MODELLING NH_3 VOLATILISATION FROM A URINE PATCH AND UREA APPLICATION USING NZ-DNDC

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Abstract

Correct simulation of ammonia (NH_3) loss through volatilisation is important for process-based models of soil N cycling as this can have a significant effect on the soil mineral-N concentration and subsequent N-transformation processes. In addition, volatilised NH_3 represents a significant loss of N from pasture soils, and can act as a secondary source of nitrous oxide (N_2O) emissions when redeposited on soil.

In this study we use data from two field experiments on the same soil (Tokomaru silt loam) to test the process-based NZ-DNDC model. In the first experiment, cattle urine was applied at 530 kg N ha^{-1}, and NH_3 emissions, soil pH, and mineral-N were monitored over 30 days. In the second experiment, urea was applied at either 0 (control), 30 or 60kg N ha^{-1}. The urea was followed by either 5 mm, or 10 mm of irrigation applied after a delay of 8, 24, or 48 hours. NH_3 emissions and soil mineral N were collected for 2 weeks following urea application.

Both these data sets revealed processes within the NZ-DNDC model that need improving. For the urine application, the model over-estimated the increase in the soil pH (simulated maximum ~8.7 compared with observed 6.7) and of the NH_3 emissions. Modifying the model to use observed pH changes improved the simulated NH_3 loss. For the urea plus irrigation experiments, the model simulations showed a much lower effect of irrigation timing on NH_3 EF compared with the experiments. This is because NZ-DNDC does not simulate the physical transport of urea down the soil profile.

Our model results show that better representation of soil pH in NZ-DNDC is required to improve simulation of NH_3 emissions from urine patches and applied urea. This will involve explicit accounting for the different buffering capacities of soils. Additionally, a urea transport process needs to be added to simulate the potential mitigation of NH_3 emissions by irrigation. These improvements are the focus of future work.

Introduction

Ammonia (NH_3) volatilisation following urea or urine deposition can result in losses of ~5–66% of the applied-N (Sherlock et al. 2008). When this volatilised N is re-deposited it can act as a secondary source of nitrous oxide (N_2O) emissions. However, this lost N also represents a significant (but variable) reduction in the soil mineral-N available for subsequent leaching or nitrification/denitrification. Therefore, it is important for process-based models of soil N processes to correctly simulate NH_3 emissions in order to accurately simulate the downstream processes.

Giltrap et al. (2015) compared model simulations of soil mineral-N and N_2O emissions following urine patch application using two process-based models: NZ-DNDC and APSIM. Both models varied in their simulations of N_2O emissions. However, even when both models simulated N_2O emissions well there were large differences in the simulated NH_3 emissions. Unfortunately for these experiments NH_3 data were not available, so it was not possible to tell which model simulated NH_3 emissions more accurately.

In this study we compared the NZ-DNDC model with NH_3 emissions from two field experiments conducted in the Manawatu region. In the first experiment dairy cattle urine was applied at 530 kg N ha^{-1}, and NH_3, pH, and soil NH_4^+ and NO_3^- were measured. The second experiment aimed to look at the effectiveness of irrigation following fertiliser application as a means of reducing NH_3 emissions. In this experiment urea fertiliser was applied at 0, 30 and 60 kg N ha^{-1} followed by either 5 mm or 10 mm irrigation applied 8, 24, or 48 hours after urea application.

Methodology

Urine application experiment

Experiment design

The experiment was conducted in April 2013 on a commercially managed dairy farm at Massey University that had been fenced off for a year before the start of the experiment. The soil was a Tokomaru silt loam (Table 1) and rainfall and temperature data were collected from a weather station located on site. The experiment is described in full in Rodriguez (2014).

Table 1. Physical and chemical properties of the soil at the experimental site

Soil properties	Data
Soil pH	6.1*
Bulk Density (g cm^{-3})	1.2
Total C (mg kg^{-1} soil)	34
Total N (mg kg^{-1} soil)	2.7
NH_4^+-N (mg kg^{-1} soil)	73
NO_3^--N (mg kg^{-1} soil)	4.4

*Values are mean (*n* = 4).

