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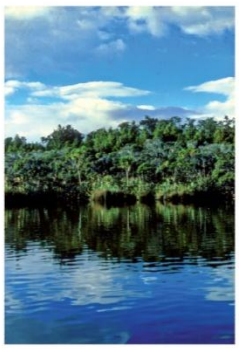

Ammonia from Animal Excreta

Final Report

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Contents

Summary

Project

- Two field experiments were carried out to determine ammonia (NH_3) emission rates from cattle excreta, in the first from a regular pattern of realistically-sized urine patches, in the second from a real distribution of urine and dung as excreted by 12 cattle over 3 days.
- The key deliverable was to provide new data for validating the country-specific value of 0.1 for the emissions factor $Frac_{GASM}$, which was recently adopted by NZ.

Objectives

- The first experiment had three specific objectives. The first was to compare three micro-meteorological methods to establish their suitability and accuracy for determining emission rates from treated circular plots.
- The second objective was to obtain an accurate estimate of the amount of NH_3 volatilised from a known amount of nitrogen (N), deposited with a known amount of urine, at the paddock scale in undisturbed atmospheric flow conditions.
- The third objective was to formulate and test a simple yet physically realistic process model to predict the emission rates from urine-treated soil. If successful, such a model would provide an alternative means for estimating NH_3 emission rates, based on collection of soil samples.
- The second experiment aimed to obtain a good estimate of the amount of NH_3 volatilised from cattle excreta in-situ in a realistic farming situation. The amount of N deposited with the excreta was estimated from the feed intake of the animals.

Methods

- In both experiments, the excreta were deposited inside a circle of 16 m radius, on a previously mown paddock surface. Horizontal fluxes of NH_3 were sampled quasi-continuously at five heights in the centre of the treated circle.
- In the first experiment, three micrometeorological methods were used to derive the NH_3 emission rate from these horizontal fluxes: the mass-budget (MB) method, the backward-Lagrangian stochastic (BLS) method, and the ZINST (height, *z*, *in*dependent of *st*ability) method. In the second experiment, the MB method only was used, as the most accurate.
- In the first experiment, soil temperature was measured at 20 mm depth, and samples were taken from the upper 5 mm of soil within selected urine patches, a few times daily, to measure pH, ammoniacal-N (NH_x-N) and moisture contents in the topsoil, providing input parameters for a volatilisation model. The model describes a chain of three processes: the phase equilibrium between aqueous NH_x in the soil solution and gaseous NH_3 at the liquid-air interface (within the soil pores), the diffusion of gaseous NH_3 in the soil layer, and the diffusion of gaseous NH_3 in the atmospheric surface layer between ground and sampling height.
- In the second experiment, the excreta were created by 12 non-lactating cattle, which were kept inside the circle and fed with known amounts of fresh grass ("cut and carry"). Grass samples were analysed for N content and digestibility. A few urine patches and dung pats were created outside the circle, for measurements of the pH of urine surface, dung surface

and dung interior, and for sampling of NH_x-N and moisture contents of the dung. Soil temperature and soil moisture inside and outside the urine patches were measured continuously.

Results

- In the first experiment, 25.7 (±0.5) % of the applied urine-N volatilised as NH_3 over the first 6 days. After that, the pH had dropped below 7, implying that NH_3 emissions were probably insignificant. Mean soil temperature was 18 °C.
- The ZINST method provided emission rate estimates that did not differ systematically from the MB method, with 50 % larger random error. The BLS method underestimated the emission rate systematically, not because the method is flawed but because the specific implementation that was used is optimised for time-averaged atmospheric gas concentrations as inputs, not time-accumulated horizontal gas fluxes as provided here.
- The volatilisation model was found, in diagnostic mode, to provide physically realistic magnitudes of NH_3 source depth. However, in order to use it for accurately predicting NH_3 emission rates, the vertical distribution of NH_x-N within the urine patches must be well-characterised by soil sample analyses.
- In the second experiment, 19.8 % of the excreted N volatilised as NH_3 over the first 8 days (the 3 days with cattle presence and the 5 following days). This amount is interpreted as a good approximation of the total N volatilised from urine only. From Days 9 to 13, another 2.6 % of the excreted N volatilised, interpreted as the emissions from dung. This interpretation is based on the observed temporal evolution of pH in urine and dung, respectively. Mean soil temperature was 18 °C, as in the first experiment.

