FIELD-SCALE VERIFICATION OF NITROUS OXIDE EMISSION REDUCTION WITH DCD IN DAIRY-GRAZED PASTURE USING MEASUREMENTS AND MODELLING

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Nitrous oxide (N_2O) from agricultural soils is a major source of greenhouse gas emissions in New Zealand. N_2O is produced by the microbial break-down of animal excreta and fertiliser N applied to agricultural soils. Nitrification inhibitors are seen in New Zealand as a potential technology to reduce N_2O emissions from agricultural soils. A review of lysimeter and field studies using the nitrification inhibitor dicyandiamide (DCD) reported an average reduction in N_2O emission of 67 ± 6% from animal urine (Kelliher et al. 2007). In these studies DCD was directly applied to urine. However, farmers apply DCD to grazed pastures shortly before or after grazing rather than applying it specifically to the urine patches.

Accordingly, the objectives of this study were: 1) to test whether the same level of N_2O reduction is achieved under grazed conditions where excretal-N is non-uniformly deposited, and 2) to apply the process-based NZ-DNDC model to simulate the effect of DCD on emission reductions. Two circular 1260-m^2 treatment plots at Massey University Dairy Farm 4 were grazed simultaneously for 5 h, by 20 cattle on each plot. The following day, DCD was applied in 800 L water to one of the plots at 10 kg ha^{-1}. N_2O emissions were measured periodically for 20 days following a grazing event, using equal arrays of 20 soil chambers in either plot, and soil and environmental variables were monitored.

The cumulative N_2O emissions over the 20 day period were 220 ± 90 g N_2O-N $ha^{-1}$and 110 ± 20 g N_2O-N ha^{-1} (based on the arithmetic mean and standard error of the chambers) for the untreated and DCD-treated plots respectively. This suggests a reduction in N_2O emission from DCD application of ~50 ± 40% from a single grazing event. However, this result should be treated with caution, because the possibility of sampling error due to the chamber distribution cannot be excluded.

NZ-DNDC simulated N_2O emissions of 185 g N_2O-N $ha^{-1}$and 73 g N_2O-N ha^{-1} for the untreated and DCD-treated areas respectively, corresponding to a reduction in N_2O emissions from DCD application of 60%. This level of reduction is consistent with that found in experiments with individual urine patches.

A sensitivity analysis was conducted on the NZ-DNDC model to find the variability in the predicted N_2O emissions that would result from uncertainty in the input parameters. Varying the parameters' initial soil NO_3^- and NH_4^+, soil organic carbon and bulk density within plausible ranges resulted in N_2O emissions from the no-DCD area ranging from 120 to 259 g N_2O-N ha^{-1}. This range is in good agreement with the measured emissions.

Introduction

Nitrous oxide (N_2O) from agricultural soils is a major source of greenhouse gas emissions in New Zealand accounting for 15.2% of total greenhouse gas emissions on a CO_2 equivalent basis (Ministry for the Environment 2010). N_2O is a by-product of the microbial breakdown of N-compounds applied to soil (typically as animal excreta or N-fertiliser). In New Zealand N_2O emissions from agricultural soils rose from 30.3 to 35.8 Gg/annum between 1990 and 2008 due to increase fertiliser and excretal N inputs (Ministry for the Environment 2010)

Nitrification inhibitors such as dicyandiamde (DCD) inhibit the nitrification process where soil microbes convert ammonium ions (NH_4^+) to nitrate (NO_3^-). Inhibiting the nitrification process can potentially reduce the N_2O emitted both by the nitrification process itself, and from subsequent denitrification of NO_3^- (Abbasi and Adams, 2000; Cookson and Cornforth 2002).

A review of lysimeter and field studies using the nitrification inhibitor dicyandiamide (DCD) in New Zealand reported an average reduction of 67 ± 6% in N_2O emission from animal urine (Kelliher et al. 2007). The effects of using DCD have been incorporated into the national inventory assuming a reduction of 67% in direct N_2O emissions from animal excreta when DCD is applied (Ministry for the Environment 2010).