The experiment was divided into 0.5 m × 0.5 m plots (separated by a 0.5-m buffer), each receiving a particular treatment. Soil samples were taken and ammonia was sampled from the acid trap for each plot. In this study we will consider only the urine treatment.

Urine was collected from Friesian cows during milking. After collection, the urine was transferred to 20-L containers, and stored below 4°C to avoid urea hydrolysis before field application. The urine application rate was 530 kg N ha^{-1}. Urine was applied to the chambers and soil plots with a watering can. The pasture was mowed before the urine application to simulate grazing.

The treatment was replicated 6 times and the plots were sampled nine times following urine application, on days 1, 3, 5, 9, 12, 15, 18, 21 and 30. At each sampling, three soil cores of 25-mm diameter and 100-mm depth were taken from each plot and bulked to produce one sample. Before soil analysis, soil samples were sieved (2 mm) to remove plant roots. A sub-

sample of 5 g of field moist soil was extracted with 50 mL of 2 M potassium chloride (KCl) solution by shaking for 1 h. The extract was analysed for nitrate (NO_3^-) and ammonium (NH_4^+) concentrations colorimetrically using Technicon AutoAnalyzer (Blakemore, 1987).
Soil pH was measured at a 1:2.5, soil: water ratio using a pH meter (pHM83, Autocal pH meter; Blakemore 1987).

As chambers and soil plots were covered during the first week to avoid any rainfall events, rainfall did not influence NH_3 losses during the first week.

Ammonia emission measurement
Ammonia volatilisation in this experiment was measured using the dynamic chamber method (Kissel et al. 1977), comprising a volatilisation chamber, an acid trap to capture the ammonia, and a manifold consisting of 6 air valves to regulate the flow rate inside the chambers. PVC chambers (0.15 m diameter × 0.04 m total height) with a transparent top (to allow photosynthesis) were inserted into the soil to a depth of 0.01 m that gave a headspace volume of 0.5 m^3. The chamber had a vent on the chamber′s vertical surface that was connected to an acid trap (250 mL, 0.025 M H_2SO_4) using a tube connected to the manifold through to a vacuum cleaner. Air from the chambers was sucked at a constant flow rate (at 6 L min^{-1}, monitored daily) and was passed through the acid trap. Sub-samples of the H_2SO_4 solution in the acid traps were analysed for NH_4^+-N concentrations and were performed as described below. Samples were taken every day for the first 12 days and then on days 15, 18, 21, 24, 27, and 30.

Urea plus irrigation experiment

Experiment design
This field experiment was set up in the same site as the urine application experiment described above. Two separate trials with the same treatments were laid out in December 2012 and January 2013 in a randomised block design with all treatments each replicated two times. Urea was applied at either 0 (control), 30 or 60 kg N ha^{-1}. The urea was followed by either 5 mm, or 10 mm of irrigation applied after a delay of 8, 24, or 48 hours. The soil plots were adjacent to the gas trapping chambers and were sampled nine times following N application, from 8 hours to 14 days. Ammonia losses were measured as described in the first experiment. Further details of this experiment are given in Zaman et al. 2013.

NZ-DNDC simulations

The DNDC (DeNitrification Decomposition) model is a process-based model developed to simulate greenhouse gas fluxes from agricultural soils (Li et al. 1992). Since its original development it has been adapted, expanded, and applied to a wide range of systems around the world (Giltrap et al. 2010a). NZ-DNDC is the New Zealand specific version that has been adapted to perennial grazed pasture systems (Saggar et al. 2004, 2007). NZ-DNDC was adapted from DNDC version 8.6K.

NZ-DNDC consists of a number of interacting sub-models that control the soil thermal-hydraulic flows, plant growth, and microbial processes such as decomposition, nitrification and denitrification. The sol is modelled as a number of thin layers with soil properties assumed to be homogeneous within a layer. Figure 1 shows the processes leading to NH_3 volatilization as modelled by NZ-DNDC.