Conclusions

- Expressed as fractions of deposited N, the N losses were 25.7 (±0.5) % from the urine-patch pattern, and 22.4 (±1.3) % from the cattle excreta created in-situ.
- As both experiments were conducted at the warmest time of the year, the emission rates were at the upper end of the range that can occur in NZ. Taking the positive correlation between temperature and volatilisation rate into account, the observed emission rates are compatible with an annually-averaged emissions factor $Frac_{GASM}$ of 10 %, for urine-N and dung-N combined.
- Of the three micrometeorological methods, the MB method has the best precision. In combination with the horizontal-flux samplers used here, the ZINST method is the best-suited method for comparative studies of different treatments.

Recommendations

- It is appropriate for NZ to keep using the currently adopted value of 0.1 for $Frac_{GASM}$.
- It should be considered to introduce separate emission factors for urine-N and dung-N, provided the same is done for the direct nitrous oxide emissions from animal excreta.
- Further research into the role of soil moisture in the volatilisation process is required.

1 Introduction

Urine and dung from farm animals cause emissions of both nitrous oxide (N_2O) and ammonia (NH_3). The latter appear indirectly in the inventory of N_2O emissions by assuming that the volatilised NH_3 is re-deposited and a fraction of it converted into N_2O. In New Zealand's greenhouse gas inventory, reported under the United Nations Framework Convention on Climate Change (UNFCCC), both the fraction of deposited nitrogen that is volatilised as NH_3 and the fraction that is converted into N_2O after re-deposition are accounted for by constant emission factors, even though both are subject to variation with soil and weather conditions.

This project is concerned with the factor "$Frac_{GASM}$" that quantifies the amount of nitrogen (N) volatilised as NH_3. New Zealand (NZ) used to use a default value, defined by the Intergovernmental Panel on Climate Change (IPCC), of $Frac_{GASM}$ = 0.2, until a review by Sherlock et al. (2008) of available experimental data relevant for NZ's farming conditions suggested that a value of 0.1 instead was likely to be more accurate, upon which the inventory estimate was adjusted accordingly. The net result of this adjustment is a reduction of the reported total N_2O emissions from agriculture of order 5 %.

The research undertaken in this project has collected new experimental data to determine $Frac_{GASM}$ in controlled but realistic farming situations. Given the considerable experimental effort required, this had to be restricted to two well-designed field experiments. The new data add to those collated in the Sherlock et al. (2008) review, and perhaps more importantly, they are supplemented by measurements of the pH, ammonium (NH_4^+) concentration, temperature and moisture of the soil in order to interpret the obtained emission rates in the context of the chemistry and physics of the volatilisation process.

The first experiment and its results were described in detail in a progress report to MAF (Laubach et al. 2010) and have since been further analysed in a recently submitted manuscript (Laubach et al. 2011). In that experiment, animal urine was collected and applied to a paddock surface in a controlled pattern. The reasons for this approach were that urine contributes a much larger fraction than dung to the total NH_3 emissions (Ryden et al. 1987, Jarvis et al. 1989, Sherlock et al. 2008), and that the total amount of N deposited on the ground could then be accurately known. This campaign aimed to, firstly, establish suitability and accuracy of two micrometeorological methods (ZINST and BLS, see below) versus the mass-budget method as a reference, and, secondly, determine NH_3 emission rates from a controlled urine patch distribution that closely represented real patch distributions from grazing cattle. A summary of the results is given in Section 5.1.

The second field experiment was conducted one year after the first, in weather conditions comparable to those during the first experiment. NH_3 emissions from the excreta of a group of 12 cattle were measured in situ, representing the combined effect of emissions from urine and dung. This experiment is reported here for the first time, with the results presented in Section 5.2.