In many of the previous studies DCD has been applied directly to the urine patch. However, farmers apply DCD to grazed pastures shortly before or after grazing rather than specific application to the urine patches. In this study we attempted to measure the effectiveness of DCD in reducing N_2O emissions under grazing conditions using both gas chambers and micrometeorology, and modelled the results using the process-based NZ-DNDC model. The micrometeorological results have been published by Harvey et al. (in prep), so this paper will focus on the gas chamber and modelling approaches.

DNDC (Li et al. 1992) is a process-based model that simulates the soil physical, chemical and biological processes that produce greenhouse gas emissions. NZ-DNDC is the New Zealand specific model that has been adapted for use in New Zealand grazed pasture conditions and tested on dairy and sheep grazed pastures (Saggar et al. 2004, 2007). Giltrap et al. (2010) modelled the effect of DCD on N_2O emissions from a urine patch assuming that the nitrification inhibitor caused a constant percentage reduction in the nitrification rate. Reasonable agreement between measured and modelled results was found when 70% reduction in nitrification rate with DCD was used.

Methodology

Study Site

The study site was Massey University Dairy Farm 4 in Palmerston North, New Zealand. The soil was a poorly drained Tokomaru silt loam. Two circular plots of 40 m diameter (0.126 ha) were each grazed by 20 cows for 5 hours on 11 June 2009. The following day, DCD was applied in 800 L water to one of the plots at 10 kg ha^{-1}. N_2O emissions were measured periodically for 20 days following a grazing event, using 20 soil chambers in each plot. The period of 20 days was chosen to align with a concurrent micrometeorology study (described in Harvey et al. (in prep)). Chambers were placed in a regular circular pattern in either plot, which constitutes random placement with respect to the distribution of cattle excreta. Soil and environmental variables were also monitored.

Chamber measurements

N_2O fluxes were measured using 20 gas flux chambers in each plot. On each sampling day the chamber was closed with a lid for 1 h, and the air above the soil sampled through a three-way tap on the chamber lid using a 60-ml syringe at 0, 30 and 60 minutes after sealing the chamber. Gas samples were then analysed using a Shimadzu GC-2010 gas chromatograph and flux rates calculated based on a linear regression of the three sampled concentrations using the method described in Saggar et al. (2010).

NZ-DNDC model

The NZ-DNDC model was used to simulate the N_2O emissions from both treatments (with and without DCD). The model was run using the parameter values listed in Table 1.

Table 1: Parameters used in the NZ-DNDC simulations

Parameter	**Value**
Bulk density	1.3 g/cm^3
Clay content	23%
Initial soil NH_4^+-N	10 mg N/kg soil
Initial soil NO_3^-–N	15 mg N/kg soil
Initial WFPS	85%
pH	6
Soil organic carbon at surface	0.047 kg C/kg soil
Soil texture	Silt loam
Soil WFPS at field capacity	80%
Soil WFPS at wilting point	28%
Depth of Water Retention Layer	5 cm
Nitrification inhibitor effectiveness	70%

The soil WFPS at field capacity and depth of water retention layer were set to minimise the root mean square error of the prediction for soil WFPS from 0 to 10 cm (Figure 1a). In the absence of measurements, the initial soil NH_4^+ and NO_3^- were selected to minimise the root mean square error in the N_2O emissions for the urine-only treatment (Figure 1b). The same soil conditions were then used for the urine + DCD treatment. A previous field study on the same soil had found that DCD reduced the nitrification rate by between 60 and 80% (Giltrap et al. 2010), so the effect of DCD was simulated by reducing the nitrification rate by 70%. Note that as N_2O is produced by both nitrification and denitrification processes, the reduction in the N_2O emissions will not be the same as the reduction in the nitrification rate. It was assumed that the inhibitor effectiveness remained constant over the 20-day measurement period.