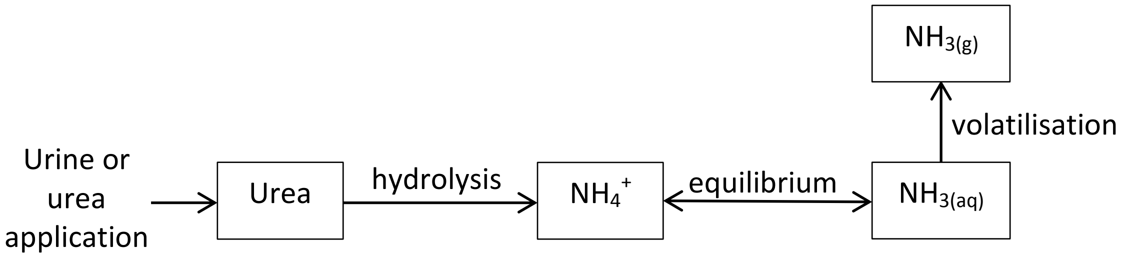

Figure 1. NZ-DNDC representation of NH_3 volatilisation.

The urea hydrolysis occurs rapidly and results in an increase in pH proportional to the amount of urea hydrolysed. The amounts NH_4^+ and $NH_{3(aq)}$ are then adjusted to their equilibrium values (with high pH favouring more $NH_{3(aq)}$). The volatilisation rate is then proportional to the soil temperature, the air-filled pore space and the amount of $NH_{3(aq)}$ (but decreases with depth in soil). The original DNDC model used a semi-empirical formula for NH_3 volatilisation that had been formulated for typical fertiliser application rates (~20–50 kgN/ha) rather than the extreme N concentrations in a urine patch (up to 1000 kg N/ha). Giltrap et al. (2010b) found that when modelling N_2O emissions from a urine patch it was necessary to increase the base volatilisation rate by a factor of 50 to get a good fit between observed and modelled N_2O. We also used this higher volatilisation rate in these simulations.

After urea hydrolysis the soil pH may change as a result of the reaction $NH_4^+ \leftrightarrow NH_{3(aq)} + H^+$ or by dilution due to rainfall.

Table 2 shows the parameters used in the NZ-DNDC model to describe the Tokomaru soil.

Table 2: Soil parameters used in NZ-DNDC simulations

Soil parameter	Value
Bulk Density (g cm^{-3})	1.2
Clay fraction	23%
SOC	3.4%
Soil pH	6.1
WFPS at field capacity*	62%
WFPS at wilting point*	28%

*Adjusted to produce good fit with the measured WFPS for the control treatment in the urine application experiment.

For initial soil WFPS and NH_4^+ and NO_3^- concentrations, the values for each experiment were based on the initial values measured in the control treatments.

For the urea plus irrigation experiment it was not possible to model an 8-hour delay between urea application and irrigation as NZ-DNDC applies all applications at the start of the day of application. Therefore for these treatments the model used a 0-hour delay.

Results and Discussion

Urine application

The total NH_3 measured from the urine patch over the 30-days following application was 80 ± 3 kg $N.ha^{-1}$. In NZ-DNDC the pH remained much higher than was measured resulting in an estimate of NH_3 emissions during this time period of 231 kg $N.ha^{-1}$ (Fig. 2). The model was then modified by setting the pH to the measured value on each day for which the pH was measured. This reduced the modelled NH_3 emissions to 94 kg $N.ha^{-1}$. The NZ-DNDC model therefore needs to be improved so that it correctly simulates soil pH changes following urine addition over a range of soils with different buffering capacity.