2 Background

The central question of this research is what fraction of the total N, contained in animal excreta that are deposited on a paddock surface, is volatilised as NH_3. Experimentally-determined values for this fraction can then be compared to the emissions factor, $Frac_{GASM}$, used in the national greenhouse gas inventory to determine the indirect N_2O emissions from agricultural soils. As mentioned above, NZ recently lowered its $Frac_{GASM}$ to 0.1, following the recommendation of Sherlock et al. (2008). The majority of experiments reviewed by Sherlock et al. (2008) used chambers or wind tunnels placed above small plots treated with animal excreta. Such setups alter the microclimate of these plots and it is thus not guaranteed that the measured NH_3 emissions represent real-world paddock emissions. This potential lack of representativeness is avoided by "micrometeorological" methods. Such methods measure, at one or more points downwind of the emission source, the vertical profiles of wind speed and NH_3 concentration, to then allow calculation of the emission rate using the theory of turbulent transport in the atmospheric surface layer. These methods can easily be run continuously from the time of excreta deposition to the time the NH_3 emission rate has dropped to a negligible value. Thereby, they measure the complete integral of NH_3 emissions caused by the original excreta deposition.

Still, such measurements require considerable effort and can only be performed in a few locations and for limited time periods. When comparing measured NH_3 emission fractions to $Frac_{GASM}$, it needs to be taken into account that such a single emissions factor is supposed to be a representative mean for a range of soil and climate conditions, but an experiment at a single site for a single period of excreta application cannot represent such a range of conditions. It would thus be highly desirable to have a model of the volatilisation process that allowed the prediction of NH_3 emission rate from a few accessible parameters, such as soil temperature, soil pH and ammoniacal-N concentration (NH_3 and NH_4^+ combined) in the soil surface layer. These were identified by Sherlock and Goh (1985) as the key variables

required to successfully model NH_3 emissions for a given site. This modelling approach is based on the chemical processes in the soil surface layer, using parameters measurable in soil samples.

A point of considerable uncertainty is if and how the distribution pattern of the excreta influences the net emission rate from a given plot. Such an influence can be imagined because a urine patch creates an extremely high, localised N concentration in the topsoil and a steep concentration gradient towards the surrounding soil, both vertically and horizontally. The net emissions from a pattern consisting of very high and very low N application rates may differ from those observed either using small chambers to measure the NH_3 emission rate directly over a patch (Sherlock & Goh 1984), or from a plot where urine was homogeneously spread (Sherlock et al. 1995).

Sherlock et al. (1995) had observed NH_3 volatilisation rates in two experiments with similar circular setups on short vegetation and using the same method as in the experiments reported here, however they had used homogeneous N source distributions, with evenly-spread urea granules in one experiment and evenly-spread artificial urine in the other. They then applied the "bulk-aerodynamic" model of Leuning et al. (1984), which relates the observed NH_3 emission rates via linear regression to the product of wind speed and NH_3 equilibrium in solution. This appeared reasonably successful, as they found regression slopes of similar magnitude in both experiments, and squared correlation coefficients (R^2) of 0.76 and 0.77, respectively. However, conceptually the regression slope is the inverse of an aerodynamic resistance (hence the name of this model), and the magnitude of the resistance observed by Sherlock et al. (1995) was two magnitudes larger than physically plausible. It is thus clear that a more correct resistance model would need to account for the resistance to NH_3 transport in the soil layer. Such a model has been formulated by Laubach et al. (2011) and is tested with the data of the first experiment.

3 Objectives

Four specific objectives were addressed in the two experiments, as follows:

1) To establish suitability and accuracy of two micrometeorological methods (ZINST and BLS, see below) versus the mass-budget (MB) method as a reference. The reason for applying these two additional methods is that they require fewer NH_3 samplers

than the MB method. This means not only that future experiments can deliver more emission estimates from fewer samples; crucially, it offers the option of duplicating treatment plots, which means that two types of treatments can be compared side-by-side with identical meteorological conditions.

2) In the first experiment, to determine NH_3 emission rates from a controlled urine patch distribution of a density similar to real patch distributions from grazing cattle. Since with this approach the amount of applied N is accurately known, it allows to obtain an accurate estimate of the N fraction volatilised from urine.

3) In the second experiment, to measure NH_3 emissions from cattle excreta created in situ. This advances the approach from the first experiment by including both urine and dung emissions, and by representing real excreta distributions, not simulated ones. The disadvantage is that the N content of the excreta needs to be estimated indirectly, from knowledge of animal physiology combined with estimates of the animals' feed intake and analysis of feed samples for protein contents. The obtained N emissions fraction is thus expected to be less accurate than in the first experiment.

