1008 measurements for agricultural soils, Stehfest and Bouwman (2006) also concluded EF_1 averaged 0.009. As a result of Stehfest and Bouwman (2006), the IPCC decided to recommend a new default value for $EF_1 = 0.01$ (de Klein, 2006). We believe these international data support New Zealand's country specific EF_1 value of 0.01.

5. Literature review on effectiveness of nitrification inhibitors

Nitrogen (N) is applied to agricultural soils in two forms; namely, excreta deposited as urine and dung by sheep and cattle during year-round grazing outdoors and fertilizer. This review is related to N losses from soil as nitrous oxide (N_2O) emissions. These occur directly to the atmosphere and indirectly because of nitrate leaching. For computation of New Zealand's N_2O emissions inventory, urine and dung excreta are aggregated but these components are available separately on monthly bases. For the 2003 inventory, fertiliser application to agricultural soils was 337 Gg N (14 % of the total N input to these soils). Corresponding values for urine and dung excreta were 796 (32 % of the total) and 408 Gg N (16 %) for sheep, 217 (9 %) and 111 Gg N (5 %) for beef cattle and 444 (18 %) and 159 Gg N (6 %) for dairy cattle. The percentage of N applied to soils which is directly emitted as N_2O is called the direct N_2O emissions factor. For urine and urea fertiliser, based on 17 field trials conducted in New Zealand, the direct N_2O emissions factors were indistinquishable and the overall average was 1.0 % (Kelliher et al. 2005a, Kelliher and de Klein 2006). For dairy cattle and sheep dung, the corresponding averages from six field trials were 0.2 % and zero (Kelliher et al. 2005a). To our knowledge, there have been no measurements of N leaching following dung excretion onto soils. Because dung N content is only 3 – 4 %, we'd expect no N leaching associated with its application to soils. Returning to the 2003 inventory and

keeping in mind the N_2O emissions factors and N leaching, urine and fertiliser applications to agricultural soils were 1,457 and 337 Gg N, respectively. For this reason, we will focus our review on urine excreta.

A large number of chemical compounds are marketed as nitrification inhibitors and these are used in agricultural systems including dicyandiamide (DCD), 3, 4-dimethylpirazol phosphate (DMPP), neem oil, sodium thiosulfate, sulphur, acetylene, thiourea, 2-amino-4-chloro-6-methylpyrimidine (AM), 4-chloro-3-methylpyrazole (CIMP) and nitrapyrin amongst others. Nitrification inhibitors, through the inhibition of nitrification of ammonium, reduce leaching losses of nitrate. By slowing nitrification, N_2O production rate is reduced as a by-product of nitrification. Reduction of nitrate also reduces potential for the denitrification of nitrate and the production of N_2O, an intermediary in the denitrification pathway.

Most nitrification inhibitors have not been assessed for their effectiveness in reducing N_2O emissions from grazed pasture systems. This rendered much of the international literature irrelevant to the project. Further, it is essential that application of the nitrification inhibitor to New Zealand soils is sustainable including no deleterious environmental consequences. Dicyandiamide (DCD) (chemically written as $C_2H_4N_4$) has been studied for more than 80 years (for example, McGuinn 1924) and it has been subject to many tests with no reported environmental side effects (Suter et al. 2006). Suter et al. (2006) determined that DCD and DMPP were the available nitrification inhibitors most suited for use in pastoral systems. In New Zealand, Suter et al. reported DMPP is only available as a coated ammonium nitrate fertiliser. They concluded that this form of DMPP delivery would greatly limit its efficacy with respect to urine excreta patches in soils beneath grazed pasture and also make the inhibitor's use cost prohibitive. Research trials using DCD have recently been conducted in New Zealand's pastoral agricultural system and, in agreement with Suter et al. (2006), we focus our review on DCD.

The literature relating to DCD is extensive. An examination of the CAB International bibliographic database provided >500 abstracts for articles related to 'dycandiamide and soil' in agricultural systems over the period 1910 through January 2007. However < 20 of these are relevant because they deal with either urine and/or pasture systems.

We have excluded DCD literature that does not apply to grazed pastoral systems and in particular its use in conjunction with urine or dung. We do not include slurry (stored animal excreta) as the practice of storing excreta and applying it as slurry onto soils is not done in New Zealand, and slurry is chemically distinct from freshly deposited manure. We also excluded literature covering the use of DCD in rice paddies and for arable and horticultural crop production. Finally, comparative trials of DCD with other nitrification inhibitor chemicals/products and urease inhibitors are not considered here.

Sparseness of the literature led us to make some exceptions to our selection criteria for two key factors relevant to the effectiveness of DCD application to soils. This more catholic approach was necessary to obtain enough data to independently analyse the crucial and controversial relation between DCD decomposition and soil temperature. This was deemed essential for the review and synthesis of seasonal DCD efficacy field trials that have been conducted across New Zealand.

Dicyandiamide (DCD)

DCD is a white or colourless crystal that inhibits the first stage of nitrification (Amberger 1989). For application to soils at 10 kg/ha, DCD is considered to have a low water solubility. This can be illustrated by a simple calculation using the water solubility of DCD, 23 grams/litre at 13 °C according to Amberger (1989). At this temperature, DCD application in aqueous solution to one hectare of soil includes 435 litres of water! In contrast, the water solubility of sucrose at 13 °C is around 190 kg/litre. DCD contains 65% nitrogen and in soils, it is decomposed via guanyle urea and guanidine to urea, a conventional nitrogen fertilizer (Amberger, 1989). DCD is practically non-toxic according to Amberger (1989) (LD50/LC50: Oral, mouse: LD50 = >10 g/kg). In comparison, for salt (sodium chloride), the LD50: Oral, mouse = 4 g/kg. After DCD has decomposed to urea, it ultimately hydrolyses, catalysed by the enzyme urease, to form ammonium bicarbonate and hydroxide ions. DCD has a bacteriostatic mode of action, so it does not kill soil bacteria but rather inhibits or reduces their activity. In soils, microbes use the DCD molecule as a nitrogen source, and it is biotically mineralised or decomposed by specific enzyme activity (Schwarzer and Haselwandter, 1991).

New Zealand peer-reviewed literature

Effects on nitrate leaching ($Frac_{LEACH}$)

In a lysimeter study that used a free-draining Lismore stoney silt loam soil the use of DCD decreased nitrate leaching by 76% for urine applied in the autumn and by 42% for urine applied in the spring (Di and Cameron, 2002). In this trial, urea was also applied in eight split dressings to the lysimeters (200 kg N/ha/y). DCD was applied in solution form at the rate of 7.5 kg/ha after each split application of urea or at the higher rate of 15 kg/ha with each urine application (Di and Cameron, 2002).

Concentrations of inorganic-N were monitored in Wakanui silt loam soil over 100 days in urine-amended plots with and without DCD at either 10 or 25 kg/ha (Cookson and Cornforth, 2002). Commencing in March (day 60 of the year), at a depth of 0.075 m, daily average soil temperature decreased from 18 ^{o}C to 6 ^{o}C. In the urine only plots soil ammonium decreased to the background level found in control plots within 28 days. When urine was applied with DCD it took 60 days for soil ammonium concentrations to reach the levels seen in the control plots. DCD application reduced nitrate leaching (below a depth of 0.2 m) by 46 % (10 kg DCD/ha) and 74 % (25 kg DCD/ha).

Lysimeters, containing Templeton fine sandy loam soil, were treated with cow urine (1000 kg N/ha) and urea N (200 kg N/ha/y split into 8 applications) and then treated with DCD (15 kg/ha) in autumn or treated with DCD in autumn and spring, in solution form (Di and Cameron, 2004b). These treatments were designed to determine the effectiveness of DCD in reducing nitrate leaching as affected by one or two applications. There was no difference in the quantity of nitrate leached for the two DCD treatments with a 76% reduction in nitrate leaching.

Lysimeters, containing Templeton fine sandy loam soil, were treated with urea N (200 kg N/ha/y split into 8 applications) and urine (1000 kg N/ha) applied in a single application in the autumn. DCD treatments applied included ‘no DCD’, and DCD applied as a fine particle

suspension at either 5 or 10 kg/ha of DCD (Di and Cameron, 2005). Nitrate-N leaching losses were not significantly reduced when DCD was applied at 5 kg/ha but they were significantly reduced at 10 kg/ha with nitrate-N leaching losses reduced by 68%.

Smith et al. (2005) found that DCD (15 or 30 kg N/ha) applied with synthetic urine (580 kg N/ha) was effective in limiting nitrification in a poorly-drained Pukemutu soil for more than 100 days. This indicated the potential for reduced nitrate leaching when treatments were applied in late spring. At a depth of 0.1 m, daily average soil temperature increased from 10 ^{o}C to 18 ^{o}C by day 80 of the year (21 March).

A summary of experimental protocols for relevant published field studies performed in New Zealand, and their treatments, is presented in Table 1. (Note the field study of Smith et al. (2005) is presented and discussed separately below).

Table 1: Experimental overviews and treatments of lysimeter and field studies using DCD. Fertiliser N (urea) was applied to all treatments, at a rate of 200 kg N ha^{-1} y^{-1} split into 8 dressings, the exception to this was in (Di and Cameron, 2002), where treatment 1 received nil fertiliser, and treatments 7 and 8, where the urea was split evenly into 4 dressings. Urine-N was applied in all treatments unless stated, in the season shown, at rate of 1000 kg N ha^{-1}. DCD was applied as a solution in studies except in Di and Cameron (2005; 2006) and Di et al. (2006) where a fine particle suspension (FPS) was used.

Reference[a]	Soil surface texture	Soil pH	Pasture age[b] (y)	Irrigation (mm)	Treatments	Urine application season	Total N (kg)	DCD[c] (kg ha^{-1})	Total DCD (kg)
(Di and Cameron, 2002)	silt-loam	5.9	4	100 mm flood every 3 weeks 1364 total 564 rain 800 irrig'n	1	nil	0	0	0
					2	nil	200	0	0
					3	Aut.	1200	0	0
					4	Aut.	1200	7.5[d]/15.0[e]	75
					5	Aut.	1200	0	0
					6	Aut.	1200	7.5[d]/15.0[e]	75
					7	Spr.	1200	0	0
					8	Spr.	1200	7.5[d]/15.0[e]	45
(Di and Cameron, 2003)	silt loam	5.9	5	50 mm spray every 2 weeks 850 total 490 rain 360 irrig'n	1	Aut.	1200	0	0
					2	Aut.	1200	15[f]	15
					3	Aut.	1200	15[g]	30
					4	Aut.	1200	15[h]	15
					5	Spr.	1200	0	0
					6	Spr.	1200	15[f]	15
					7	Spr.	1200	15[i]	75
					8	Spr.	1200	7.5[j]	75

[b]Pastures were all perennial ryegrass (*Lolium perenne*) - white clover (*Trifolium repens*). [c]DCD = dicyandiamide, [d]kg per urea application, [e]kg per urine application, [f]after urine application, [g]15 kg after urine application and 15 kg in late winter, [h]mixed with urine, [i]15 kg mixed with urine application then 15 kg quarterly, [j]7.5 kg after urine application and 7.5 kg after each urea application.

Table 1 continued: Experimental overviews and treatments of lysimeter and field studies using DCD. Fertiliser N (urea) was applied to all treatments, at a rate of 200 kg N ha^{-1} y^{-1} split into 8 dressings. The exception to this was in (Di and Cameron, 2002), where treatment 1 received nil fertiliser, and treatments 7 and 8, where the urea was split evenly into 4 dressings. Urine-N was applied in all treatments unless stated, in the season shown, at rate of 1000 kg N ha^{-1}. DCD was applied as a solution in studies except in Di and Cameron (2005; 2006) and Di et al. (2006) where a fine particle suspension (FPS) was used.

Reference[a]	Soil surface texture	Soil pH	Pasture age[b] (y)	Irrigation (mm)	Treatments	Urine application season	Total N (kg)	DCD[c] (kg ha^{-1})	Total DCD (kg)
(Di and Cameron, 2004b)	silt loam	5.8	>10	50 mm spray every 2 weeks 1600 total	1	Aut.	1200	0	0
					2	Aut.	1200	15[f]	15
					3	Aut.	1200	15[k]	30
(Di and Cameron, 2005)	Sandy loam	5.8	>10	50 mm spray every 2 weeks 1200 total 500 rain 700 irrig'n	1	Aut.	1200	0	0
					2	Aut.	1200	5[k]	15
					3	Aut.	1200	10[k]	30
(Di and Cameron, 2006)	silt loam sandy loam	5.9	5	30 mm spray every week 1200 total 500 rain 700 irrig'n	1	Aut.	1200	0	0
					2	Aut.	1200	7.5[k]	15
					3	Aut.	1200	10[k]	20
					4	Aut.	1200	15[k]	30
					5	Win.	1200	0[k]	0
					6	Win.	1200	10[k]	20
					7	Aut.	1200	0[k]	0
					8	Aut.	1200	10[k]	20
					9	Aut.	1200	10[l]	20

[b]Pastures were all perennial ryegrass (*Lolium perenne*) - white clover (*Trifolium repens*). [c]DCD = dicyandiamide, [d]kg per urea application, [e]kg of per urine application, [f]15 kg after urine application, [g]15 kg after urine application and 15 kg in late winter, [h]15 kg mixed with urine application, [i]15 kg mixed with urine application then 15 kg quarterly, [j]7.5 kg after urine application and 7.5 kg after each urea application, [k]after urine application and in mid-winter, [l]ten days after urine application and mid-winter.

Table 1 continued: Experimental overviews and treatments of lysimeter and field studies using DCD.
Urine-N was applied in all treatments unless stated, in the season shown, at rate of 1000 kg N ha^{-1}. DCD was applied as a FPS.

Reference[a]	Soil surface texture	Soil pH	Pasture age[b] (y)	Irrigation (mm)	Treatments	Urine application season	Total N (kg)	DCD[c] (kg ha^{-1})	Total DCD (kg)
(Di et al., 2006)	fine-sandy-loam	5.8	not stated	Supplementary rainfall	1	nil	0	0	0
					2	nil	0	10	10
					3	Win.	1000	0	0
					4	Win.	1000	10	10
	stony-silt-loam	5.9	not stated	Supplementary rainfall	1	Aut.	1000	0	0
					2	Aut.	1000	10	20[a]
	Silt Loam	5.5	Not Stated	nil	1	nil	0	0	0
					2	nil	0	10	20 [a]
					3	Aut.	1000	0	0
					4	Aut.	1000	10	20 [a]
	pumice Sand	5.6	Not Stated	nil	1	nil	0	0	0
					2	nil	0	10	10
					3	Win.	700	0	0
					4	Win.	700	10	10

[a]DCD applied in autumn and in winter.

Table 2 summarises nitrate leaching from studies where DCD was applied with urine.

The reduction in nitrate leaching ranged from 13 to 77%. If the lowest rate of DCD is excluded (i.e. the 5kg/ha rate used in treatment 2 by Di and Cameron (2005)), the range becomes 42 to 77%. All the leaching measurements were performed after autumn/winter applications of urine, the sole exception being Di and Cameron (2002), treatment 8 where the urine was applied in spring. A spring application severely reduces the likelihood of nitrate leaching and it could be considered that there is also greater opportunity for plant uptake of urine-N over the growing season. DCD should be most effective in reducing nitrate leaching when application coincides with the lowest soil temperatures (see below) and highest drainage rates, i.e. during from autumn through winter.

We thus eliminate the spring data (42% from Di and Cameron (2002), treatment 8), so the range becomes 68 to 77% with **a mean of 74% reduction in nitrate leaching ($Frac_{LEACH}$) when DCD was applied (n=5, Std Dev. 4 %)**. The average result coincides with 75% reduction in nitrate leaching reported by Cookson and Cornforth (2002). The DCD application rates were 10 and 15 kg/ha with the lower rate achieving the minimum leaching reduction (68%). The application dose effect will be explored later.