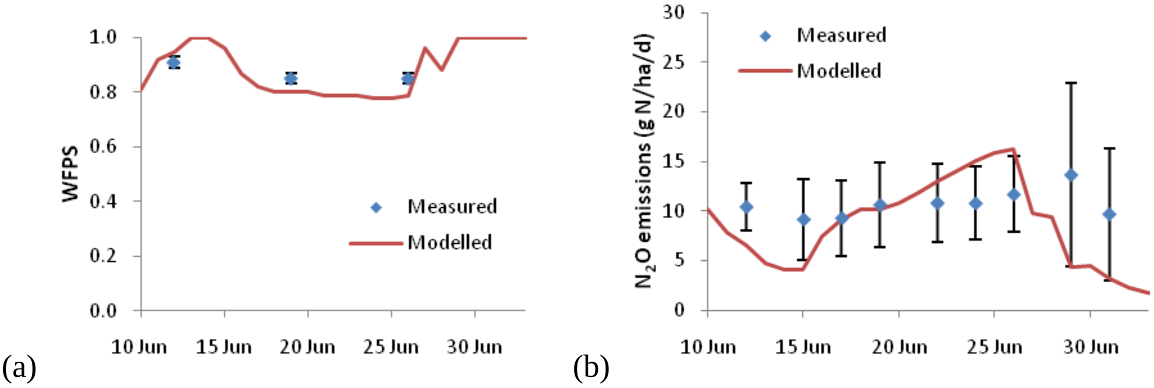


Figure 1: Measured and modelled (a) soil WFPS (0–10 cm) and (b) N_2O emissions for a cattle grazed pasture with no DCD applied. Error bars represent the standard error of chamber measurements.

Sensitivity analysis

The N_2O emissions predicted by the NZ-DNDC model are sensitive to the choice of initial soil parameter values. For the sensitivity analysis we examined the effects of uncertainty in soil NH_4^+, NO_3^-, organic carbon and bulk density on the simulated N_2O emissions. The effect on N_2O emissions of varying each parameter was examined individually, then a high and low scenario were generated using the extreme values of all four parameters. Table 2 shows the parameter ranges considered.

Table 2: Parameter ranges considered in uncertainty analysis

Parameter	Range
Soil NO_3^-	13–17 mg NO_3^-–N/kg soil
Soil NH_4^+	8–12 mg NH_4^+–N/kg soil
Soil Organic Carbon (SOC)	0.043-0.051 g C/g soil
Bulk density	1.20–1.35 g/cm^3

In addition to the direct effect that bulk density has in NZ-DNDC, bulk density is also used to convert the measured soil moisture to WFPS. As the WFPS at field capacity and water retention layer depth were adjusted to provide a good model simulation of WFPS the uncertainty in the bulk density would also affect these parameters. However, these secondary effects have not been quantified.

Sensitivities of individual parameters were quoted as (% change in N_2O emission)/(% change in parameter).

Results

Chamber measurements

Figures 2(a) and (b) are box-plots of the chamber emissions from the grazing-only and grazing + DCD plots respectively. The measured emissions were positively skewed, as was expected given the highly patchy nature of urine deposition. In particular, for the grazing-only treatment the highest emissions come from a single chamber and are likely to be the result of a urine patch.

To calculate the total emissions over the 20-day period, the fluxes from each chamber were integrated using linear interpolation between measurement days and then the arithmetic mean and standard error calculated. Taking the mean and standard error of all 20 chambers, for the grazing only treatment the total N_2O emission was 220 ± 90 g N_2O-N/ha, while for the DCD treatment it was 110 ± 20 g N_2O-N/ha. From these figures the calculated reduction due to DCD application was 50 ± 40%.