4) To formulate a process model to predict the emission rates that is still simple yet physically more realistic than the empirical "bulk-aerodynamic" approach of Sherlock et al. (1995). If successful, such a model would provide an alternative means for estimating NH_3 emission rates, based on collection of soil samples.

4 Methods

The methods to measure NH_3 emission rates are adaptations of micrometeorological techniques that have been applied successfully by the authors (e.g. Laubach et al. 2008, Sherlock et al. 2002) and many other workers to a range of dispersion problems, including the determination of greenhouse gas emission rates. The primary method is based on the physical principle of conservation of mass. Two other methods, based on micro-meteorological theory, are compared against the mass-budget (MB) method as the reference. The micrometeorological approach was chosen so that the measurements could be made on real paddock surfaces, in real weather conditions (unaffected by chamber or tunnel setups), and in the second field campaign while real animals were present, without intruding into their natural behaviour.

4.1 Measurements of NH_3 profile, wind and turbulence

In both experiments, a vertical NH_3 profile was measured in the centre of a circular plot treated with animal excreta, and background NH_3 concentration was measured upwind of this plot (Fig. 1). A vertical wind speed profile, wind direction and turbulence parameters were measured in parallel. From these data, the NH_3 emission rates were derived as described in 4.2. Supporting measurements required to interpret these emission rates are detailed in the following subsections.

4.1.1 Ammonia collection

Vertical profiles of NH_3 were measured with "Leuning samplers" (Leuning et al. 1985), which are collection devices that point into the wind and completely remove the NH_3 contents from the airstream that enters the device at the front and leaves it through an orifice at the rear. Sampling heights for the profile, in the centre of the marked 15 m circle (Fig. 1), were 0.25, 0.50, 0.75, 1.25 and 2.10 m above ground. Four masts were set up at 50 (±5) m distance from the circle's centre to the NW, NE, SE and SW. Dependent on wind direction forecast, for any given collection period one of these masts was anticipated to be upwind of the circular plot, and an additional NH_3 sampler was mounted at 2.1 m height on this mast to determine the upwind background concentration.

Each NH_3 sampler contains an elaborate array of surfaces, coated with a thin film of solid oxalic acid. As the airstream impacts on these coated surfaces, the NH_3 molecules react with the oxalic acid, forming $(NH_4)_2C_2O_4$ (ammonium oxalate) crystals. At the end of the collection period, these, together with any excess oxalic acid, must be washed off the surfaces and analysed for NH_4^+ concentration. The mass of collected NH_4^+ is proportional to the horizontal flux of NH_3 at the sampling location, integrated over the collection period. At the end of a collection period, the samplers were replaced by identical ones and transported to the lab where they were subjected to extraction of the previously collected NH_4^+ and prepared for another collection period. With two sets of 6 samplers available, sampling was near-continuous (the 5 samplers at the profile mast were opened or closed for collection within less than 1 min from each other, and total changeover times including the background mast sampler were less than 5 min).