The experiments reviewed here did not include cattle grazing following DCD application. The reduction in nitrate leaching thus did not account for recycling of 'conserved' nitrogen via animal excreta. It follows that plant ingestion by grazing cattle leads to N excretion onto soils. The soil thus receives further N application(s) but no accompanying DCD application(s). Hence, for grazing after DCD application, nitrate leaching may be greater than expected from the reviewed experiements. This is predicated on the 'conserved' nitrogen being taken up by pasture plants. We note that on high fertility soils, ryegrass begins growth at 5 °C according to (Kerr, 2000). Pasture growth can thus be limited by low temperature during May - September. Finally, we note the experiments reviewed included multiple urea fertiliser dressing following DCD application, although these dressing involved only 25 kg N/ha, while urine application was 700 – 1200 kg N/ha..

The experiments reviewed here are intended to represent the results of DCD application onto agricultural pasture. For dairy farms, in the South Island and possibly the Waikato and Taranaki regions in future, grazing may take place during May – September on 'support' land. This land may not be located within a farm's boundary. There may also be a 'cut and carry' feeding regime during 'May – September' including feed produced outside the farm's boundary. This may involve 'stand off' and feed pads. We do not know the importation rate of palm kernel (by-product of the palm oil industry in South East Asia, mainly in Malaysia) that may be used as cattle feed, but this may be another consideration.

Finally, we analyse the tabulated data to determine FracLEACH. As stated earlier, the New Zealand-specific value for FracLEACH is 0.07. Following urine application in autumn 2001 to the free-draining Lismore stoney silt loam, where no DCD was applied, 43% of the applied N leached from the soil as nitrate according to Di and Cameron (2002)(Table 2). Consequently, FracLEACH was 0.43. Following urine application in autumn 2002 and 2003 to the free-draining Templeton fine sandy loam, where no DCD was applied, 7 and 11 % of the applied N leached from the soil as nitrate according to Di and Cameron (2004b) and Di and Cameron (2005), respectively. Hence, FracLEACH averaged 0.09 in these studies.

Table 2: Summary of the mass of NO_3-N leached, the percentage reduction in NO_3-N leaching when DCD was used, the fraction of N applied leached; N_2O-N emissions and their respective reductions in emissions when DCD was used in the various research trials following cow urine application to lysimeters and field plots[a]

Reference[b]	Soil	Treatment	Total N Applied (kg)	DCD[c] (kg ha^{-1})	NO_3-N leached (kg)	Leaching reduction (%)	Fraction of N applied leached	N_2O-N (kg ha^{-1})	Reduction in N_2O Loss (%)
(Di and Cameron, 2002)	**Lismore**	**1**	**0**	**0**	**4.8**	**-**	**-**	**-**	**-**
	Lismore	**2**	**200**	**0**	**7.9**	**-**	**0.040**	**-**	**-**
	Lismore	**3**	**1200**	**0**	**516**	**-**	**0.430**	**-**	**-**
	Lismore	**4**	**1200**	**7.5[d]/15[e]**	**128**	**75**	**0.107**	**-**	**-**
	Lismore	**5**	**1200**	**0**	**488**	**-**	**0.407**	**-**	**-**
	Lismore	**6**	**1200**	**7.5[d]/15[e]**	**112**	**77**	**0.093**	**-**	**-**
	Lismore	**7**	**1200**	**0**	**397**	**-**	**0.331**	**46.0**	**-**
	Lismore	**8**	**1200**	**7.5[d]/15[e]**	**230**	**42**	**0.192**	**8.5**	**82**
(Di and Cameron, 2003)	**Lismore**	**1**	**1200**	**0**	**-**	**-**	**-**	**26.7**	**-**
	Lismore	**2**	**1200**	**15[f]**	**-**	**-**	**-**	**7.0**	**74**
	Lismore	**3**	**1200**	**15[g]**	**-**	**-**	**-**	**7.6**	**72**
	Lismore	**4**	**1200**	**15[h]**	**-**	**-**	**-**	**4.5**	**83**
	Lismore	**5**	**1200**	**0**	**-**	**-**	**-**	**18.0**	**-**
	Lismore	**6**	**1200**	**15[f]**	**-**	**-**	**-**	**4.5**	**75**
	Lismore	**7**	**1200**	**15[i]**	**-**	**-**	**-**	**4.8**	**73**
	Lismore	**8**	**1200**	**7.5[j]**	**-**	**-**	**-**	**2.5**	**86**

[b]Pastures were all perennial ryegrass (*Lolium perenne*) - white clover (*Trifolium repens*). [c]DCD = dicyandiamide, [d]kg per urea application, [e]kg per urine application, [f]15 kg after urine application, [g]15 kg after urine application and 15 kg in late winter, [h]15 kg mixed with urine application, [i]15 kg mixed with urine application then 15 kg quarterly, [j]7.5 kg after urine application and 7.5 kg after each urea application, [k]after urine application and in mid-winter, [l]ten days after urine application and mid-winter.

Table 2 continued: Summary of the mass of NO_3-N leached, the % reduction in NO_3-N leaching, the fraction of N applied leached; N_2O-N emissions and their respective reductions in emissions.

Reference [b]	Soil	Treatment	Total N Applied (kg)	DCD[c] (kg ha^{-1})	NO_3-N leached (kg)	Leaching reduction (%)	Fraction of N applied leached	N_2O-N (kg ha^{-1})	Reduction in N_2O Loss (%)
(Di and Cameron, 2004b)	Templeton	1	1200	0	85	-	0.071	-	-
	Templeton	2	1200	15[f]	22	74	0.018	-	-
	Templeton	3	1200	15[k]	20	76	0.017	-	-
(Di and Cameron, 2005)	Templeton	1	1200	0	134	-	0.112	-	-
	Templeton	2	1200	5[k]	116	13	0.097	-	-
	Templeton	3	1200	10[k]	43	68	0.036	-	-
(Di and Cameron, 2006)	Lismore	1	1200	0	-	-	-	23.1	-
	Lismore	2	1200	7.5[k]	-	-	-	8.2	65
	Lismore	3	1200	10[k]	-	-	-	6.9	70
	Lismore	4	1200	15[k]	-	-	-	6.2	73
	Lismore	5	1200	0[k]	-	-	-	31	-
	Lismore	6	1200	10[k]	-	-	-	8.4	73
	Templeton	7	1200	0[k]	-	-	-	37.4	-
	Templeton	8	1200	10[k]	-	-	-	14.6	61
	Templeton	9	1200	10[l]	-	-	-	16.3	56

[b]Pastures were all perennial ryegrass (*Lolium perenne*) - white clover (*Trifolium repens*). [c]DCD = dicyandiamide, [d]kg per urea application, [e]kg per urine application, [f]15 kg after urine application, [g]15 kg after urine application and 15 kg in late winter, [h]15 kg mixed with urine application, [i]15 kg mixed with urine application then 15 kg quarterly, [J]7.5 kg after urine application and 7.5 kg after each urea application, [k]after urine application and in mid-winter, [l]ten days after urine application and mid-winter.

Table 2 continued: Summary of the mass of NO_3-N leached, the % reduction in NO_3-N leaching, the fraction of N applied leached; N_2O-N emissions and their respective reductions in emissions[a]

Reference[b]	Soil	Treatment	Total N Applied (kg)	DCD[c] (kg ha^{-1})	NO_3-N leached (kg)	Leaching reduction (%)	Fraction of N applied leached	N_2O-N (kg ha^{-1})	Reduction in N_2O Loss (%)
(Di et al., 2006)	**Templeton**	**1**	**0**	**0**	**-**	**-**	**-**	**1.0**	
	Templeton	**2**	**0**	**10**	**-**	**-**	**-**	**0.8**	**20**
	Templeton	**3**	**1000**	**0**	**-**	**-**	**-**	**20.9**	
	Templeton	**4**	**1000**	**10**	**-**	**-**	**-**	**5.7**	**73**
	Lismore	**1**	**1000**	**0**	**-**	**-**	**-**	**8.7**	
	Lismore	**2**	**1000**	**10**	**-**	**-**	**-**	**2.9**	**67**
	Horotiu	**1**	**0**	**0**	**-**	**-**	**-**	**0.27**	
	Horotiu	**2**	**0**	**10**	**-**	**-**	**-**	**0.12**	**56**
	Horotiu	**3**	**1000**	**0**	**-**	**-**	**-**	**6.2**	
	Horotiu	**4**	**1000**	**10**	**-**	**-**	**-**	**2.4**	**61**
	Taupo	**1**	**0**	**0**	**-**	**-**	**-**	**0.18**	
	Taupo	**2**	**0**	**10**	**-**	**-**	**-**	**0.15**	**17**
	Taupo	**3**	**700**	**0**	**-**	**-**	**-**	**1.01**	
	Taupo	**4**	**700**	**10**	**-**	**-**	**-**	**0.31**	**69**

[b]Pastures were all perennial ryegrass (*Lolium perenne*) - white clover (*Trifolium repens*). [c]DCD = dicyandiamide, [d]kg per urea application, [e]kg per urine application, [f]15 kg after urine application, [g]15 kg after urine application and 15 kg in late winter, [h]15 kg mixed with urine application, [i]15 kg mixed with urine application then 15 kg quarterly, [J]7.5 kg after urine application and 7.5 kg after each urea application, [k]after urine application and in mid-winter, [l]ten days after urine application and mid-winter.

Effects on direct N_2O emissions from urine applied to soils ($EF_{3(PRP)}$)

Table 3 summarises direct N_2O emission factors obtained from field studies of four soils based on various treatments with DCD.

In the lysimeter study that used a free-draining Lismore stony silt loam soil, DCD application decreased direct N_2O emissions (hereafter, N_2O emissions) by 82% from urine patches over the course of two spring urine deposition events (Di and Cameron, 2002). Urea was also applied in eight split dressings to the lysimeters (200 kg N/ha/y). DCD was applied in solution form at the rate of 7.5 kg/ha after each split application of urea or at the higher rate of 15 kg/ha with each urine application.

A lysimeter study, that also used a free-draining Lismore stony silt loam, showed DCD reduced N_2O emissions by 76% following urine application in autumn and by 78% following a spring urine application (Di and Cameron, 2003). Repeated applications of DCD after urine application or mixing DCD with urine had effects similar to a single application immediately after urine deposition. DCD was applied in solution form at the rate of 15 kg/ha after each urine application.

Templeton and Lismore soils were again used in lysimeter studies where urea (eight split dressings; 200 kg N/ha/y) and cow urine (1000 kg N/ha) were applied (Di and Cameron, 2006). Urine treatments were applied in late autumn or winter. DCD was applied twice, initially in late autumn and again in winter to all treatments. Where urine was applied in late autumn the first DCD application was applied immediately after the urine except for one treatment where the DCD was applied 10 days after the urine. Where urine was applied in winter the first DCD application occurred in late autumn followed by the second application in winter. DCD was applied at three rates to the Lismore soil (7.5, 10 and 15 kg/ha) when urine was applied in late autumn and at 10 kg/ha to late autumn urine applications on the Templeton soils. The DCD was applied as a fine particle suspension and sprayed evenly over the soil surface prior to irrigation (10 mm). On the Lismore soils all three rates of DCD were effective in reducing N_2O emissions from the urine applied in late autumn by 65-73% while the 10kg/ha rate of DCD also reduced N_2O emissions from the Lismore soil in winter by 73%. In the Templeton soil DCD (10 kg/ha) reduced late autumn applied urine emissions by 61%. DCD applied 10 days after urine deposition was equally effective with a 56% reduction in N_2O emissions.

Di et al. (2006) examined the effectiveness of DCD in reducing N_2O emissions from urine patches on four different soil types located in the Waikato (Horotiu silt loam), Canterbury (Templeton fine sandy loam and a Lismore stony loam) and Taupo (Taupo pumice sand) regions. The authors noted that soil temperatures differed between soils over the experimental periods. Analysis of these data indicated that, on average, the Horotiu soil was 2 – 3 ^{o}C warmer but no differences were statistically significant (see further discussion of these data in a subsequent section). At all sites urine was applied (1000 kg N/ha) either in autumn or winter. DCD was applied as a fine particle suspension on the same day as the urine treatments with the exception of the Templeton soil where an 18 day delay was instigated to simulate the possible delay between the end of a grazing event and a DCD application. Reductions in the N_2O emissions for the Templeton, Lismore, Horotiu and Taupo soils were 73, 67, 61 and 69% respectively.

When DCD was applied, the reduction in N_2O emissions ranged from 56 to 86% (n = 17, mean 71 %, Std. Dev. 8 %). This data analysis includes the four soils called Lismore (n = 12), Templeton (n = 3), Horotiu (n = 1) and Taupo (n= 1). Excluding the value of 56 % obtained for the Templeton soil when DCD was applied 10 or 18 days after the urine, the range becomes 61 to 86% (n = 16, mean 72 %, Std. Dev. 7 %).

We now refine the data analysis by considering the soils separately. For the Templeton soil, N_2O reductions ranged from 56 to 73 % (n = 3, mean 63 %, Std. Dev. 9 %). The largest data set is available for the Lismore soil where N_2O reduction ranged from 65 to 83 % (n = 12, mean 74 %, Std. Dev. 6 %). For the Horotiu and Taupo soils, single trials for each soil yielded N_2O emission reductions of 61 and 69% respectively. **Combining the mean and single values of the direct N_2O emissions reduction ($EF_{3(PRP)}$) when DCD was applied to the four soils, the range was 61 to 74 % (n = 4, mean 67 %, Std. Dev. 6 %).**

As before, the experiments reviewed here did not include cattle grazing following DCD application. Smith et al. (2007) provided a draft manuscript reporting the effectiveness of DCn™ to reduce soil nitrate accumulation and N_2O emissions within a grazed pasture system. In the first year, during late April 2004, urea or urea+DCD treatments were applied after grazing. Both treatments had a urea application rate of 50 kg/ha and the DCD application rate was 10 kg/ha (42 kg DCn™/ha). Plots were grazed (for 3 hours by 2.7 dairy cattle/ha as described by de Klein et al., 2006; confirmed by personal communication on 18 April 2007) prior to and one month after treatment applications. In year two the same treatments were applied three times on 4th March, 18th April, and 25th August. The plots were grazed just before each of the three treatment application and one month after the third treatment application (for one day, less time spent being milked twice, by 2.7 dairy cattle/ha). **The experimental design of Smith et al. (2007) is thus unique because grazing took place after DCD application and direct N_2O emissions were measured.**

In year 1 N_2O emissions were generally insignificant and spatially variable. This may have reflected the water content exceeding field capacity in the poorly drained soil throughout 2004. In year 2 with an elevated number of replicates, differences in N_2O emissions were detected for 70% of the measurement sets and DCD application corresponded with significantly lower emissions. The soil remained very wet but drier than year 1, especially during the spring of year 2. In year one few differences in soil ammonium N were detected, with a brief period where soil nitrate-N was elevated in the urea only treatment. In year 2 soil ammonium-N varied little in March and April but was higher in the DCD treated plots in spring. Soil nitrate-N was reduced significantly with DCD use, but not after a second grazing following the August application in spring (29th September). Reductions in N_2O emissions ranged between 75 and 91% over a 2 to 3 month period following application (n = 3, mean 82%, Std. Dev. 8). These results should also be considered for judgement about direct N_2O emissions reduction ($EF_{3(PRP)}$) following DCD application.