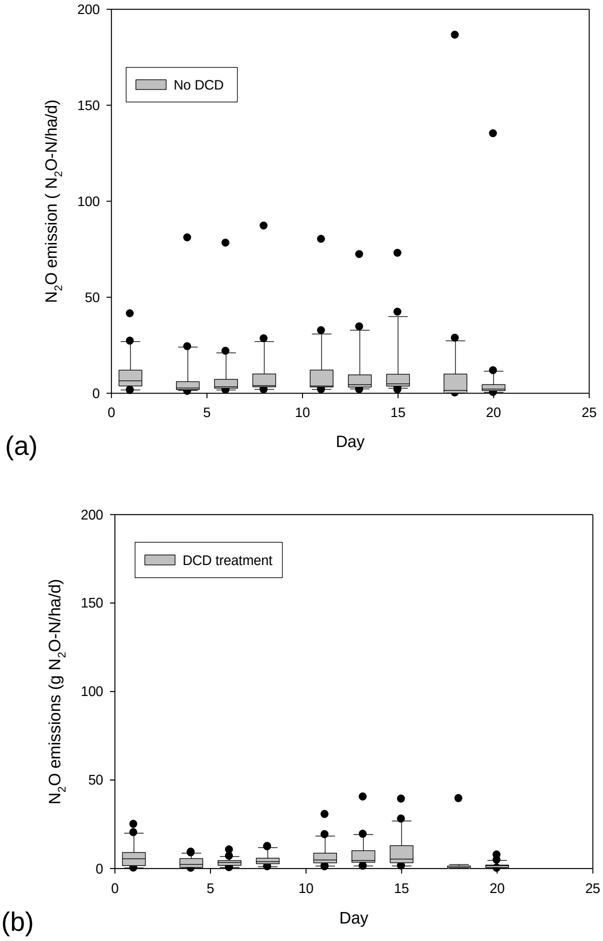


Figure 2: Box-plots of chamber N_2O fluxes from (a) grazing only (no DCD) and (b) grazing + DCD treatments. The boxes show the inter-quartile range, with a horizontal line drawn at the median. The lines extend from the 10th percentile to the 90th percentile. Dots represent the values of the upper and lower 10% of chambers.

Modelled emissions

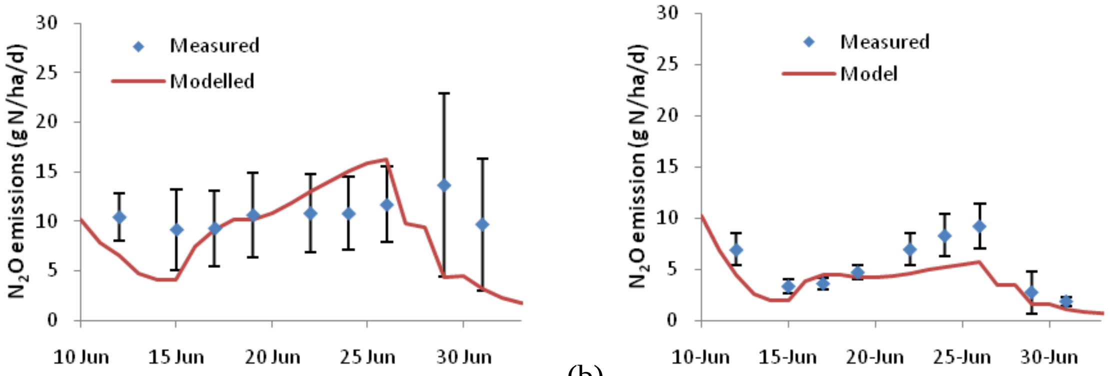
Figures 3(a) and (b) show the N_2O emissions from the grazing-only treatment (which was used to establish some initial parameter values) and the grazing + DCD treatment.

Table 3 compares the measured and modelled N_2O emissions for the two treatments.

The model mean error (ME) is the average difference between the predicted and observed values. The model RMSE (Root Mean Square Error) is defined as:

$$RMSE = \sqrt{\frac{\sum_i (P_i - O_i)^2}{n}}$$

where P_i is the predicted value, O_i is the observed value and n is the number of observations. Note that both the ME and RMSE are measures of the model deviation from observation on a point-by-point basis. It is possible that the model could have high errors for predicting the emissions on a given day, but still produce accurate emissions estimates over a longer time period.