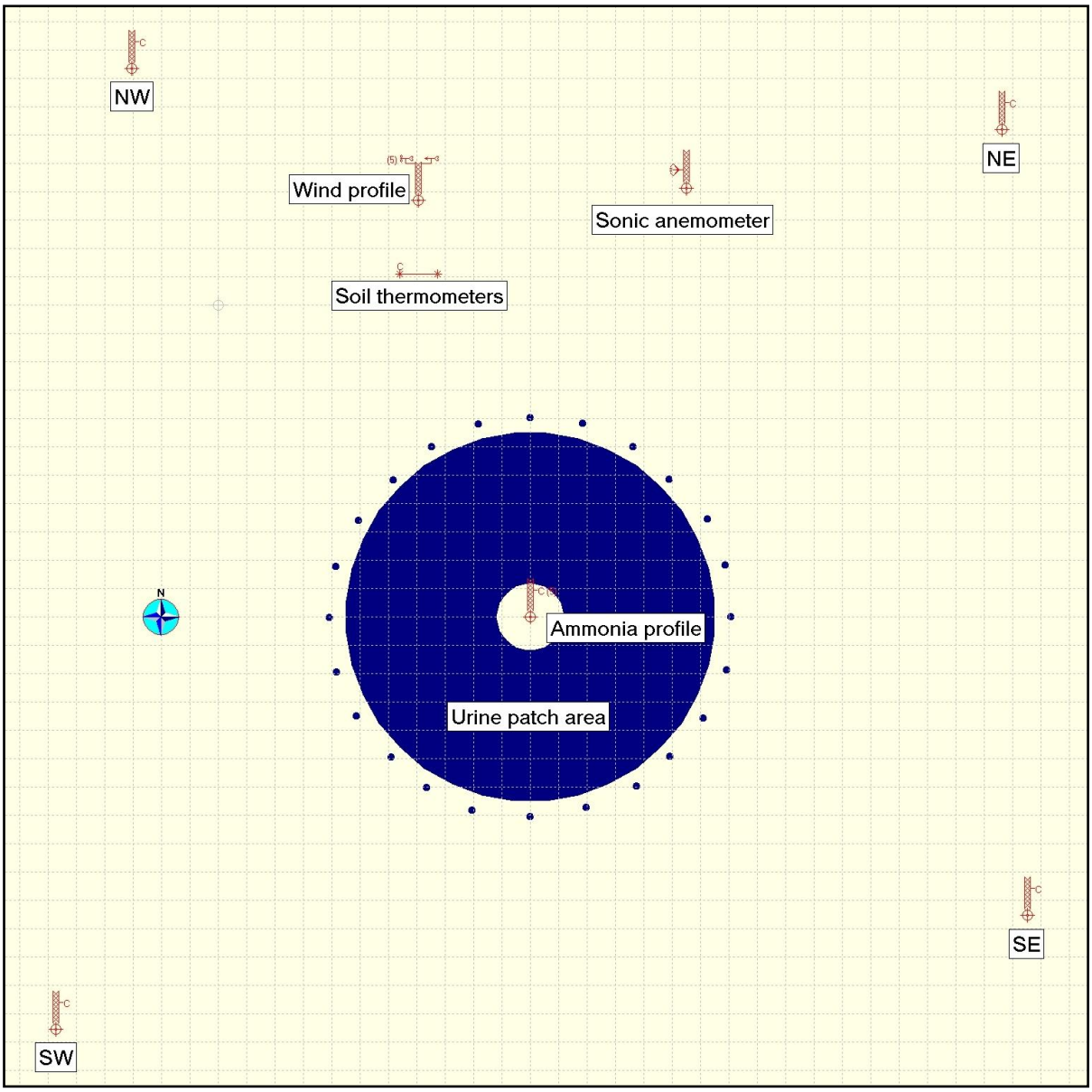

Fig. 1 Scale diagram of the experimental setup. In the first experiment, 132 urine patches were created within the dark area, one at each grid point (grid cell size is 2.3 m by 2.3 m). From 24 extra urine patches (dots surrounding the dark area), soil samples were repeatedly taken for measurements of pH, soil moisture, and mineral-N. Atmospheric samples of NH_3 were collected at five heights in the centre of the circular area, and at one of the four locations labelled NW, NE, SE, and SW (the one closest to the anticipated upwind direction). In the second experiment, no grid pattern of urine patches was created. Instead, 12 cattle were held within the dark area for 3 days and fed twice daily with freshly-cut grass from a nearby paddock. The urine patches and dung pats created by the cattle provided the NH_3 sources.

4.1.2 Wind and turbulence measurements

Wind speed was measured by five cup anemometers (A101M, Vector Instruments, Rhyl, Clwyd, UK) with matched calibrations. They were installed at the same five heights as the NH_3 samplers, on a separate mast away from the circle (Fig. 1), in order to not disturb the rotational symmetry of the plot. Wind speed data were recorded by a datalogger (Campbell Scientific, Logan, Utah). An ultrasonic anemometer (81000V, RM Young, Traverse City, Michigan) was mounted on a separate mast, also outside the circle. It sampled the fast fluctuations of the wind vector and temperature at a frequency of 20 Hz. These data were transmitted via a serial port to a laptop computer for storage and processing. The parameters derived from the raw wind and temperature data are wind direction, velocity standard deviations, friction velocity (u_*) and the temperature flux required to compute the stability parameter (Obukhov length, L).