Table 3: Emission factors for N_2O-N calculated as the mass of N_2O-N divided by the mass of N applied, either gross-N (fertiliser + urine) or urine-N only

Reference	Treatment	DCD[c] (kg ha^{-1})	EF (gross N)	EF (urine-N)	Reduction in EF (%)
(Di and Cameron, 2002)	**7**	**7.5[d]/15[e]**	**0.038**	**0.02**	**82**
	8	**0**	**0.007**		
(Di and Cameron, 2003)	**1**	**0**	**0.022**	**-**	**-**
	2	**15[f]**	**0.006**	**-**	**74**
	3	**15[g]**	**0.006**	**-**	**72**
	4	**15[h]**	**0.004**	**-**	**83**
	5	**0**	**0.015**	**-**	**-**
	6	**15[f]**	**0.004**	**-**	**75**
	7	**15[i]**	**0.004**	**-**	**73**
	8	**7.5[j]**	**0.002**	**-**	**86**
(Di and Cameron, 2006)	**1**	**0**	**0.019**	**0.023**	**-**
	2	**7.5[k]**	**0.007**	**0.008**	**65**
	3	**10[k]**	**0.006**	**0.007**	**70**
	4	**15[k]**	**0.005**	**0.006**	**73**
	5	**0[k]**	**0.026**	**0.027**	**-**
	6	**10[k]**	**0.007**	**0.007**	**73**
	7	**0[k]**	**0.031**	**0.036**	**-**
	8	**10[k]**	**0.012**	**0.014**	**61**
	9	**10[l]**	**0.014**	**0.016**	**56**
	1	**0**	**-**	**-**	**-**
	2	**10**	**-**	**-**	**-**
	3	**0**	**-**	**0.020**	**-**
	4	**10**	**-**	**0.005**	**75**
	1	**0**	**-**	**0.008**	**-**
	2	**10**	**-**	**0.003**	**63**
	1	**0**	**-**	**-**	**-**
	2	**10**	**-**	**-**	**-**
	3	**0**	**-**	**0.006**	**-**
	4	**10**	**-**	**0.002**	**67**
	1	**0**	**-**	**-**	**-**
	2	**10**	**-**	**-**	**-**
	3	**0**	**-**	**0.009**	**-**
	4	**10**	**-**	**0.003**	**67**

[e]kg per urine application, [f]15 kg after urine application, [g]15 kg after urine application and 15 kg in late winter, [h]15 kg mixed with urine application, [i]15 kg mixed with urine application then 15 kg quarterly, [j]7.5 kg after urine application and 7.5 kg after each urea application, [k]after urine application and in mid-winter, [l]ten days after urine application and mid-winter.

Effects on herbage yields

In a lysimeter study that used a free-draining Lismore stoney silt loam soil the use of DCD increased herbage yields in all treatments relative to non-DCD treatments (Di and Cameron, 2002). Urea was also applied in eight split dressings to the lysimeters (200 kg N/ha/y). DCD was applied in solution form at the rate of 7.5 kg/ha after each split application of urea or at the higher rate of 15 kg/ha with each urine application (Di and Cameron, 2002). The application of DCD increased annual herbage yields in the autumn treatments by an average 49% and by an average 18% in the spring treatments.

Using a free-draining Templeton fine sandy loam soil, lysimeters were treated with cow urine (1000 kg N/ha) and urea N (200 kg N/ha/y split into 8 applications) and then treated with DCD (15 kg/ha) in autumn or treated with DCD in autumn and spring, in solution form (Di and Cameron, 2004d). Following DCD application to urine patches, the annual herbage dry matter yields increased by 19-24%.

For a poorly-drained Pukemutu soil, Smith et al. (2005) found no significant differences in pasture production for treatments that included artificial urine (580 kg N/ha) and DCD at 15 or 30 kg N/ha in a solution form. A urine-only treatment was not included, so it is not possible to compare the effect of urine +DCD against urine only in terms of DM yield. In addition this study was performed in late spring when pasture production rate should be at a maximum (the 156-day-long trial began 30 October 2003). Rainfall maintained soil water content near the field capacity for the trial's first 30 days but thereafter, soil water content was only about one-quarter of the field capacity. At a depth of 0.1 m, minimum, maximum and mean soil temperatures were 7, 18 and 15 ^{o}C, respectively. The relatively dry and warm soil may have affected pasture herbage response to the additional N by DCD treatment. Also with respect to the earlier studies, these 156-day-long results may not be directly comparable to those obtained over an entire year.

There has been one New Zealand field trial quantifying the effects of repeated use of DCD on pasture production and quality (Moir et al. 2007). For four years (2002 – 2006 at the Lincoln University Dairy Farm), DCD was applied to a Wakanui silt loam soil beneath pasture at 10 kg ha^{-1} in early May in addition to dairy cattle urine (1000 kg N ha^{-1}) with DCD applied again in early August. **A herd of dairy cattle (3.3 cows/ha in year one increasing annually up to 4.3 cows/ha in year four) grazed the plots at approximately 21 day intervals during September - May (9 months) each year with no grazing during June – August.** Comparisons were made with control plots that received no DCD. All plots had an area of 100 m^2 and a ('nova flow') drainage pipe installed at a depth of 0.6 m. Each year, DCD applications consistently corresponded with increased pasture herbage dry matter yield that ranged from 19 to 36 % (n = 8, mean 24 %, Std. Dev. 6 %) on an annual basis including urine patches and inter-urine areas. On average, calculated on whole paddock and annual bases, application of DCD corresponded with a 21 % increase of dry matter production. Pasture nitrogen, metabolisable energy and fibre contents were not affected by the DCD applications.

Table 4 summarises the herbage yield data with respect to DCD treatment.

Table 4: Increases in DM yields under DCD applications and the average total annual yields.

Reference	Treatment	DCD[c] (kg ha^{-1})	Increase in DM (%)	%N	Average DM yield (tonne ha^{-1} y^{-1})
(Di and Cameron, 2002)	**1**	**0**	**-**	**3.5[c]**	**11[c]**
	2	**0**	**-**	**-**	**-**
	3	**0**	**-**	**-**	**-**
	4	**7.5[d]/15[e]**	**49[a]**	**4.1[d]**	**15[d]**
	5	**0**	**-**	**-**	**-**
	6	**7.5[d]/15[e]**	**-**	**-**	**-**
	7	**0**	**-**	**-**	**-**
	8	**7.5[d]/15[e]**	**18[b]**	**-**	**-**
(Di and Cameron, 2004d)	**1**	**0**	**-**	**3.3**	**15.9**
	2	**15[f]**	**14**	**3.5**	**18.2**
	3	**15[k]**	**33**	**3.1**	**21.1**
(Smith et al., 2005)	**1**	**0[l]**	**-**	**1.9**	**3.0[m]**
	8	**10[l]**	**-**	**3.6**	**6.7[m]**
	9	**20[l]**	**-**	**3.6**	**7.2[m]**
(Di and Cameron, 2006)	**1**	**0**	**-**	**2.9**	**15.3**
	2	**5[k]**	**0**	**2.9**	**15.3**
	3	**10[k]**	**33**	**3.1**	**20.3**

[a]average of autumn urine treatments + DCD [b]average of spring urine treatments + DCD
[c]without DCD [d]with DCD [e]kg per urine application, [f]15 kg after urine application, [k]after urine application and in mid-winter, [l] artificial urine applied at nil (treatment 1) or 580 kg N/ha with DCD in solution form), [m]DM yield is for tonnes/ha over 156 days.

Table 4 continued: Increases in DM yields under DCD applications and the average total annual yields.

Reference	Treatment	DCD (kg ha^{-1})	Increase in DM (%)	%N	Average DM yield (tonne ha^{-1} y^{-1})[e]
(Moir et al., 2007) Year 1	**1[a]**	**0**		**3.5**	**10.2**
	2[b]	**10**	**21**	**3.5**	**12.3**
	3[c]	**0**		**3.6**	**11.6**
	4[d]	**10**	**30**	**3.4**	**15.1**
(Moir et al., 2007) Year 2	**1**	**0**		**3.6**	**9.0**
	2	**10**	**17**	**3.6**	**10.5**
	3	**0**		**3.8**	**10.0**
	4	**10**	**23**	**3.8**	**12.3**
(Moir et al., 2007) Year 3	**1**	**0**		**3.5**	**10.3**
	2	**10**	**25**	**3.7**	**12.9**
	3	**0**		**3.9**	**13.3**
	4	**10**	**36**	**4.0**	**18.1**
(Moir et al., 2007) Year 4	**1**	**0**		**3.6**	**11.8**
	2	**10**	**19**	**3.8**	**14.1**
	3	**0**		**4.1**	**14.9**
	4	**10**	**23**	**4.3**	**18.4**

[a]Inter-urine, no DCD, [b]Inter-urine + DCD
[c]Urine, no DCD, [d]Urine + DCD, [e]DM yield is tonnes/ha over 365 days, determined by harvesting the herbage at approximately 21 day intervals as described by Moir et al. (2007).

Effects on ammonia volatilization

Using a free-draining Templeton fine sandy loam soil, lysimeters were treated with cow urine (1000 kg N/ha) and urea N (200 kg N/ha/y split into 8 applications) and then treated with DCD (15 kg/ha) in autumn or treated with DCD in autumn and spring, in solution form (Di and Cameron, 2004d). Ammonia volatilization losses were not increased by the DCD treatment with ammonia-N volatilization losses equal to 1.7 - 3.5% of the urine-N applied. The authors suggested that since urine is a liquid it would rapidly permeate into the soil after deposition.

It is understood that ammonia volatilization is affected by temperature, wind speed and soil pH, buffer capacity and the concentrations of ammonia or ammonium in soil solution. The factors affecting ammonia volatilization have been reviewed elsewhere (Haynes and Sherlock, 1986; Jarvis and Pain, 1990). For urine applied at 500 kg N/ha during summer, autumn and winter trials at Lincoln with Templeton silt loam soil, and including no DCD applications, ammonia volatilisation ranged from 10 to 37 % of the applied N (n = 9, Ave. 20 %, Std. Dev 8 %)(Sherlock, 1984).

Given that the use of DCD slows down the rate of nitrification in the urine patch and thus prolongs the presence of ammonium and the period of elevated soil pH, it might be expected that such conditions would favour volatilization. However, the extra ammonium available could also undergo other transformations and be fixed, immobilized or be taken up by plants, rather than be volatilized. In fact a prolonged elevation of soil pH was observed when urine was treated with DCD but this did not translate into higher ammonia losses (Di and Cameron, 2004d). The field study of Wakanui silt loam by Cookson and Cornforth (2002) included measurement of soil pH following the application of DCD at 10 or 25 kg/ha with urine (450 kg/ha). The controls had a pH of 5.3. After DCD application, the soil's pH increased by less than 1 pH unit. These measurements were made on sieved samples, taken from the surface to a depth of 0.1 m, in the laboratory.

Effects on other soil cations

Using a free-draining Templeton fine sandy loam soil, lysimeters were treated with cow urine (1000 kg N/ha) and urea N (200 kg N/ha/y split into 8 applications) and then treated with DCD (15 kg/ha) in autumn or treated with DCD in autumn and spring, in solution form (Di and Cameron, 2004d). In the DCD treated urine patches, there were 38 – 56 % and 21 – 42 % reduction in the leaching of calcium and magnesium, respectively, but no change in potassium leaching. Decreased cation leaching was postulated to be attributable to decreased nitrate leaching and a reduced leaching requirement for counter ions.

Lismore stoney silt loam lysimeters were treated with urea (200 kg N/ha/y) split into 8 applications throughout the year and urine (1000 kg N/ha) applied in the autumn. DCD was applied in solution form 7.5 kg/ha after each urea application and immediately after urine application (15 kg N/ha). Leaching losses of calcium, potassium and magnesium were reduced by 50, 65 an 53% respectively when DCD was applied to urine treated lysimeters DCD (Di and Cameron, 2004c).

Templeton fine sandy loam lysimeters were treated with urea N (200 kg N/ha/y split into 8 applications) and urine (1000 kg N/ha) applied in a single application in the autumn. DCD treatments applied included 'no DCD', and DCD applied as a fine particle suspension at

either 5 or 10 kg/ha of DCD (Di and Cameron, 2005). Calcium and magnesium leaching was reduced by 51 and 31 %, respectively, when DCD was applied at 10 kg/ha (Di and Cameron, 2005).

Effects on the soil microbial community

In an incubation study DCD (7.5 or 15 kg/ha) was applied in conjunction with urea (25 kg N/ha) and urine (1000 kg N/ha) to a Lismore silt loam at field capacity field, at either 8 or 20 ^{o}C. Soil microbial biomass carbon and nitrogen contents were not affected by DCD treatment (Di and Cameron, 2004e).

Effects on nitrate accumulation in pastoral soils and herbage

Smith et al.(2005) found no difference between the solid and liquid forms of DCD applied with urine onto pasture in terms of slowing nitrate formation in 0.1 m surface layer of soil (Table 5). A 'urine- nil DCD' treatment would have been beneficial and enabled the effect of the DCD treatment relative to urine only to be determined.

Smith et al. (2005) also found that DCD application reduced nitrate accumulation in herbage to safe levels for ingestion by grazing stock, as well as a trend to increasing herbage magnesium and calcium concentrations.

Table 5 from Smith et al. (2005) showing the treatments used in the spring formulation study

Treatment	DCD rate	N application rate (kg/ha)		
	(kg/ha)	DCD	Urea	Urine
Control	Nil		nil	nil
Urea	Nil		50	nil
Urea+urine	Nil		50	580
Super U®[a]	1	0.7	50	nil
Super U® + urine	1	0.7	50	580
Coated N (25%)[b]	30	20	42	nil
Coated N (25%) + urine	30	20	42	580
Liquid DCD + urine[c]	15	10	50	580
Liquid DCD + urine	30	20	50	580
Zeolite (25% DCD w/w) + urine[d]	15	10	50	580
Zeolite (25% DCD w/w) + urine	30	20	50	580

International peer-reviewed literature

Effects of DCD on direct N_2O emissions from urine applied to soils ($EF_{3(PRP)}$)

Williamson and Jarvis (1997) applied cow urine to grassland, in autumn, to a silty clay loam at the extremely low rate of 60 kg N/ha along with 7.9 kg DCD/ha and N_2O emissions were reduced by 74%. Mean soil temperature was 10 ^{o}C.

De Klein and Van Logtestijn (1994) measured N_2O emission rates following the application of artificial urine (400 kg urine-N/ha) to a perennial rye-grass sward on sandy soil in the Netherlands. Urine was also applied with DCD to distinguish between N_2O emission from denitrification and nitrification. When DCD was added to the urine, N_2O emissions over the following 14 days were reduced by 50 to 89 % compared to the urine only treatment.

Akai et al. (2001) conducted an experiment on a pasture sown with Italian ryegrass (*Lolium multiflorum*), tall fescue (*Festuca arundinacea*) and red clover (*Trifolium pratense*). The treatments included cow urine and cow urine + DCD. The nitrogen application rate was 50 kg/ha except for the urine + DCD, which had a nitrogen application rate of 55 kg/ha. Nitrous oxide generation was reduced by 66 and 40% in 1998 and 1999, respectively, in the cow urine + DCD treatment, compared to that in the cow urine treatment. Soil temperature was not reported in the abstract.

There is a dearth of international literature on the interaction between DCD, bovine urine, nitrate leaching ($Frac_{LEACH}$) and N_2O emissions ($EF_{3(PRP)}$). The three studies above included very low N application rates, compared to that associated with cattle urine excretion during grazing in New Zealand. Nevertheless, as under New Zealand conditions, DCD was effective in reducing N_2O emissions in these international pastoral soils trials.

DCD degradation and microbiology

It has been reported that DCD is degraded in soil via guanylurea, guanidine and urea to yield carbon dioxide and ammonium (Rathsack, 1955; Rodgers et al., 1985; Vilsmeier, 1980). The first step in the degradation cascade was assumed to be catalyzed by the interaction of metal oxides, e.g. $Fe(OH)_3$, rather than being due to microbial and hence enzymatic mineralization (Amberger and Vilsmeier, 1979; Hauser and Haselwandter, 1990). However, some soil bacteria species can utilise and thus degrade DCD (Schwarzer and Haselwandter, 1991). One of the most efficient isolates is strain EK1 of *Mycobacterium sp*. (Teaumroong et al., 1997). DNA probes have been developed to detect EK1 and related or identical species of soil bacteria (Teaumroong et al., 1997). Bacterial cultures have also been isolated from composts (*Mycobacterium sp*., *Pseudomonas sp.*) and shown to degrade DCD (200mg N/ml) within 3 days, with two metabolic pathways observed, one being consistent with guanyl urea metabolism (Hallinger et al., 1990). DCD mineralization in culture (strain EK1) was also shown to be enhanced under anaerobic conditions with the rate of mineralization decreasing with increasing concentration of DCD, following normal degradation kinetics in batch cultures as will be discussed further below (Hauser and Haselwandter, 1990).

DCD-N is only slowly mineralized in acid soils ca. pH 4.0 (Rodgers et al., 1985).

The interim products of DCD decomposition (guanylurea and guanidine) have been reported to have little if any effect on nitrification compared with DCD (McCarty and Bremner, 1989).

In laboratory experiments with nitrifying cultures of *Nitrosomonas sp*. nitrification was completely inhibited , but numbers of ammonium oxidizing bacteria were not significantly affected by a 48 h treatment with DCD (Rodgers and Ashworth, 1982).