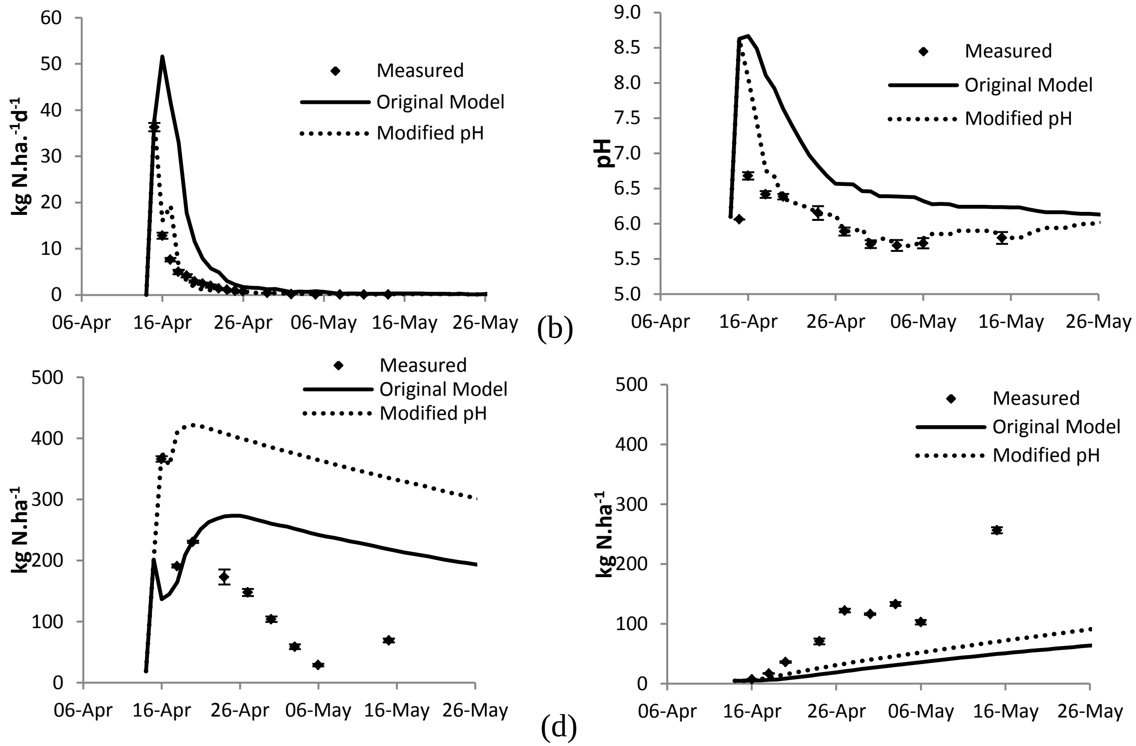

Figure 2: Measured and modelled (a) NH_3 emissions, (b) pH, (c) soil NH_4^+ (0–10 cm), and (d) soil NO_3^- (0–10 cm) following the application of 530 kg $N.ha^{-1}$ urine. “Modified pH” model refers to the model run with the pH set to the measured values.

Figure 2(c)–(d) show that even with the pH correctly simulated the modelled soil NH_4^+ and NO_3^- concentrations are not quite correct. This indicates that there may be a problem with some other process (e.g. nitrification) which should also be investigated.

Urea plus irrigation

Figure 3 (a)–(d) shows the measured and modelled cumulative NH_3 emissions for the 14 days following a urea application. The measured emissions showed an increase with increasing N application rates, but application of 5–10 mm of irrigation 8 hours after fertiliser application reduced the emissions by 30–70% compared to when the irrigation was delayed by 24–48 hours.