(a) (b)

Figure 3: Measured and modelled N_2O emissions from (a) grazing-only and (b) grazing + DCD plot. Model assumed DCD reduced nitrification rate by 70% for duration of trial. Fig. 3(a) is identical to 1(b), repeated for easy comparison between the two plots.

Table 3: Measured and modelled N_2O emissions between 12 June and 1 July 2009 for grazing-only and grazing + DCD treatments

	Measured (± SE) (g N_2O–N/ha)	**Modelled (g N_2O–N/ha)**	**Model ME g N_2O–N/ha/d**	**Model RMSE g N_2O–N/ha/d**
Grazing only	220 ± 90	185	2.2	9
Grazing + DCD	110 ± 20	73	–1.6	2
% Reduction in N_2O emissions using DCD	50 ± 40 %	60		

The modelled N_2O emission for the grazing-only treatment is within the uncertainty range of the measured emission. The RMSE is larger than the ME, indicating that the differences between measured and modelled predictions can be quite high on a daily basis, but that under-predictions and over-predictions tend to cancel out. The ME is positive, so overall the model may slightly overestimate N_2O emissions.

For the grazing + DCD treatment, the model slightly under-predicted N_2O emissions. The most likely reason is that the 70% reduction in nitrification assumed was slightly too high. The measured and modelled reduction in N_2O emissions using DCD agreed within the large uncertainty limits.

Sensitivity analysis

Figures 4(a)–(d) show the range of modelled N_2O emissions as initial soil NO_3^-, NH_4^+, SOC, and bulk density are individually varied within the ranges listed in Table 2, while Figure 4 (e) shows the effect of varying all four parameters simultaneously.