DCD has been shown to not inhibit growth and respiration of N-fixing bacteria (*Rhizobium leguminosarum* and *Azotobacter chroococcum*) in cell suspensions with 400 μg/ml of DCD (Zacherl and Amberger, 1990). While DCD applied at high rates had the potential to affect the N_2 fixation process in nodules of alfalfa it was not likely to be of practical significance if DCD was used at rates normally required to inhibit nitrification (Rice and Olsen, 1988).

Laboratory experiments have demonstrated that repeat applications of DCD to soil have little or no effect on the rate of DCD decomposition or the ability of DCD to inhibit nitrification

(Rodgers, 1986). Repeated field application of DCD resulted in no differences in the sensitivity of ammonium oxidizing bacteria to DCD (Rodgers, 1986).

In sterile soil at 30^{o}C the applied DCD concentration remained constant after 36 days (Rajbanshi et al., 1992) when soil was reinoculated it disappeared within 7 days. Addition of Fe_2O_3 powder to the sterilized soil had no effect on DCD degradation. Suggestion of an inducible metabolic degradation occurred since pretreated soils degraded DCD faster.

A relationship was established between the nitrification capability of microscopic soil fungi and the appearance of phytotoxic properties of micromycetes. The phytotoxic activity of pure cultures of micromycetes was found to change under the influence of nitrification inhibitors. The influence of nitrification inhibitors on growth, accumulation of biomass, and formation of nitrates and nitrites by microscopic fungi appeared at concentrations 1-4 orders of magnitude higher than with regard to autotrophic nitrifying bacteria. The tested preparations were arranged in the following order in terms of effectiveness of action of fungi: nitrapyrin, carbamoylmethylpyrazole, dicyandiamide, and 4-amino-1,2,4 triazole. (Kurakov and Popov, 1996).

DCD degradation and temperature

The fate of DCD applied to soils depends strongly on temperature. This dependence is complex, in turn varying with temperature. A progressive series of analyses will be done to synthesise the available data and further develop DCD application criteria for New Zealand conditions.

Hauser and Haselwandter (1990) measured the concentration of DCD, applied as five doses, over time since application to a nutrient solution maintained at 25 °C and containing the soil bacteria strain EK1. To quantify the reported relationship, we fitted their tabulated data to a first-order exponential decomposition model. Term ‘c’ is the DCD concentration and ‘c_0’ is the initial concentration of DCD at time zero. For the representative data portrayed in Figure 1, the model predicted that DCD concentration had declined to half of its initial value (called the half life, $t_{½}$, $t_{½}$ = Ln(2)/k where Ln denotes natural logarithm (Ln(2) = 0.69) and k is a decomposition constant determined by regression analysis) in 10 days. For the five doses, additional regression analysis showed that as c_0 increased from 1.5 to 3 g/L, $t_{½}$ increased by a factor of 4.3.

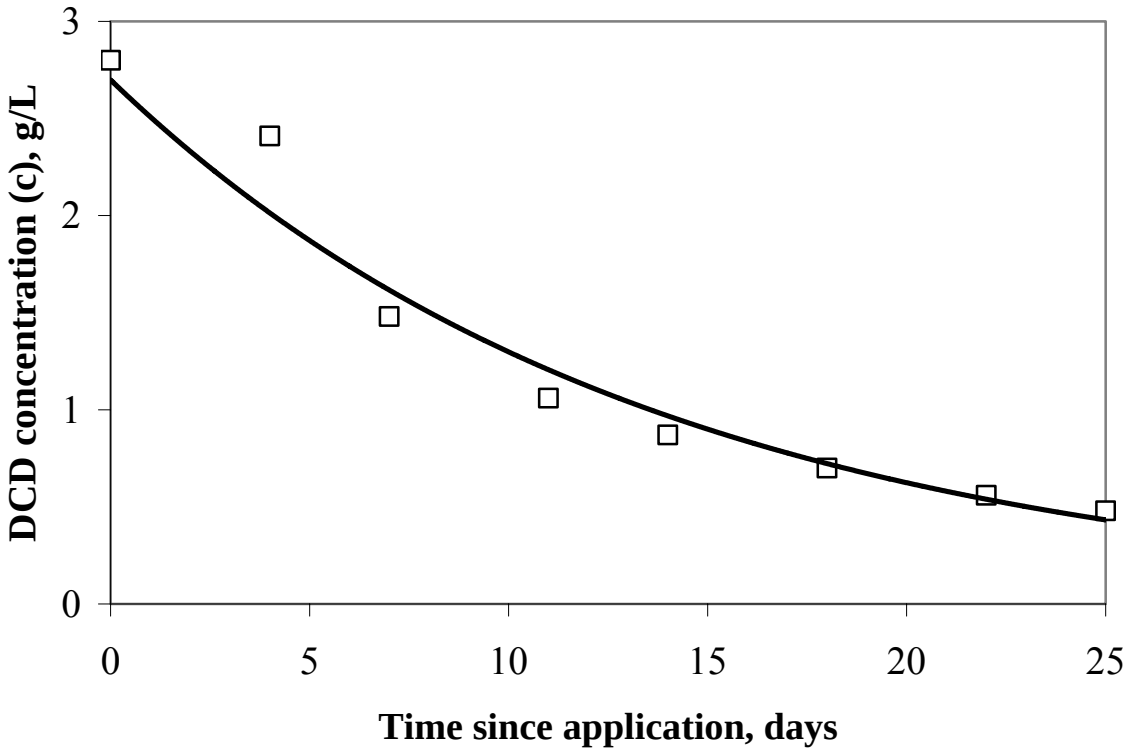

Figure 1 The relation between DCD concentration and time since application to a nutrient solution maintained at 25 °C and containing the soil bacteria strain EK1. These data came from Table 1 of Hauser and Haselwandter (1990). The curve is a first-order exponential decomposition model, $c(t) = c_0 e^{-kt}$ where c(t) is DCD concentration as a function of time, t, c_0 is DCD concentration when t is zero (0) and k is a decomposition constant. Regression analysis yielded $c(t) = 2.7 e^{-0.073t}$ with a coefficient of determination (R^2) = 0.97.

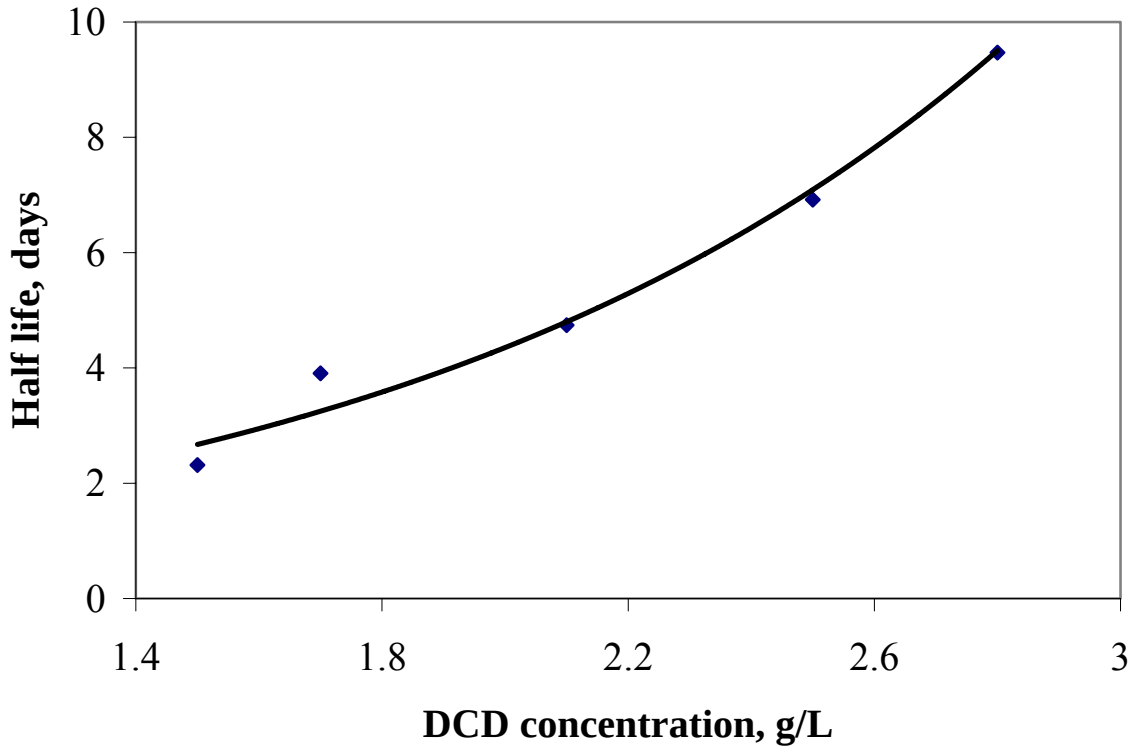

Figure 2 The relation between the half life ($t_{½}$) of DCD, and the initial DCD concentration applied to a nutrient solution (c_0) maintained at 25 °C and containing the soil bacteria strain EK1. Using a model explained in the caption of Figure 1, $t_{½}$ values were calculated from the data in Table 1 of Hauser and Haselwandter (1990). Regression analysis yielded the exponential curve, $t_{½}$ (c_0) = 0.62 $e^{0.976c}{}_0$, that explained 95 % of the variance.

The rate of a biologically mediated process can also be described using Michaelis-Menton kinetics. For DCD, under constant environmental conditions, kinetics can define a relation between decomposition rate (D) and substrate concentration (S). When S is low, D increases with S as a hyperbolic curve, indicating a first-order reaction. For DCD, as shown, this means its decomposition rate in soil can depend on the applied quantity. However, when S is high, D is relatively constant, indicating a zero-order reaction. When saturated with substrate, D is at a maximum (D_{max}). A parameter, K_m, is the substrate concentration corresponding with D equal to half of D_{max}. The relation, exhibited by the data of Schwarzer and Haselwandter ((1991); see their Figure 1) based on pure culture studies with the soil bacteria strain EK1, may be written as:

$$D = [D_{max} + S] / [K_m + S].$$

To determine D_{max} and K_m, data are plotted according to the Lineweaver-Burke transformation with 1/S on the abscissa (X axis) and 1/D on the ordinate. The relation is thus transformed to a line with slope and intercept equal to K_m/D_{max} and $1/D_{max}$, respectively.

Schwarzer and Haselwandter (1991) reported that DCD decomposition occurred only in a temperature range between 10 and 33 °C. They did not specify the incubation period(s) nor report half lives. At 25 °C, they obtained an optimum (fastest decomposition) rate, meaning

the rate increased with increasing temperature between 10 and 25 °C but declined with increasing temperature between 25 and 33 °C. In contrast, they noted the inorganic DCD decomposition rate increased with increasing temperature up to at least 90 °C. Earlier, Amberger (1989) tabulated data (but did not quantitatively analyse it) showing that DCD decomposition occurred in an unspecified soil over a temperature range between 0 and 12 °C. Zero- and first-order decomposition models fitted these data well and yielded similar half lives (Figure 3). For 0 and 12 °C, $t_{½}$ was 147 and 42 days, respectively.

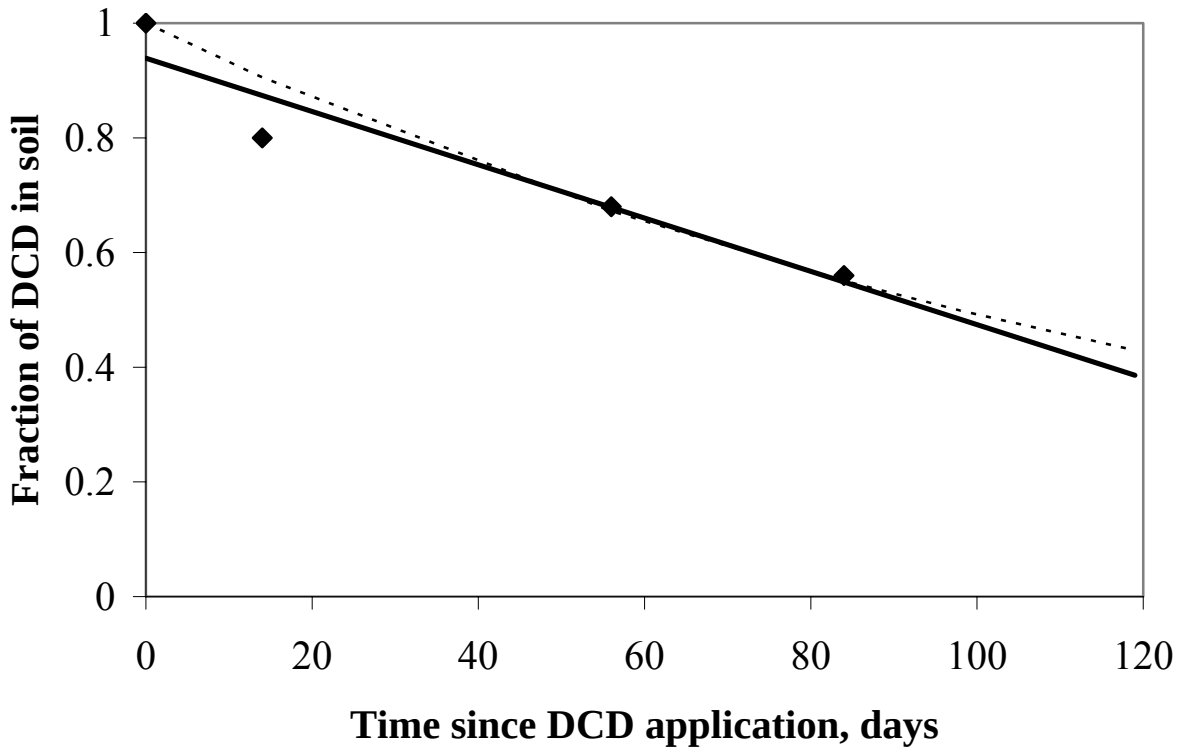

Figure 3 Relations between the mass of DCD remaining in soil, maintained at 6 °C, and time since its application (the rate was not given) based on data (shown here as symbols) tabulated by Amberger (1989). The data were fitted to a first-order decomposition model by regression that accounted for 94 % of the variance. This is portrayed as the dashed curve, $M(t) = M_0 e^{-kt}$ where M(t) is mass of DCD in the soil as a function of time, t, M_0 is mass of DCD applied to the soil when t is zero (0)(M_0 was normalised to unity on the ordinate) and k is a decomposition constant (0.0071 per day). The first-order model predicted that inhibitor mass had declined to half its application value in 98 days, $t_{½}$, = Ln(2)/k where Ln denotes natural logarithm. A zero order decomposition model was also fitted to the data by regression ($M(t) = M_0 – kt$, so $t_{½} = 1/[2k]$) that accounted for 91 % of the variance and yielded $t_{½}$ = 109 days.

For a Lismore silt loam soil sampled beneath grazed pasture near Lincoln and incubated for 135 days at 8 and 20 °C, DCD decomposition was measured on six occasions (Di and Cameron, 2004a). These data were fitted to the first-order first-order exponential decomposition model. The soil was fertile with organic carbon and total nitrogen contents of 36.5 and 3.5 grams per kg of soil, respectively, and a pH of 5.9. The DCD application rates were 5.77 and 11.54 mg per kg of soil, equivalent to 7.5 and 15 kg DCD per hectare over a

soil depth of 0.1 m and bulk density of 1.3 Mg m^{-3}. The samples were maintained near the field capacity water content of 0.3 kg of water per kg of soil. For 8 °C, with 7.5 and 15 kg DCD per hectare, $t_{½}$ was 111 and 116 respectively, while for 20 °C, $t_{½}$ was 26 and 18 days (Figure 4). Consequently, doubling the DCD application rate did not correspond with a significant increase of $t_{½}$ as portrayed in Figure 2 based on the data of Hauser and Haselwandter (1990). For the data of Di and Cameron (2004a) at 8 and 20 °C, regression accounted for 70 and 94 % of the variance, respectively. Confidence limits were not stated for $t_{½}$ but an approximation of k ± 10 %, based on the data of Irigoyen et al. (2003), see Table 3), suggested a $t_{½}$ confidence interval of 100 – 122 days at 8 °C.