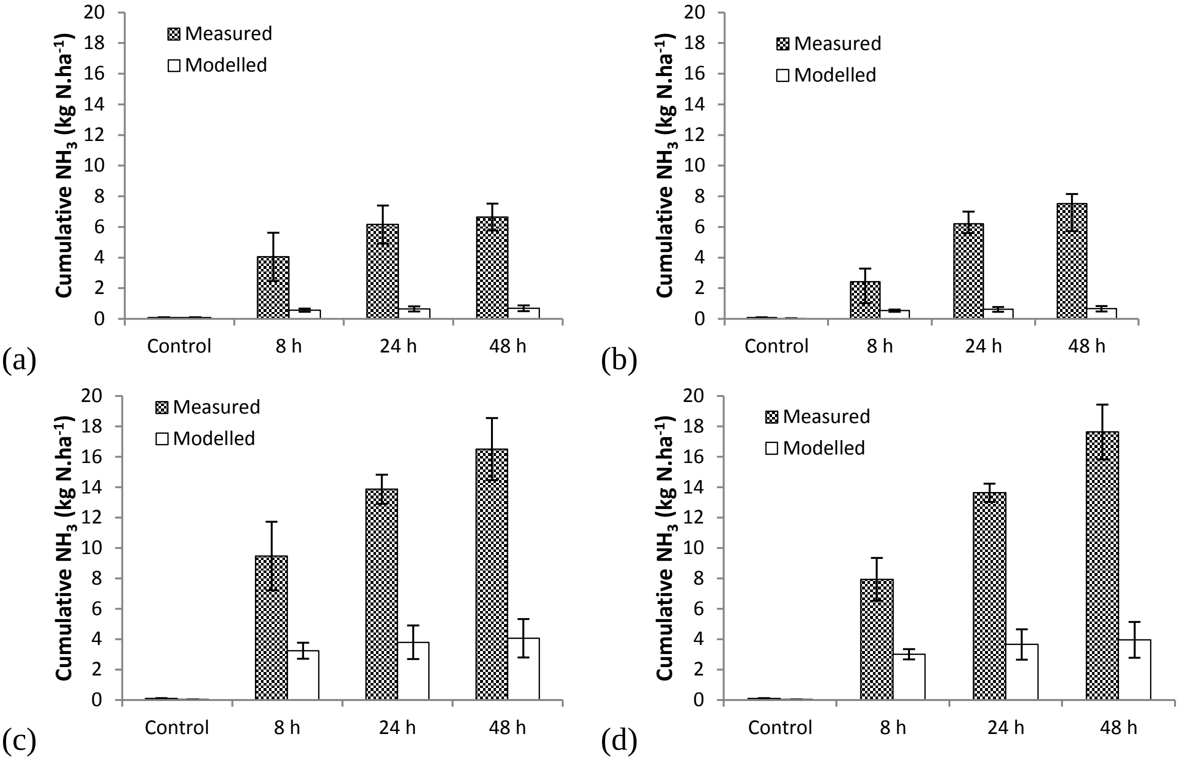

Figure 3: Measured and modelled cumulative NH_3 emissions for the 14 days after urea application followed by irrigation (irrigation was delayed by 8, 24, or 48 hours). (a) urea applied at 30 kg N.ha^{-1} and 5 mm irrigation; (b) 30 kg N.ha^{-1} urea and 10 mm irrigation; (c) 60 kg N.ha^{-1} urea and 5 mm irrigation; (d) 60 kg N.ha^{-1} urea and 10 mm irrigation. Note that the model could not simulate an 8 hour delay between fertiliser application and irrigation, so in this case the modelled delay was actually 0 hours.

The modelled emissions were lower than the measured emissions, although the model still predicted increased emissions with increased urea application. Unfortunately pH measurements were not made during this experiment, so it is not possible to tell whether the model under-prediction of NH_3 emissions was due to incorrect simulation of pH or some other problem.

NZ-DNDC did not simulate the decrease in NH_3 emissions when the urea application was followed by irrigation within 8 hours. This is because NZ-DNDC does not currently simulate the transport of urea down the soil profile with irrigation. More recent versions of DNDC do include urea leaching and this process needs to be incorporated into NZ-DNDC if mitigation of NH_3 emissions by irrigation following urea application is to be simulated.

Conclusions

These modelling exercises have illustrated areas where the NZ-DNDC model needs to be improved to better simulate NH_3 emissions. The first area for improvement is the simulation of the soil pH following urine or urea application allowing for the different buffering capacities of different soils. The second improvement is the inclusion of a urea leaching process which should be relatively straight forward. These improvements are the focus of future work.

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