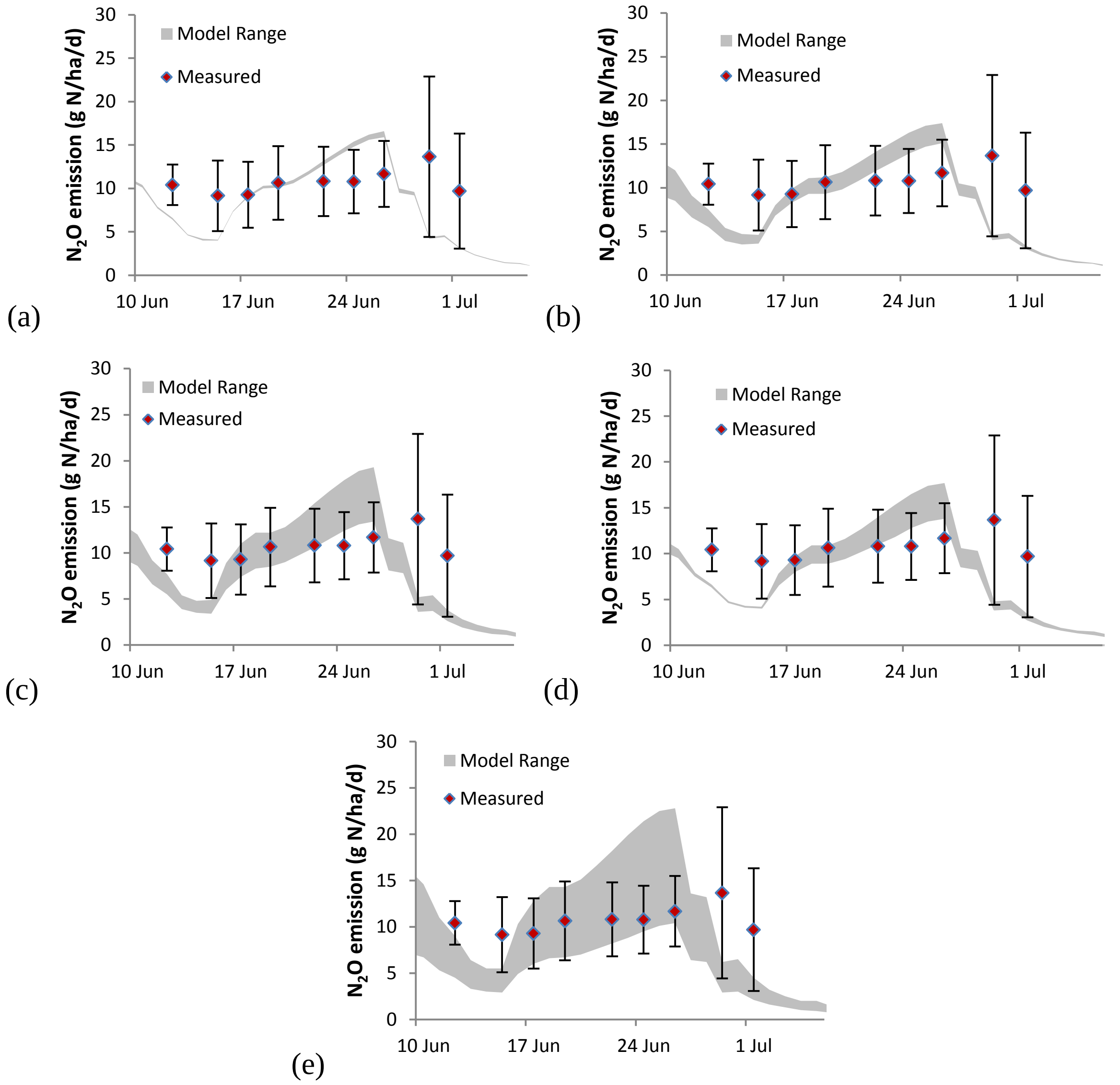


Figure 4: Range of modelled N_2O emissions for control plot compared with measured values as initial values of (a) soil NO_3^-, (b) soil NH_4^+, (c) SOC, and (d) bulk density used in model are individually varied according to Table 4. (e) Shows the effect of varying all four parameters simultaneously

The range in the modelled N_2O emissions for the combined effect of variability in the input parameters was noticeably larger than the range produced by varying any one parameter. Table 4 shows the sensitivity (defined as (% change in N_2O emission)/(% change in parameter)) of the total modelled N_2O emissions to each of the input parameters.

SOC and bulk density had sensitivities > 1, meaning that uncertainty in these parameters produces an even larger relative uncertainty in the modelled N_2O emissions. In contrast, soil NO_3^- and NH_4^+ parameters had sensitivities < 1, so the modelled N_2O emissions are relatively insensitive to uncertainties in these parameters.

The combined effect of the uncertainty in all 4 parameters produced a 55% uncertainty in the total N_2O emissions modelled. While this is quite high, it is of a similar magnitude to the variability found in the field.

Table 4: Sensitivity of modelled 20-day N_2O emissions to changes in initial soil NO_3^-, NH_4^+, SOC, and bulk density

Parameter	**Nitrous oxide (% change)**	**Parameter (% change)**	**Sensitivity**
Soil NO_3^-	4	27	0.13
Soil NH_4^+	18	40	0.44
SOC	36	17	2.1
Bulk density	19	12	1.6
All parameters	55		
Measured uncertainty	40		

Discussion

In a grazed pasture N_2O emissions tend to be highly variable and positively skewed due to the uneven deposition of animal excreta creating emission “hot spots” around urine patches. As many statistical tests require normally distributed data, a common technique is to log-transform results (with the mean of the log-transformed data being equivalent to the geometric mean). However, in this study our aim was to estimate the total N_2O emissions from the field. In a grazed pasture high emitting hot spots are responsible for a large proportion of the total N_2O emissions. Measures such as the geometric mean and median, which lessen the influence of extreme values, will tend to underestimate the total field emissions. Therefore we have used untransformed data to calculate the arithmetic mean emission and standard error. Accordingly, it was not possible to apply many common statistical probabilities, which assume a normal distribution, to our data (e.g. t-statistics to calculate 95% confidence intervals).