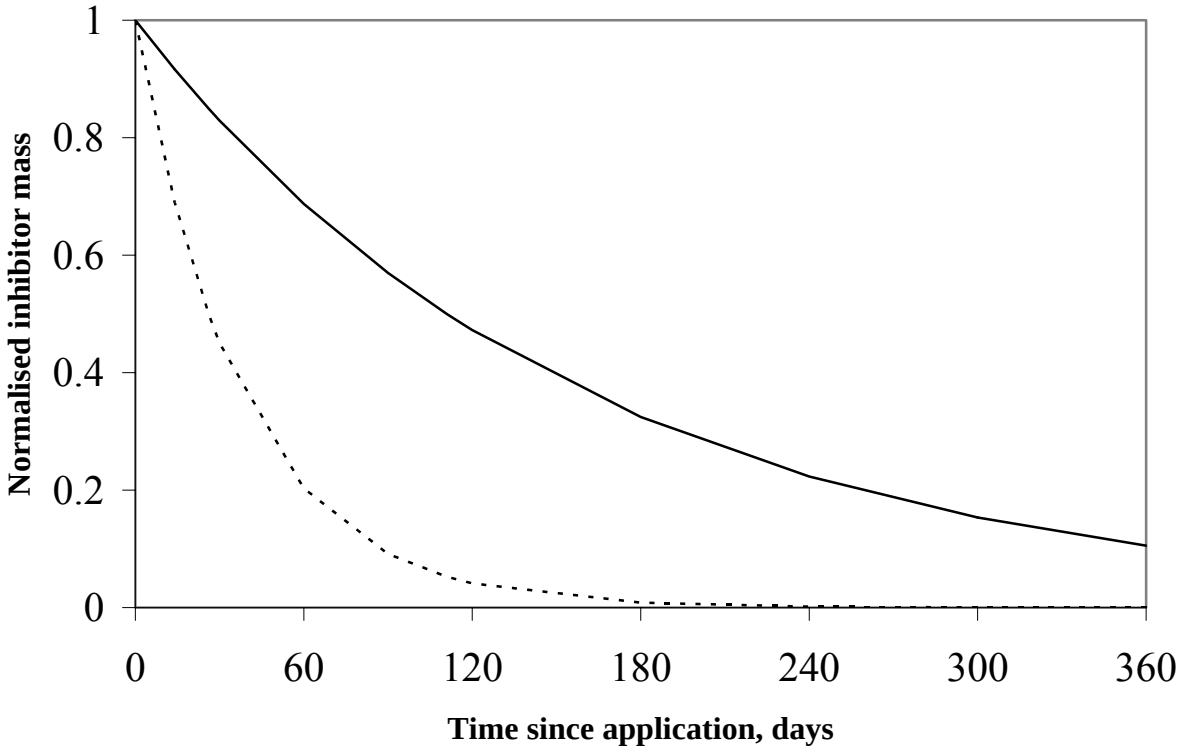

Figure 4 Relationships between the mass of DCD remaining in a Lismore silt loam soil, maintained near the field capacity water content (approximately 0.3 kg water per kg soil), and time since its application for two temperatures after Di and Cameron (2004a). These data were fitted to a first-order exponential model, $M(t) = M_0 e^{-kt}$ where M(t) is mass of DCD in the soil as a function of time, t, M_0 is mass of DCD applied to the soil when t is zero (0)(M_0 was normalised to unity on the ordinate) and k is a decomposition constant determined by regression analyses (0.00625 per day and 0.0266 per day for 8 and 20 °C and portrayed as solid and dashed curves, respectively, when M_0 was 5.77 mg DCD per kg soil, equivalent to 7.5 kg DCD per hectare over a soil depth of 0.1 m and bulk density of 1.3 Mg m^{-3}). For 8 and 20 °C, the model predicted that inhibitor mass had declined to half its application value (called the half life, $t_{½}$, $t_{½}$ = Ln(2)/k where Ln denotes natural logarithm) in 111 and 26 days, respectively.

For silt loam soil sampled beneath pasture near Giessen, Germany, DCD decomposition was measured over 90 days at 10, 20 and 30 °C (Rajbanshi et al., 1992). These data were fitted to

a zero-order decomposition model recognising three time points; namely at DCD application, at the end of a lag between application and the beginning of active mineralisation and at the end of active mineralisation. The model may be written as an equation, $M_E = M_L - kt$ where M_E is mass of DCD in the soil at the end of active mineralisation, M_L is mass of DCD in the soil at the end of the lag, k is again a decomposition constant obtained by regression analysis and t is time since application. The equation may be used to determine $t_{½}$ from k when M_E is zero and M_L normalised to unity, so re-arrangement yields t ($t_{½}$) equal to 1/k. The application rates were equivalent to 10, 25 and 50 mg DCD per kg soil including the reported values of DCD-N mass, where N denotes nitrogen, divided by 0.65 for conversion to DCD mass. For comparison with Di and Cameron (2004a), these DCD application rates corresponded to 13, 32 and 65 kg DCD per hectare over a soil depth of 0.1 m and bulk density of 1.3 Mg m^{-3}. This soil had organic carbon and total nitrogen contents of 29 and 2.5 g/kg of soil, respectively, and a pH of 6.1. During incubation, the samples were maintained at 0.4 kg of water per kg of soil. For 10, 20 and 30°C, with 13 and 32 kg DCD per hectare, corresponding values of $t_{½}$ were 52, 16 and 13 days and 70, 18 and 12 days. For 20 and 30°C with 65 kg DCD per hectare, $t_{½}$ was 22 and 15 days.

The value of $t_{½}$ reported by Rajbanshi et al. (1992) for 10 °C with 13 kg DCD per hectare (*ie* 52 days) was about half that reported by Di and Cameron (2004a) for 8 °C with 15 kg DCD per hectare (*ie* 116 days). The Giessen soil contained significantly less nitrogen than the Lismore soil. If the Giessen soil's microbial community was relatively N-limited, it follows that the N-rich DCD would be mineralised faster following its application. Rajbanshi et al. also found that pretreatment of the soil with DCD reduced $t_{½}$ to 7 and 13 days at 10 °C with 13 and 32 kg DCD per hectare, respectively, and there was no lag between application and mineralisation. In contrast, Rogers (1986) found no pretreatment effect when applying 10 mg DCD per kg of soil for 4 years.

For a Decatur silt loam soil sampled in Alabama, USA, DCD decomposition was measured for 75 days at three temperatures by Bronson et al. (1989). The cropping soil had an organic carbon content of only 8.0 g/kg of soil and a pH of 6.2. The soil's nitrogen content was not reported but the very low organic carbon content should be indicative. During incubation, the samples were maintained at 0.2 kg of water per kg of soil. These data were fitted to a zero-order model. The application rate, M_0, was 2 mg DCD per 20 g soil, equivalent to 130 kg DCD/ha over a soil depth of 0.1 m and bulk density of 1.3 Mg m^{-3}. The decomposition constant, k, was 0.0382, 0.0775 and 0.1276 mg DCD per 20 g soil per day for 8, 15 and 22 °C, respectively, and the corresponding values of $t_{½}$ ($t_{½} = M_0/2k$, equivalent to 1/k given the units used for M_0 and k) were 26, 13 and 8 days. These short half lives were exceptional and may reflect a very N-limited microbial community.

For a sandy loam soil sampled in Spain, following DCD application, ammonium ammonium was considered a proxy for DCD and its decomposition was measured for 105 days at three temperatures (Irigoyen et al., 2003). These data were fitted to the zero-order model according to Bronson et al. (1989). The application rate of DCD was 4 mg/kg soil, equivalent to 5.2 kg/ha over a soil depth of 0.1 m and bulk density of 1.3 Mg m^{-3}. The cropping soil had organic carbon and Kjeldahl nitrogen contents of 7.3 and 1.3 g/kg of soil, respectively, and a pH of 7.5. During incubation, samples were maintained at 75% of field capacity or 0.1 kg of water per kg of soil. For 10, 20 and 30 °C, $t_{½}$ was > 105, 18 and 7 days, respectively. At 10 °C, the $t_{½}$ of ammonium was broadly similar to that expected for DCD in Lismore silt loam (Di and Cameron, 2004a).

For a soil sampled in France, following DCD application, ammonium decomposition was measured for 364 days at three temperatures (Guiraud and Marol, 1992). These data were fitted to a first-order model. The DCD application rate was 15 mg/kg soil, equivalent to 19.5 kg/ha over a soil depth of 0.1 m and bulk density of 1.3 Mg m^{-3}. An equal measure of ammonium thiosulphate was applied with the DCD in order to increase its effectiveness according to the authors. The cropping soil contained 21% clay, had organic carbon and total nitrogen contents of 11 and 1.3 grams per kg of soil, respectively, and a pH of 7.9. During incubation, samples were maintained at 67% of the field capacity water content. For 10, 15 and 20°C, the respective regressions accounted for 72, 98 and 94% of the variance and $t_{½}$ was 231, 77 and 14 days. Thus, when ammonium thiosulphate was applied with DCD, ammonium half lives were longer than generally found for DCD when DCD was applied to soils alone (e.g. Di and Cameron, 2004a).

To synthesise the data reviewed here, an inverse exponential relation was fitted to a plot of DCD half life and soil temperature (Figure 5). The sixteen measurements included a temperature range of 0 – 30 °C but with only five < 10 °C (Amberger, 1989; Di and Cameron, 2004a; Irigoyen et al., 2003). To quantify the decrease in half life per unit increase of temperature, the function portrayed in Figure 5 was differentiated with respect to temperature (Figure 6). This showed that the half life change is inversely proportional to the temperature but also that the change depends strongly on the temperature. At weather stations throughout New Zealand, beneath grass that was mowed regularly, soil temperature was measured daily (at 0900 h) at depths of 0.1 and 0.3 m (New Zealand Meteorological Service, 1983). Measurements at the 0.l m depth were considered most representative of a pasture plant root zone. During autumn, winter and early spring, soil temperature ranged from 4 – 13 °C according to the climatological data in Tables 6 and 7. For the efficacy of DCD, this is a significantly wide temperature range. For example, during May, average soil temperature varied from 7 °C at Invercargill up to 13 °C at Dargaville (Table 7). The relation fitted to the data in Figure 5 suggested that the corresponding values of DCD half life nearly halved from 81 to 44 days. Our analysis was based on data obtained under controlled temperatures. To our knowledge, there have been no reported measurements of DCD decomposition in the field. Moreover, the field efficacy of DCD application in reducing direct nitrous oxide emissions has not been statistically analysed with respect to soil temperature.

Finally, five of six DCD application field trials conducted in NZ had an average soil temperature of 8 °C and recorded 75 ± 11 % (average ± 95 % confidence limit) reduction in direct N_2O emissions, while corresponding values for the sixth trial were 11 °C and 61 % (Table 8, Di and Cameron 2006, Smith et al. 2007). The differences were not statistically significant. During late spring and summer, soil temperature in New Zealand ranges from 9 – 21 °C (Table 9).

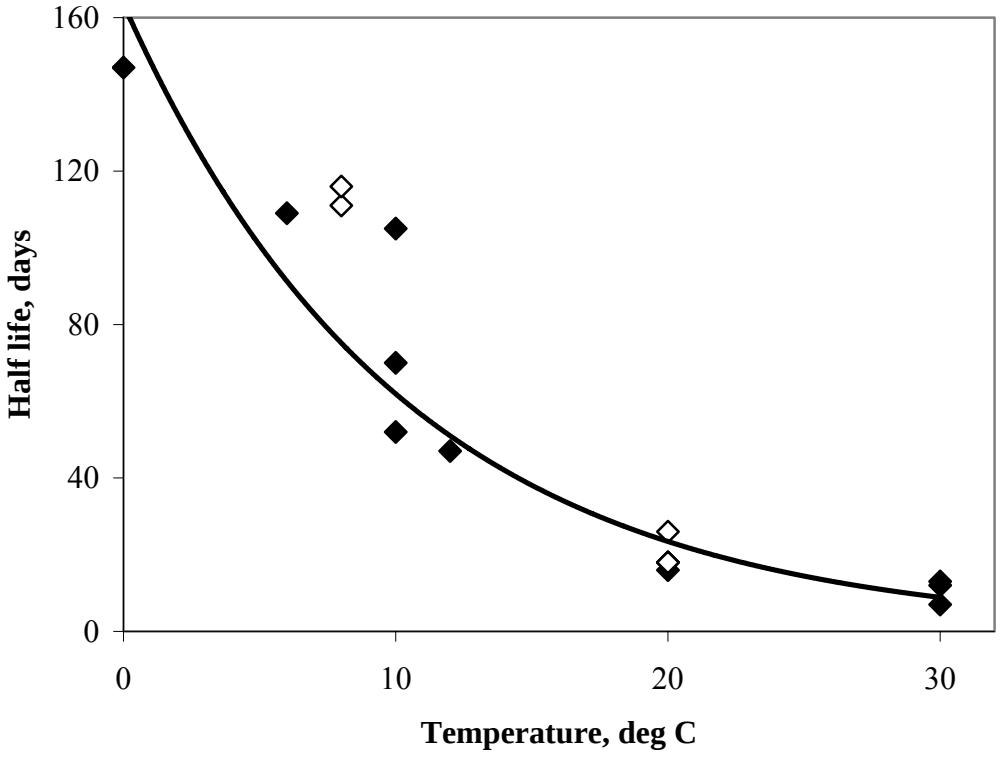

Figure 5 Relation between the half life ($t_{½}$, days) of DCD mixed into soil samples, incubated under controlled conditions, and the corresponding temperature (T, °C). Over the period denoted $t_{½}$, the mass of DCD had declined to half its application value. These data are described in the text but exclude those of Bronson et al. (1989), Guiraud and Marol (1992) and the 65 kg DCD per hectare treatment data of Rajbanshi et al. (1992)) The New Zealand data of Di and Cameron (2004a) are portrayed by open symbols. The range of application rates was 5 – 32 kg DCD ha^{-1} based on a soil depth of 0.1 m and bulk density of 1.3 Mg m^{-3}. Regression, portrayed as the curve, yielded the function $t_{½}(T) = 163\ e^{-0.1T}$ that accounted for 91% of the variance.

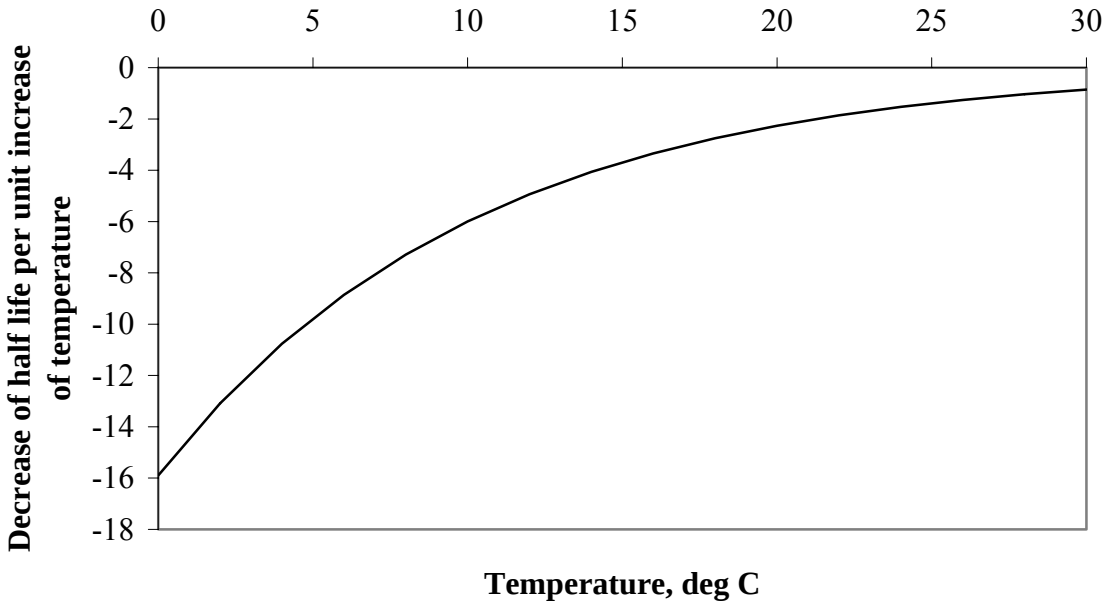

Figure 6 Relation between the decrease of DCD half life ($t_{½}$, days) and soil temperature (T, °C) based on differentiating the functional relation portrayed in Figure 5. The derivative, $dt_{½}/dT = -16\ e^{-0.1T}$, is portrayed here as the curve.

Table 6 Five former weather stations of the New Zealand Meteorological Service located along a North to South transect and the period (years) of soil temperature measurement (New Zealand Meteorological Service, 1983).

Weather station	Latitude, Longitude, elevation (masl)	Period
Dargaville	35° 57’ S, 173° 50’ E, 20	1951 - 1980
Rukuhia	37° 50’ S, 175° 18’ E, 66	1946 - 1980
Palmerston North DSIR	40° 23’ S, 175° 37’ E, 34	1939 - 1980
Lincoln	43° 39’ S, 172° 28’ E, 11	1943 - 1980
Invercargill Airport	46° 25’ S, 168° 20’ E, 0	1951 - 1980

Table 7 Monthly average soil temperature during autumn, winter and early spring at five locations along a North to South transect described in Table 1. Measurements were made daily at 0900 hours and the thermometer was located at a depth of 0.1 m beneath mown grass. The averages were computed from 30 – 41 years of data. During these months, rainfall generally exceeds evaporation (Scotter and Kelliher 2004), so soils become wet. If the soil’s water storage capacity is exceeded, there will be drainage.

Month	May	Jun	Jul	Aug	Sep
Location					
Dargaville	12.8	10.9	9.6	10.4	12.2
Rukuhia	11.1	8.7	7.6	8.5	10.7
Palmerston North	10.1	7.7	6.7	7.6	9.9
Lincoln	7.4	4.5	3.9	5.0	7.5
Invercargill	6.7	4.6	3.5	4.3	6.5

Table 8 Data from Di and Cameron 2006 and Smith et al. 2007

Location	Soil	Soil temperature (°C), depth of 0.1 m			% direct N_2O emissions reduction	Date of DCD treatment application	Period (days) when N_2O emissions from urine-amended soils greater than urine-amended soils treated with DCD
		Max.	Min.	Mean (± Std Dev)			
Lincoln	Templeton	12.2	3.4	7.9 ± 2.2	73	23 Jun. 2005	82
Lincoln	Lismore	11.6	3.4	7.4 ± 2.1	67	29 Apr 2005	88
Hamilton	Horotiu	15.7	5.7	10.7 ± 2.8	61	15 May 2005	33
Taupo	Taupo	13.8	2.9	8.5 ± 2.4	69	3 Aug 2005	56
Invercargill	Pukemutu	16.2	3.6	7.2 ± 1.8	75	27 Apr 2004	55
Invercargill	Pukemutu	12.4	5.8	9.5 ± 1.5	91	25 Aug 2005	62

Table 9 Monthly average soil temperatures during late spring and summer. Measurements were made daily at 0900 hours and the thermometer was located at a depth of 0.1 m beneath mown grass. The averages were computed from 30 – 41 years of data.

Location	Month	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Dargaville		14.9	17.4	19.5	20.8	20.4	18.6	15.6
Rukuhia		13.4	15.8	18.1	19.5	19.5	17.6	14.3
Palmerston North		12.5	15.1	17.3	18.5	18.1	16.3	13.2
Lincoln		10.8	13.8	16.4	17.4	16.7	14.3	10.9
Invercargill		9.0	11.1	13.3	14.1	13.6	12.1	9.5

6. Inventory revisions for pasture treated with nitrification inhibitors

We re-iterate that the direct N_2O emission factor for N fertiliser, EF_1, is the fraction of N applied to soils that is emitted directly into the atmosphere (the New Zealand specific value is 0.01 kg N_2O-N/kg fertiliser N). Likewise, the direct N_2O emission factor for excreta deposited by farmed animals during grazing, $EF3_{PR\&P}$, is the fraction of N excreted onto soils that is emitted directly into the atmosphere (the New Zealand specific value is also 0.01 kg N_2O-N/kg excreta N). Indirect N_2O emissions are mainly associated with N leaching. This depends on the total N applied to soils as fertiliser and excreta. The fraction of N applied to soils that is leached is called *Frac*$_{LEACH}$ and the New Zealand specific value is 0.07 (Thomas et al., 2005)).

N_2O emissions and NO_3^- leaching depend on the quantity of N applied to soils. DCD should last the longest and be most effective when soil temperature is lowest. Field trials demonstrated that DCD application significantly reduced direct N_2O emissions and NO_3^- leaching from urine applied to pasture when the soil temperature averaged < 12 °C. During May - September, the soil temperature ranges from 4 – 13 °C according to climatological data (Table 7).

New Zealand's agricultural soils N_2O emissions inventory could readily be computed on a monthly basis. The nitrogen excretion rates are determined on a monthly basis by animal type and we believe credible estimates could be made for the corresponding nitrogen fertiliser rates.

Application rate for nitrification inhibitors

Based on the peer-reviewed literature, we conclude that a DCD application rate of 10 kg/ha most effectively reduced direct N_2O emissions and nitrate leaching (Di and Cameron, 2005). This rate was predominantly based upon two applications per year in the autumn and late winter. The effective period following DCD application is discussed below as well as the effect of repeated applications.

Formulation and application of nitrification inhibitors

Smith et al. (2005) compared various granular formulations of DCD and DCD in solution. They found no formulation effect on pasture herbage dry matter response in synthetic urine patches. However, there was no urine-only treatment for comparison. As discussed earlier, the results may have been affected by relatively warm and dry soil for most of the trial. The response to N applied may have been reduced due to a relatively high soil organic matter mineralization rate. Nevertheless, all the DCD formulations containing 15 and 30 kg DCD/ha were effective in limiting the nitrification of ammonium-N to nitrate-N for more than 100 days. These results suggested granular- and solution-based formulations of DCD may be effectively applied to soils.

Di and Cameron (2005) compared three methods of DCD application; namely, (1) DCD dissolved in water and irrigated onto the soil surface, (2) DCD dissolved in cattle urine and irrigated onto the soil surface and (3) DCD ground into a fine powder then made into a suspension (FPS) and sprayed evenly across the soil surface. The soil treated by FPS was irrigated after application, per recommended practice to simulate rainfall. The three methods maximised DCD coverage of the soil and they were found to be equally effective in reducing nitrate leaching.

The optimum timing for DCD application is concurrently or as close as possible to the deposition of urine-N. In practice on the farm this will not always be possible. However, a 10 day lag between urine and DCD applications to Templeton silt loam soil at Lincoln did not significantly affect DCD performance because N_2O emissions were reduced by 56%, compared with 61% for concurrent applications of urine and DCD (Di and Cameron, 2006). For the same soil, an 18 day lag between urine and DCD applications corresponded with N_2O emissions reduced by 73% (Di et al., 2006).

In principle, maximum contact with soil bacteria should make DCD most effective. For perspective, we begin with some linear dimensions. In the rhizosphere, soil located in the vicinity of plant roots, the average distance between bacteria cells is 10 μm according to Watts et al. (2006). Following rainfall or irrigation, pores in soils that are drained by the suction of gravity (1 metre of suction) have diameters larger than 30 μm. One day after drainage, the soil obtains a water content called its field capacity. We can use this linear perspective to examine the application of DCD to soils. As an example, we consider a granular formulation. From a sample of 260 zeolite grains containing the DCD product called DCn^{TM}, the average weight was 2.3 mg. If the application rate was 50 kg/ha, on average, there would be 2174 grains/m^2 on the soil surface. For this hypothetical situation, assuming the sample measurements are representative, the average distance between grains would be 21 mm. This distance is 2,100 times greater than 10 μm, the average distance between bacteria cells in the rhizosphere. However, a distribution of distances between grains is more useful for analysis. A distribution statistic is the coefficient of variation (CV), a ratio of standard deviation and average values, commonly reported as a percentage. For a centrfugal fertilizer spreader, the CV in application to a rectangular paddock was 43 % according to Lawrence and Yule (2007). If the average distance between grains, containing DCD, was 21 mm and CV 43 %, the standard deviation was 9 mm. With 95 % confidence, this statistic indicates the minimum and maximum distance between grains was 3 (21 – [2 X 9]) and 40 (21 + [2 X 9]) mm, respectively. Because the applied DCD will horizontally disperse into non-treated areas of soil between grains by the process called diffusion, we can do further analysis. We begin by assuming DCD in the grain dissolves completely to create a

point on the soil surface where DCD concentration is equal to the application rate. We then solve the so-called continuity equation, including Fick's law of diffusion, to obtain a useful one-dimensional expression relating distance travelled by a diffusing solute and time (Nobel 1983, see page 16). The relation shows that the distance depends on the square root of time divided by a term called the diffusion coefficient (equal to 2.2 X 10^{-9} m^2 s^{-1} for DCD dissolved in water, based on the molecular weight, 84 grams/mole). The dependence is also determined by the fraction of solute that has diffused away from the point of application. For DCD solute diffusing horizontally in the soil between grains on the surface, located as close as 3 mm apart, the distance of interest is 1.5 mm or the halfway point between grains closest to one another. The relation shows, for example, that it would take 1.4 hours for 95 % of the DCD solute to diffuse from a grain to a point 1.5 mm away. Although for simplicity the solution and relation considers diffusion in one dimension (that is, horizontally along a line), the process take place throughout the soil. For grains located as far apart as 40 mm apart, the distance of interest is 20 mm and it would take 10 days for 95 % of the DCD solute to diffuse 20 mm. In summary, these calculations support two seminal results from studies of DCD formulation and application; namely, (i) granular-, solution- and fine powder suspension-based formulations of DCD have been effectively applied to soils and (ii) a 10 day lag between urine and DCD applications did not significantly affect DCD performance.

Recording the area where nitrification inhibitors are applied

The use of DCD includes a requirement for accurate and verifiable records of the treated pasture/land/soils area. Long-term record storage and availability for independent review are also required. A GPS system associated with application seems ideal. This system should be future proof and suitable for audit and accreditation of farm scale carbon credits. The system may have wider application to monitoring N use and losses from farms.

Recording variables to estimate nitrogen fertilizer application and excretion rates

Linked to the GPS record of land area covered by DCD application, there must be a grazing stock record. Hence the number and type of animals (dairy cattle, beef cattle and sheep) 'treated' with DCD could be calculated from the record and subsequently used in the IPCC inventory for New Zealand (Clough et al., 2007). From the number and type of animals 'treated' with DCD, compared to the national population, one could proportionally determine the required N excretion rate. Alternatively, at the farm scale, animal weight and production rate could be used for determination of pasture herbage N intake and output to product. Nitrogen fertilizer rate on the land 'treated' with DCD also needs to be recorded.

As mentioned earlier, for some dairy farms, grazing may take place during much of the 'May – September period on 'support' land that may not be located within a farm's boundary. There may also be a 'cut and carry' feeding regime during 'May – September' including feed produced outside the farm's boundary. This may involve 'stand off' and feed pads.

Comparison of emissions factors from other countries

To our knowledge, no other country has revised its emission factors to account for the effect(s) of nitrification inhibitor application onto soils. However, in the absence of nitrification inhibitors, we can compare New Zealand's specifc values of EF_1 and $EF_{3(PRP)}$ (both equal to 0.01) with those of the IPCC and recently completed international peer-

reviewed literature data syntheses. For $Frac_{LEACH}$, the reader is directed to Thomas et al. (2005).

Revised emission factors and emissions inventory: Method 1 - 'Annualised' revisions of $EF_{3(PRP)}$, EF_1 and $Frac_{LEACH}$ using nitrification inhibitors

The revised emission factors in this section will be 'annualised' figures, compatible with the current method of emissions inventory calculation that was described earlier. In turn, the revised emission factors will be used to revise the N_2O emissions inventory calculation. This revision of the emissions inventory will be called Method 1. Our recommendations are predicated on application criteria that have proved successful for DCD in research trials. Firstly, the nitrification inhibitor should thoroughly cover the soil. Each application rate should be at least 10 kg/ha. There should be two applications each year following grazing in autumn (May) and again in late winter (August). Given soil temperatures throughout New Zealand during May – September, we believe that effectiveness can be expected for these 5 months of the year. Hence, DCD is not used for seven months of the year (October – April), so the NZ specific values for emission factors do not require revision. We do not think there has been sufficient research to make recommendations for a range of application methods and rates. For the same reason, insufficient research prevents us from making recommendations based on the anticipated effects of soil drainage on nitrification inhibitor use efficacy (Kelliher et al. 2005a, 2005b). While the efficacy of nitrification inhibitor use has been evaluated in soils subjected to autumn and late winter applications, except for the pasture production data of Moir et al. (2007), the results from research trials in New Zealand that were available to us were limited to single years of study. Further research is needed to quantify the effect(s) of repeated nitrification inhibitor applications over several years.

When DCD was applied to four New Zealand pastoral soils, $EF_{3(PRP)}$ was reduced by 61 to 74 % (n = 4, mean 67 %, Std. Dev. 6 %). These statistics define the uncertainty of nitrification inhibitor application to soils with respect to $EF_{3(PRP)}$. The mean value determines our recommendation. Consequently, **when DCD is applied as recommended, we revise $EF_{3(PRP)}$ as follows**

$$EF3_{PRP}\text{ ' plus DCD'} = \left(\frac{7}{12} \times NZ\ specific\ EF3_{PRP}\right) + \left(\frac{5}{12} \times NZ\ specific\ EF3_{PRP} \times (1 - 0.67)\right) = 0.007$$

For EF_1, revision should be the same as for $EF_{3(PRP)}$. Urine is the primary N excreta constituent in the N_2O emissions inventory and there is no scientific evidence to suggest that urea from fertiliser behaves differently than urea from urine (Kelliher et al. 2005a, Kelliher and de Klein 2006). We also recommend estimating the uncertainty of EF_1 using the $EF_{3(PRP)}$ uncertainty statistics, presuming N fertiliser applications will be done in autumn and late winter. We do not think there has been sufficient research to make any further recommendations for fertiliser. Consequently, **when DCD is applied as recommended, we revise EF_1 as follows**

$$EF_1\text{ ' plus DCD'} = \left(\frac{7}{12} \times NZ\ specific\ EF_1\right) + \left(\frac{5}{12} \times NZ\ specific\ EF_1 \times (1 - 0.67)\right) = 0.007$$

When DCD was applied to New Zealand pastoral soils, $Frac_{LEACH}$ was reduced by 68 to 77 % (n = 5, mean = 74% Std Dev. 4 %). These statistics define the uncertainty of nitrification

inhibitor application to soils with respect to $Frac_{LEACH}$. The mean value determines our recommendation. **Consequently, when DCD is applied as recommended, we revise $Frac_{LEACH}$ as follows:**

$$Frac_{LEACH}\text{ ' plus DCD'} = \left(\frac{7}{12} \times NZ\ specific\ Frac_{LEACH}\right) + \left(\frac{5}{12} \times NZ\ specific\ Frac_{LEACH} \times (1 - 0.74)\right) = 0.05$$

Revised emission factors and emissions inventory: Method 2 - Disaggregating nitrogen application onto soils for nitrification inhibitor responses

This method uses the same 'annualised' emission factors developed in the previous section. However, N application onto soils will be disaggregated for this emissions inventory method into two periods; namely, May – September when DCD is used and effective and October – April when DCD is not used. This method recognises that N excretion as urine and dung is computed monthly for dairy cattle, beef cattle, sheep and deer. This facilitates sums of figures for the seven months of October – April when DCD would not be applied according to our recommendations. Figures can also be summed for the five months of May – September when DCD would be applied and effective. We recognise that the monthly figures can be summed for other periods as well.

The application of N fertiliser onto soils also has to be disaggregated. Our figures come from expert judgement (Hilton Furness, FertResearch, Personal Communication, 8 March 2007). We begin by disaggregating N fertiliser application by animal type. Currently, 70 % of all N fertiliser that is sold annually is applied to soils associated with dairy cattle. Further, and currently, 10 % of all N fertiliser that is sold is applied to soils associated with beef cattle, sheep and deer. We approximate the partitioning as 5 % applied to soils associated with beef cattle and 5 % to sheep. Consequently, no N fertiliser is applied to soils associated with deer. Finally, in this report, we do not include 20 % of the N fertiliser sold annually because it is applied to soils associated with arable and horticultural crops. To re-iterate, this report includes only 80 % of the N fertiliser sold annually because this is the quantity thought to have been applied to soils associated with grazing animals. Finally, the current percentages of N fertiliser applied to soils associated with dairy cattle (70 %), beef cattle (5 %) and sheep (5 %) are used in our calculations for the years 1990, 2004 and 2010. To monitor these percentages, we recommend that FertResearch is the best available source of information.