The accuracy of chamber measurements depends on the distribution of urine patches among the chambers being representative of the distribution of urine patches across the field. We are unable to ascertain whether this was the case for our experiment. In the grazing-only trial there was one very highly emitting chamber that was most likely due to a urine patch. However, there was no correspondingly high emitting chamber in the grazing + DCD treatment. This could either be because the DCD reduced the emissions from the urine patch, or because the random sample did not include any urine patches. As we were unable to distinguish between these explanations, the possibility exists that the differences observed were an artefact of sampling error. However, the fact that the level of reduction measured agreed with that measured in a urine patch trial (50 ± 20%, Giltrap et al. 2010) and the NZ-DNDC simulation is encouraging.

Previous studies have attempted to empirically determine the number of chambers required to adequately sample a grazed pasture. The results from two intensive 6-week measurements using 20 small (Ø250 mm, 300 mm high, used in this study) and 6 large (1m × 0.5 m, 300 mm high) chambers reported in Saggar et al. (2008) showed no significant differences in gaseous emissions between two types of chambers but the spatial variability was higher from small chambers than large chambers. Subsequently, Saggar et al. (2010) performed another grazing experiment using 40 chambers in a 0.48 ha plot grazed by 205 cows.ha^{-1} for a total of 12 hours and found for that experiment, 20 chambers appeared to produce a representative emissions estimate.

The methodology for using chambers to estimate N_2O emissions at field scale is continuously undergoing refinement. A simple test for sampling errors in future experiments would be to conduct simultaneous emissions measurements from chambers on known urine patches for both treatments. If the N_2O emissions from the urine patch were substantially higher than any individual chamber in the corresponding plot this could indicate the sample did not include any urine patches. Another possible approach for future trials is a targeted placement, with a defined number of chambers representing urine patches and another group of chambers representing urine-free areas, combined with an attempt to estimate the area fraction in the plot covered by urine. Such an approach allows weighted upscaling of the chamber fluxes to a paddock flux estimate.

The mean daily N_2O emission rates obtained here are small, 11 ± 4.5 g N_2O-N/ha/d for grazing-only and 5.5 ± 1 g N_2O-N/ha/d for grazing + DCD. Harvey et al. (in prep) attempted simultaneously to measure these emission rates with a micrometeorological flux-gradient technique. They obtained a mean daily emission of 13 ± 30 g N_2O-N/ha/d for grazing-only and 12 ± 27 g N_2O-N/ha/d for grazing + DCD. The magnitude of the error shows that, in the present experiment, the flux-gradient method was unable to resolve a difference between the two plots; but that does not mean no difference existed.

This study looked only at the effects of DCD on N_2O emissions from a single grazing event, with the DCD applied the following day. However, DCD has a limited lifetime in soil as it is subject to microbial decay. For example Kim et al. (2011) studied the half-life of DCD in Tokomaru soil following applications in March, April and October and found the mean half-life varied from 7 to 12 days depending upon weather conditions. It is therefore unlikely that a single application of DCD would be effective at reducing emissions from subsequent grazings.

The NZ-DNDC is sensitive to variability in the soil input parameters and the uncertainty in input parameters leads to large errors in the modelled N_2O emissions. This uncertainty reflects an underlying spatial variability in the soil properties. Reducing the uncertainty in the model estimates may require characterising the soil properties in terms of a probability distribution function rather than using average values. A better knowledge of the underlying distribution of urine patches would also be useful both for modelling and for experimental design.

Conclusion

DCD applied to a grazing pasture appeared to reduce the N_2O emissions from a single grazing event by 50 ± 40% over a 20-day period. However, this result should be treated with caution, because the possibility of sampling error due to the chamber distribution cannot be excluded.

The effectiveness of DCD in reducing N_2O emissions over the longer term is a matter of ongoing research. NZ-DNDC simulated a reduction in N_2O emissions due to DCD of a similar magnitude (60%). This level of reduction is consistent with that found in experiments with individual urine patches.

The NZ-DNDC model was sensitive to uncertainty in the input parameters, particularly SOC and bulk density. The combined effect of typical uncertainty in soil NO_3^-, NH_4^+, SOC and bulk density was a 55% uncertainty in the cumulative N_2O emissions.

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