The application of N fertiliser onto soils also has to be disaggregated for the calculation of nitrification inhibitor response. We re-iterate that there is no scientific evidence to suggest that urea from fertiliser behaves differently than urea from urine. For this report, N fertiliser was applied in two equal dressings (each half of the annual quantity) in early May and early August along with the DCD applications.

Revised emission factors and emissions inventory: Method 3 - Disaggregating the $EF_{3(PRP)}$ and EF_1 data for revision by nitrification inhibitor response

This method uses the same (two period) disaggregation of N application onto soils as Method 2; namely, May – September when DCD is used and effective and October – April when DCD is not used. In addition, Method 3 uses this (two period) disaggregation for $EF_{3(PRP)}$, EF_1 and $Frac_{LEACH}$.

For dairy cattle urine, data from the 17 NzOnet trials given in Table A.1 were disaggregated into the two seasonal periods; namely, spring + summer, representing the seven months of October – April, and autumn + winter, representing the five months of May – September. For spring + summer, the 9 trials yielded a geometric average of 0.006. For autumn + winter, the 8 trials yielded a geometric average of 0.014. For Method 3, these two seasonal values should be used when nitrification inhibitors are NOT applied to soils. In the absence of nitrification inhibitors, these two seasonal values should also be used for $EF_{3(PRP)}$ of beef cattle urine excreted onto soils and EF_1 of nitrogen fertiliser applied to soils (fraction of applied nitrogen emitted to the atmosphere as nitrous oxide).

For dairy cattle dung, the 6 trials yielded a geometric average of 0.002 (Table A.2). There were not enough data for seasonal disaggregation. Consequently, a constant $EF_{3(PRP)}$ value of 0.002 should be used throughout the year when nitrification inhibitors are NOT applied to soils. In the absence of nitrification inhibitors, this constant value should also be used for $EF_{3(PRP)}$ of beef cattle dung excreted onto soils.

For sheep urine, the 4 trial values yielded a geometric average of 0.002 (Table A.3). The corresponding value for sheep dung was 0.0001 based on 2 trials. These values should be used throughout the year for the $EF_{3(PRP)}$ of sheep urine and dung when nitrification inhibitors are NOT applied to soils.

We have recommended that DCD be applied to soils twice each year in autumn and late winter. We also recommended that DCD would be effective during the autumn + winter period, representing the five months of May – September. Accordingly, DCD application corresponds with no change of $EF_{3(PRP)}$ or EF_1 during the seven months of October – April. When DCD was applied to New Zealand pastoral soils, $EF_{3(PRP)}$ of cattle urine was reduced by 61 to 74 % (n = 4, mean 67 %, Std. Dev. 6 %). These statistics define the uncertainty of nitrification inhibitor application to soils with respect to $EF_{3(PRP)}$. The mean value determines our recommendation. Consequently, **when DCD is applied as recommended, we revise the cattle urine $EF_{3(PRP)}$ during the five months of May – September as follows**

Cattle urine $EF_{3(PRP)}$ ‘plus DCD’ -= [0.014 X (1 – 0.67)] = 0.0046

For EF_1, revision should be the same as for $EF_{3(PRP)}$. Urine is the primary N excreta constituent in the N_2O emissions inventory and there is no scientific evidence to suggest that urea from fertiliser behaves differently than urea from urine (Kelliher et al. 2005a, Kelliher and de Klein 2006). We also recommend estimating the uncertainty of EF_1 using the $EF_{3(PRP)}$ uncertainty statistics, presuming N fertiliser applications will be done in autumn and late winter. We do not think there has been sufficient research to make any further recommendations for fertiliser. Consequently, we write

EF_1 ‘plus DCD’ -= [0.014 X (1 – 0.67)] = 0.0046

In the absence of trials, we apply the same logic to the revision of sheep urine $EF_{3(PRP)}$ in response to DCD application. Consequently, we write

Sheep urine $EF_{3(PRP)}$ ‘plus DCD’ -= [0.002 X (1 – 0.67)] = 0.00066

Again, in the absence of trials, we cannot be sure if the same logic should be used for the revision of cattle and sheep dung $EF_{3(PRP)}$ in response to DCD application. Consequently, it can only be an approximation when we write

Cattle dung $EF_{3(PRP)}$ 'plus DCD' -= [0.002 X (1 – 0.67)] = 0.00066

Sheep dung $EF_{3(PRP)}$ 'plus DCD' -= [0.0001 X (1 – 0.67)] = 0.000033

When DCD was applied to New Zealand pastoral soils, $Frac_{LEACH}$ was reduced by 68 to 77 % (n = 5, mean = 74% Std Dev. 4 %). These statistics define the uncertainty of nitrification inhibitor application to soils with respect to $Frac_{LEACH}$. The mean value determines our recommendation. Consequently, **when DCD is applied as recommended, we revise the $Frac_{LEACH}$ during the five months of May – September as follows**

$Frac_{LEACH}$ 'plus DCD' -= [0.07 X (1 – 0.74)] = 0.0182

7. Results

Nitrogen application as excreta and fertiliser onto pastoral soils

For the Kyoto Protocol base year of 1990, we calculated there was 1,406,153 tonnes (hereafter, abbreviated as t) of N as excreta deposited onto soils by grazing animals (Table A.4 in the Appendix). We focus on sheep and dairy cattle because these animal types made the greatest contributions. Just over half of this total was calculated to have come from sheep. For sheep, 66 % of total excreta was in the form of urine and 34 % as dung. In contrast, we calculated that dairy cattle contributed 25 % of total excreta and 74 % of their excreta was urine with 26 % as dung. In 1990, the quantity of N fertiliser applied to pastoral soils was 41,429 t. This figure is 80 % of the (3 year running mean quantity of) N fertiliser sold in 1990 based on expert judgement described earlier.

By 2004, we calculated that total excreta N and fertiliser N applications had increased by 136,089 and 234,763 t, respectively (totalling 370,852 t with the increase averaging 26,489 t per year for 1990 - 2004). We calculated a similar increase for the combination of dairy cattle urine and fertiliser, 367, 217 t including increases of 161,799 t for urine and 205,418 t for fertiliser. The sheep contribution was calculated to have decreased by 124, 495 t including urine plus dung excreta decreasing by 136,233 t, while fertiliser increased by 11,738 t.

By 2010, with respect to 1990, total excreta and fertiliser were projected to have increased by 227,816 and 281,538 t, respectively (totalling 509,354 t). Between 2004 and 2010, the rate of increase of N application averaged 23,084 t per year or 87 % of that for the previous 14 years. For dairy cattle, compared to 1990, urine and fertiliser increased by 194,931 and 246,346 t, respectively, totalling 441,277 t. Compared to 1990, the sheep contribution decreased by 72,633 t including urine and dung excreta decreasing by 86,710 t, while fertiliser increased by 14,077 t. Between 2004 and 2010, the sheep contribution thus increased by 51,862 t including increases of 49,523 t for urine and dung and 2,339 t for fertiliser.

Nitrous oxide emissions inventories quantifying how the emissions are reduced below that which would have occurred in the absence of the use of the nitrification inhibitors

We developed three emissions inventory methods. Our first method, called method 1, is an aggregated N_2O emissions inventory comparable to current calculations reported by government. The effects of nitrification inhibitors are calculated using 'annualised' revisions of emissions factors $EF_{3(PRP)}$ and EF_1 and term $Frac_{LEACH}$. For the other two methods, separate calculations are done for October – April when nitrification inhibitors should not be used and May – September when nitrification inhibitors should be used because they will then be most effective. For method 2, the nitrogen applied to soils as excreta from grazing animals remains an aggregation of urine and dung, so calculations for October – April are the same as for method 1. For May – September, method 2 uses a second set of revised values for $EF_{3(PRP)}$ and EF_1 and $Frac_{LEACH}$. Method 3 includes this disaggregation plus the excreta are disaggregated into urine and dung, so a third set of revised values for $EF_{3(PRP)}$, EF_1, and $Frac_{LEACH}$ are used for each of the two periods. To summarise:

Method 1 Completely aggregated, so comparable to the current method but DCD application uses 'annualised' revisions of emissions factors and leaching fraction

Method 2 Aggregated excreta but disaggregation into October – April calculations that are identical to method 1 but the May – September calculations, including DCD application, use a second set of revised emissions factors and leaching fraction

Method 3 Completely disaggregated with excreta separated into urine and dung and a third set of revised emissions factors and leaching fraction, one set for October – April and another for May – September including the effects of DCD application

The emissions calculations are tabulated in the Appendix (Tables A.4 – A.8) with a summary at the end (Table A.9). In 1990, by methods 1 and 2, we calculated that N_2O emissions from pastoral soils totalled 31.2 Gg (Table A.9). For method 3, because lower values were used for $EF_{3(PRP)}$ of dung, this value was reduced to 18.5 Gg (Table A.9). For Kyoto Protocol accounting, a change of N_2O emissions is calculated relative to the 1990 level. Consequently, the same method must be used to compute a change of emissions. For example, a change of emissions from 1990 to 2004 cannot combine the relatively large method 1 value for 1990 with the relatively small value for 2004 from method 3. Using methods 1 and 2, in the absence of nitrification inhibitors (DCD), there were emissions increases of 7.7 and 10.6 Gg by 2004 and 2010, respectively (Table A.9). During the year 2010, N_2O emissions represent an average for the Kyoto Protocol's five-year-long Commitment Period 1 (2008 – 2012). For method 3, the corresponding emissions increases were larger at 9.7 and 11.8 Gg (Table A.9).

As case studies, we now calculate changes in the emissions between 1990 and 2004 and 2010 if DCD was applied as recommended to all land grazed by dairy cattle. This allows us to utilise the excretion and fertiliser application rates discussed above. Method 1 does not include seasonal differences in N_2O emissions (October – April versus May – September) or different emissions from urine and dung. Using method 1, there were emissions increases of 3.0 and 5.3 Gg by 2004 and 2010, respectively (Table A.9). Compared to the emissions increases in the absence of DCD, mitigation using DCD was 4.7 Gg in 2004 (7.7 – 3.0, Table A.9) and 5.3 Gg in 2010. For Commitment Period 1 according to method 1, DCD mitigation was 26.5 Gg (5.3 Gg per year multiplied by 5 years). For method 1, mitigation is

proportional to the fraction of excreta and fertiliser exposed to DCD. For example, if DCD was applied to only half the dairy cattle excreta and fertiliser, the mitigation values would be halved (Commitment Period 1 mitigation becomes 13.2 Gg, half of 26.5 Gg). As a further illustration, when DCD was applied as recommended to all land grazed by all animals, emissions were actually reduced from the 1990 level by 3.2 and 1.2 Gg in 2004 and 2010, respectively (Table A.5).

Method 2 includes seasonal differences in N_2O emissions (October – April versus May – September) but no difference made between emissions from urine and dung. If DCD was applied as recommended to all land grazed by dairy cattle, using method 2, there were emissions increases of 0.0 (that is, no increase above the 1990 level) and 1.8 Gg by 2004 and 2010, respectively (Table A.9). Compared to the emissions increases in the absence of DCD, mitigation was 7.7 Gg in 2004 and 8.8 Gg in 2010. For Commitment Period 1 according to method 1, mitigation was 44.0 Gg. For method 2, mitigation is also proportional to the fraction of excreta and fertiliser exposed to DCD.

Method 3 includes disaggregation of emissions into periods when DCD is not used (October – April) and when DCD is used (May – September). There is also disaggregation of excreta into urine and dung and different emissions factors applied to these components. If DCD was applied as recommended to all land grazed by dairy cattle, using method 3, there were emissions increases of 3.2 and 4.4 Gg by 2004 and 2010, respectively (Table A.9). Compared to the emissions increases in the absence of DCD, mitigation was 6.5 Gg (9.7 – 3.2, Table A.9) in 2004 and 7.4 Gg (11.8 – 4.4) in 2010. For Commitment Period 1 according to method 3, mitigation was 37.0 Gg. For method 3, mitigation is not simply proportional to the fraction of excreta and fertiliser exposed to DCD because of the disaggregation of excreta into urine and dung and their different $EF_{3(PRP)}$ values throughout the year.

Estimate future use of nitrification inhibitors and limitations to their use, and impact on emissions until the end of Commitment Period 1 to enable an estimate of future liabilities associated with N_2O emissions

At present, there are many unknowns related to the future use of nitrification inhibitors. One example is the possibility of a public: private partnership whereby the involved cost is shared by farmers and the government on the basis that each gains from the investment. Farmers have the potential to gain through enhanced pasture production associated with improved nitrogen use efficiency, while the government can account for a financial liability associated with its ratification of the Kyoto Protocol. Nevertheless, we re-iterate that any predictions will probably have considerable, but at this stage, intractable uncertainty. Consequently, we do not believe this aspect of the objective can be constructively analysed here. However, we described some limitations of nitrification inhibitor use and the impact on emissions through Commitment Period 1 in our draft Part I report for this project and the previous section of this report, respectively.

Recommend how the revised factors should be monitored, including the long-term effectiveness of nitrification inhibitors

While Li and Kelliher (2005) proposed an underground method to monitor direct nitrous oxide emissions ($EF_{3(PRP)}$) that allowed pasture grazing by farmed animals, this method has not yet been deployed operationally. The monitoring of nitrogen leaching ($Frac_{LEACH}$)

includes spatial and temporal integration challenges that are beyond the scope of this report. We believe that monitoring should rely on the principles of observation and generalisation because measurements must be made at smaller space and time scales. After all, the emissions inventory relies on these principles. Consequently, we recommend that monitoring should be based on field trial, despite their limitations. We believe strongly that the site network approach used by de Klein et al. (2003) serves as a constructive model.

As mentioned earlier, there has been one New Zealand field trial that included dairy cattle grazing and quantified the effects of repeated use of DCD on pasture production and quality (Moir et al. 2007). For four years (2002 – 2006 at the Lincoln University Dairy Farm), DCD was applied to a Wakanui silt loam soil beneath grazed pasture at 10 kg ha^{-1} in early May in addition to dairy cattle urine (1000 kg N ha^{-1}) with DCD applied again in early August. Comparisons were made with control plots that received no DCD. Each year, the DCD applications consistently corresponded with increased pasture herbage dry matter yield that averaged 21 % on an annual, whole paddock basis including urine patches and inter-urine areas. Pasture nitrogen, metabolisable energy and fibre contents were not affected by the DCD applications.

The production rate and number of animals (based on farm records) grazing on pastures treated and not treated with nitrification inhibitors and the soil's drainage class (based on treated area soil inspections)

As stated in our Part I draft report, DCD use includes a requirement for accurate and verifiable records of the treated pasture/soils (land) area. Long-term data storage and availability for independent review are also required. A GPS system associated with application seems ideal. This system should be future proof and suitable for audit and accreditation.

Linked to the GPS record of land area covered by DCD application, farm records of additional information would be needed to determine the N loading rate onto soils. Firstly, nitrogen fertilizer rate on the land 'treated' with DCD needs to be recorded. Next, as described earlier in our Methods, the weight, production rate and number of grazing animals determines N excretion as urine and dung that is deposited onto soils during grazing. Hence farm records could be used to determine the number and type of animals (dairy cattle, beef cattle and sheep) 'treated' with DCD including grazing period on the farm for lambs and other animals slaughtered during the year. We acknowledge that access to farm records of production rate may be controversial and animal weights may not be available. Alternatively, the number and type of animals 'treated' with DCD could be compared to the national population, facilitating a proportional calculation of the treated animal's N excretion rate.

An emissions factor, EF, that determines N_2O emissions is the direct EF for excreta, called $EF_{3(PRP)}$. As described earlier, the $EF_{3(PRP)}$ data are cumulative values of direct N_2O emissions over 5 to 10 months following an excreta application (fraction of applied nitrogen emitted to the atmosphere as nitrous oxide) based on field chamber measurements of the NzOnet field trials (Barton et al., 2000; de Klein et al., 2003, 2004; Sherlock *et al.*, 2003a,b). The data for dairy cattle urine are given in Table A.1, including the soil's drainage class. These data may be analysed to compute a statistic known as the geometric average, a robust measure of the central tendency. For the well-, imperfectly- and poorly-drained soils, the geometric average values of $EF_{3(PRP)}$ were 0.0061 (n = 7), 0.0063 (n = 3) and 0.0164 (n = 7), respectively. The well-drained and imperfectly-drained soils had virtually the same $EF_{3(PRP)}$

values, but the poorly-drained soils value was 2.7 times greater. We acknowledge the small samples sizes involved in these comparisons. To implement our comparisons, $EF_{3(PRP)}$ would need to be disaggregated by soil drainage class. Earlier, at the national scale, it was determined that 74 % of the grazed pasture land area has well-drained soils, while 17 and 9 % of the area has imperfectly- and poorly drained soils, respectively (Sherlock et al. 2001). For the land area covered by DCD application, determination of the soil's drainage class could be done by three methods. Firstly, a high-level assessment may be possible using soil maps. However, the reliability of this approach may vary widely at the scale of individual paddocks. Alternatively, the land manager is probably best able to make the assessment based on experience from observation (for example, after heavy rainfall, poor drainage is indicated by an area prone to flooding). As a refinement, soils in the treated area could be examined following excavation but a sampling strategy and assessment protocol would need to be developed. As a rule of thumb, it is reckoned that about half of the spatial variance in the variables that determine drainage is likely within one metre of a measurement or inspection point. Consequently, though we can envisage reasonable, clear and unambiguous criteria for separation of inspected soils into well-, imperfectly- and pooly-drained classes, we are wary about including the need to dig holes and inspect soils throughout the area treated with DCD. This could involve a tremendous amount of work on farms, and hence expense, and the information acquired seems likely to be uncertain.

8. Recommendations

- Because the rate of DCD degradation in soils depends strongly on temperature (i.e., slower degradation rate in cooler soils), for October – April when soil temperature beneath pasture generally exceeds 12 °C, DCD should not to be used because it is unlikely to be optimally effective. A suitable DCD application rate is 10 kg/ha and two applications each year, one following grazing in autumn and another following grazing in late winter.

- Based on the New Zealand peer-reviewed literature in conjunction with dairy cattle urine application to soils located at Lincoln, Hamilton, Taupo and a confidential trial in Southland that included dairy cattle grazing, DCD application is expected to correspond with a 67 ± 6% reduction in the direct N_2O emissions factor called $EF_{3(PRP)}$.

- Based on the New Zealand peer-reviewed literature in conjunction with dairy cattle urine application to soils located at Lincoln, DCD application is expected to correspond with a 74 ± 4% reduction in nitrate leaching ($Frac_{LEACH}$). We acknowledge that confidential trials yielded smaller and more variable percentages, but due to the relatively small absolute value of $Frac_{LEACH}$, the N_2O emissions inventory was not sensitive to its response of $Frac_{LEACH}$ to DCD application.

- The quantity of nitrogen applied to pastoral soils as excreta from grazing animals and fertiliser should be disaggregated into May – September and October – April periods. Monthly values are already available for the excreta. For nitrogen fertiliser, FertResearch should be consulted each year for advice about the required disaggregation. This involves estimation of the land area grazed by different types of animal and the fractions of fertiliser applied to this land during each of the two periods. The revised values of $Frac_{LEACH}$ and

$EF_{3(PRP)}$ should apply to May – September. The revised value of $EF_{3(PRP)}$ should be applied to EF_1.

- Because method 2 is most strongly supported by research that has been conducted in New Zealand, recognising only sparse data are available for emissions from excreta disaggregated into urine and dung components, method 2 is recommended to describe how anthropogenic N_2O emissions from pastoral agriculture soils can be reduced using nitrification inhibitors.

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11. Appendix I – Confidential literature on effectiveness of nitrification inhibitors

[Information withheld from public release]

12. Appendix II - Tables A.1 – A.9

Table A.1. Dairy cattle urine EF_3 (fraction of applied N evolved as N_2O, duration of study in days) measurements made at NzOnet trial sites located in three regions (Barton et al., 2000; de Klein et al., 2003, 2004; Sherlock et al., 2003a,b). These data represent analyses of an estimated 30,000 gas samples collected over 4 years (2000 – 2003). No data is abbreviated as n.d.

Season	Spring	Summer	Autumn	Winter
Well-drained soils by region				
Otago	n.d.	0.0146, 202	n.d.	0.0090, 149
Canterbury	n.d.	n.d.	0.0050, 224	n.d.
Waikato	0.0122, 91	0.0007, 253	0.0064, 163	0.0090, 146
Imperfectly-drained soils by region				
Canterbury	0.0037, 91	0.0020, 262	0.0330, 224	n.d
Poorly-drained by region				
Otago	0.0295, 69	0.0058, 202	0.0260, 152	0.0090, 149
Waikato	0.0261, 91	0.0075, 253	n.d.	0.0270, 146

Table A.2. Dairy cattle dung EF_3 (fraction of applied N evolved as N_2O, duration of study in days). No data is abbreviated as n.d.

Season	Spring	Summer	Autumn	Winter
Well-drained soils by region				
Waikato	0.0024, 91	n.d.	n.d.	n.d.
Otago	n.d.	n.d.	n.d.	0.001, 149
Imperfectly-drained soils by region				
Canterbury	0.0017, 91	0.0021, 262	n.d.	n.d.
Waikato	0.0043, 91	n.d.	n.d.	n.d.
Otago	n.d.	n.d.	n.d.	0.001, 149

Table A.3. Sheep urine and dung EF_3 (fraction of applied N evolved as N_2O, duration of study in days) measurements made at the Otago site. No data is abbreviated as n.d.

Season	Spring	Winter
Well-drained soil		
urine	0.0020, 69	0.0030, 149
dung	0.0001, 69	n.d.
Poorly-drained soil		
urine	0.0010, 69	0.0020, 149
dung	0.0000, 69	n.d.

Table A.4. Method 1 pastoral soils nitrous oxide (N_2O) emissions. Nitrogen (N) application to these soils is shown as urine and dung excreta deposited by grazing animals and fertiliser (80 % of total sold). Year 2010 represents an average for the Kyoto Protocol Commitment Period 1. Symbol Δ denotes a change of total from the Kyoto Protocol base year of 1990 to years thereafter including 2004 and 2010. A tonne is equivalent to 10^6 grams (g), while Gg means 10^9 g. The N_2O emissions computation based on the quantity of N applied to soils includes multiplication by the ratio of molecular weights (44/28).

N source	N Excreta (tonnes)			EF3	Gg N_2O		
	1990	2004	2010		1990	2004	2010
Dairy cattle							
Urine	245800	418480	451612	—	—	—	—
Dung	92118	150184	182149	—	—	—	—
Sub total	337918	568664	633761	0.01	7.63	12.84	14.31
Δ	0					5.21	6.68
Beef cattle							
Urine	201007	219024	205502	—	—	—	—
Dung	103088	112328	107763	—	—	—	—
Sub total	304095	331352	313265	0.01	6.57	7.16	6.77
Δ						0.59	0.20
Sheep							
Urine	481942	391892	421415	—	—	—	—
Dung	247168	200985	220985	—	—	—	—
Sub total	729110	592877	642400	0.01	15.75	12.81	13.88
Δ						-2.94	-1.87
Deer							
Urine	15963	32620	29220	—	—	—	—
Dung	8187	16729	15323	—	—	—	—
Sub total	24149	49349	44543	0.01	0.52	1.07	0.96
Δ						0.55	0.44
N source	N fertiliser (tonnes)			EF1	Gg N_2O		
	1990	2004	2010		1990	2004	2010
Fertiliser	41429	276192	322967	0.01	0.77	5.10	5.96
Δ						5.41	6.49
Grand total					31.24	38.98	41.88
Δ						7.74	10.64

Table A.5. Method 1 pastoral soils nitrous oxide (N_2O) emissions inventories with annualised DCD emission factors for all animal classes. For these two scenarios, DCD was applied as recommended to all land grazed by dairy cattle, beef cattle, sheep and deer (denoted All land) or the land grazed by dairy cattle (denoted Dairy land).

N source	Gg N_2O (All land)			Gg N_2O (Dairy land)		
	1990	2004	2010	1990	2004	2010
Dairy						
Urine	—	—	—	—	—	—
Dung	—	—	—	—	—	—
sub total	7.63	9.24	10.29	7.63	9.24	10.29
Δ		1.61	2.66		1.61	2.66
Beef						
Urine	—	—	—	—	—	—
Dung	—	—	—	—	—	—
sub total	6.57	5.13	4.85	6.57	7.16	6.77
Δ		-1.44	-1.72		0.59	0.20
Sheep						
Urine	—	—	—	—	—	—
Dung	—	—	—	—	—	—
sub total	15.75	9.19	9.95	15.75	12.81	13.88
Δ		-6.56	-5.80		-2.94	-1.87
Deer						
Urine	—	—	—	—	—	—
Dung	—	—	—	—	—	—
sub total	0.52	0.76	0.69	0.52	1.07	0.96
Δ		0.24	0.17		0.55	0.44
N source						
	1990	2004	2010	1990	2004	2010
Fertiliser	0.77	3.67	4.29	0.77	3.95	4.62
Δ		2.90	3.52		3.18	3.85
Grand total	31.24	27.99	30.07	31.24	34.23	36.52
Δ		-3.25	-1.17		2.99	5.28

Table A.6. Method 2 calculations are done separately for October – April when no DCD was used and May – September when DCD is used. The nitrogen applied to soils as excreta is an aggregation of urine and dung. Consequently, though not shown explicitly in Table A.5 because only annual values are given there, the calculations for October – April that are shown here yield the same figures as would have been obtained using method 1. For May – September, a second set of revised values are used for $EF_{3(PRP)}$ and EF_1 and $Frac_{LEACH}$. This nitrous oxide (N_2O) emissions inventory was calculated with DCD applied as recommended to the land area grazed by dairy cattle.

N source	Gg N_2O (Oct – Apr)			Gg N_2O (May – Sep)			Gg N_2O (year)		
	1990 No DCD	2004 No DCD	2010 No DCD	1990 No DCD	2004 DCD used	2010 DCD used	1990 No DCD	2004 DCD used	2010 DCD used
Dairy									
Urine									
Dung									
sub total	4.67	7.93	8.84	2.96	1.58	1.76	7.63	9.51	10.60
Δ		3.26	4.17		-1.38	-1.2		1.88	2.97
Beef									
Urine									
Dung									
Sub total	3.75	4.08	3.86	2.82	2.78	2.62	6.57	6.86	6.48
Δ		0.33	0.11		-0.04	-0.2		0.29	-0.09
Sheep									
Urine									
Dung									
Sub total	10.17	8.38	9.08	5.58	4.00	4.33	15.75	12.38	13.41
Δ		-1.79	-1.09		-1.58	-1.25		-3.37	-2.34
Deer									
Urine									
Dung									
Sub total	0.32	0.67	0.61	0.20	0.36	0.32	0.52	1.03	0.93
Δ		0.35	0.29		0.16	0.12		0.51	0.41
Fertiliser				0.77	2.03	2.37	0.77	2.03	2.37
Dairy	0	0	0	0.67	1.430	1.670	0.67	1.43	1.67
Beef & Sheep	0	0	0	0.10	0.60	0.70	0.10	0.60	0.70
Δ		0	0		1.26	1.60		1.26	1.60
Grand total	18.91	21.06	22.39	12.33	10.15	10.7	31.24	31.21	33.09
Δ									

Table A.7. Method 3 calculations are done separately for October – April and May – September. The nitrogen applied to soils as excreta is disaggregated into urine and dung, so so a third set of revised values for $EF_{3(PRP)}$, EF_1, and $Frac_{LEACH}$ are used for each of the two periods. This nitrous oxide (N_2O) emissions inventory was calculated with no DCD applied to soils.

N source	Gg N_2O (Oct – Apr)			Gg N_2O (May – Sep)			Gg N_2O (year)		
	1990	2004	2010	1990	2004	2010	1990	2004	2010
Dairy									
Urine	2.33	3.96	4.27	2.69	4.46	4.82	5.02	8.42	9.09
Dung	0.69	1.18	1.40	0.44	0.73	0.86	1.13	1.91	2.26
sub total							6.15	10.33	11.35
Δ								4.18	5.20
Beef									
Urine	1.76	1.91	1.80	2.41	2.63	2.46	4.17	4.54	4.26
Dung	0.53	0.58	0.56	0.40	0.44	0.42	0.93	1.02	0.98
Sub total							5.10	5.56	5.24
Δ								0.46	0.14
Sheep									
Urine	2.81	2.32	2.49	1.54	1.23	1.32	4.35	3.55	3.81
Dung	0.97	0.80	0.87	0.53	0.42	0.46	1.50	1.22	1.33
Sub total							5.85	4.77	5.14
Δ								-1.08	-0.71
Deer									
Urine	0.21	0.44	0.40	0.13	0.26	0.23	0.34	0.70	0.63
Dung	0.05	0.10	0.09	0.03	0.06	0.05	0.08	0.16	0.14
Sub total							0.42	0.86	0.77
Δ								0.44	0.35
Fertiliser									
Dairy	0.00	0.00	0.00	0.87	5.83	6.82	0.87	5.83	6.82
Beef & Sheep	0.00	0.00	0.00	0.13	0.83	0.97	0.13	0.83	0.97
Grand total							18.52	28.18	30.29
Δ								9.66	11.77

Table A.8. Method 3 calculations are also done separately for October – April when DCD is not used and for May – September when DCD is used. The nitrogen applied to soils as excreta is disaggregated into urine and dung, so a third set of revised values for $EF_{3(PRP)}$, EF_1, and $Frac_{LEACH}$ are used for each of the two periods. This nitrous oxide (N_2O) emissions inventory was calculated with DCD applied to the land area grazed by dairy cattle.

N source	Gg N_2O (Oct – Apr)			Gg N_2O (May – Sep)			Gg N_2O (year)		
	1990	2004	2010	1990	2004	2010	1990	2004	2010
Dairy									
Urine	2.33	3.96	4.27	2.69	1.78	1.92	5.02	5.74	6.19
Dung	0.69	1.18	1.40	0.44	0.61	0.72	1.13	1.79	2.12
sub total							6.15	7.53	8.31
Δ								1.38	2.16
Beef									
Urine	1.76	1.91	1.80	2.41	2.63	2.46	4.17	4.54	4.26
Dung	0.53	0.58	0.56	0.40	0.44	0.42	0.93	1.02	0.98
Sub total							5.10	5.56	5.24
Δ								0.46	0.14
Sheep									
Urine	2.81	2.32	2.49	1.54	1.23	1.32	4.35	3.55	3.81
Dung	0.97	0.80	0.87	0.53	0.42	0.46	1.50	1.22	1.33
Sub total							5.85	4.77	5.14
Δ								-1.08	-0.71
Deer									
Urine	0.21	0.44	0.40	0.13	0.26	0.23	0.34	0.70	0.63
Dung	0.05	0.10	0.09	0.03	0.06	0.05	0.08	0.16	0.14
Sub total							0.42	0.86	0.77
Δ								0.44	0.35
Fertiliser									
Dairy	0.00	0.00	0.00	0.87	5.83	6.82	0.87	5.83	6.82
Beef & Sheep	0.00	0.00	0.00	0.13	0.83	0.97	0.13	0.83	0.97
Grand total							18.52	21.68	22.92
Δ								3.16	4.40

Table A.9. Using the 3 methods to calculate pastoral soils nitrous oxide (N_2O) emissions, two scenarios are shown whereby either no land was treated with DCD (no DCD) or all of the land grazed by dairy cattle (denoted Dairy land) was treated with DCD as recommended.

Method	Gg N_2O (no DCD)			Gg N_2O (Dairy land)		
	1990	2004	2010	1990	2004	2010
1	31.24	38.98	41.88	31.24	34.23	36.52
Δ		7.74	10.64		2.99	5.28
2	31.24	38.98	41.88	31.24	31.21	33.09
Δ		7.74	10.64		-0.03	1.85
3	18.52	28.18	30.29	18.52	21.68	22.92
Δ		9.66	11.77		3.16	4.40