4.2 Methods to calculate NH3 emission rates

4.2.1 Mass-budget (MB) method

There are a few different micrometeorological methods that allow calculation of emission rates from measurements of downwind concentration profiles. The primary method here is the mass-budget method (Beauchamp et al. 1978, Denmead 1995). Consider a volume of air from ground level to a height high enough that background concentration of NH_3 is reached. It is assumed that all the NH_3 gas emitted from sources within the volume leaves it via the downwind side, carried by the wind. The emission rate is obtained by vertically integrating the product of horizontal wind speed and concentration (the horizontal flux) and dividing by the along-wind extension of the source area. The mass-budget method is well-suited for plot sizes of a few tens of metres (Denmead 2008), it makes optimum use of the Leuning samplers' ability to measure the horizontal flux directly, and does not require any corrections except for profile extrapolation beyond the top height if the concentration there is significantly larger than background (Laubach and Kelliher 2004). It has been successfully applied to NH_3 emissions from treated plots before (Sherlock et al. 1995, 2002). Therefore, it is used here as the reference method. Its disadvantage is that it requires all available NH_3 samplers in order to resolve the shape of the horizontal flux profile. Two methods that require fewer NH_3 samplers are the ZINST method (Wilson et al. 1982) and the backward-Lagrangian simulation (BLS) method (Flesch et al. 1995), see the following subsections.

4.2.2 ZINST method

The ZINST method is based on the theoretical finding that, for a given plot size and surface roughness, and with a constant emission rate of the gas of interest, there exists a particular height at which the horizontal flux of this gas is nearly independent of atmospheric stability (Wilson et al. 1982). In other words, the ratio of the horizontal flux at this height to the emission rate is constant. (The name ZINST was chosen to label the height (z) where independence of stability is obtained.) Once this constant ratio is determined experimentally, e.g. by comparison to the MB method, only one downwind measurement of the horizontal gas flux, at ZINST, is required to calculate the emission rate. Here, a slight modification was used, employing two samplers above and below ZINST and interpolating between them. This avoids the need to know ZINST prior to the experiment (which depends on roughness length, to be determined from the vertical wind profile), and reduces sampling error.

4.2.3 BLS method

The backward-Lagrangian simulation (BLS) method models the random nature of the turbulent airflow, given a set of statistical parameters of the turbulence (as measured by an ultrasonic anemometer or derived from a vertical wind profile). The model simulates the flight paths of many thousands of individual air parcels backward in time from a given observation point (here: the location of an NH_3 sampler) and records for each parcel where it was last in contact with the ground ("touchdown"). That way, a map of the touchdown distribution is obtained. Knowing the coordinates of the source area for gas emissions, the model computes which fraction of all simulated touchdowns occurred within the source area and uses this information to infer the gas emission rate from the concentration at the observation point (Flesch et al. 1995). Here, a freely available software implementation of the BLS model was used, named WindTrax (Thunder Beach Scientific, Nanaimo, BC, Canada) and described comprehensively by Flesch et al. (2004). Like the ZINST method, the BLS method requires only one concentration measurement downwind of the source. Advantages over the ZINST method are that the measurement height is not critical, as long as it is well within the gas plume, and that addition of further measurement heights will help to constrain the uncertainty of the computed emission rates.

4.3 Experiment 1: A grid pattern of urine patches as NH_3 sources

4.3.1 Urine application and patch pattern

This experiment began on 24 February 2010. Two days prior to the experiment, 230 litres (L) of cattle urine had been collected at the Lincoln University Dairy Farm and refrigerated. The N content of the urine, determined on duplicate subsamples using a C-N analyser, was 5.07 g L^{-1}. Water was added to obtain the required amount of 240 L, and then the N contents boosted to 10.0 g L^{-1} by addition of urea.

Within the circular plot, a rectangular grid of 132 points was marked as the locations for urine patches (Fig. 1). The distance between adjacent patches was 2.3 m. The central grid point (location of the NH_3 mast) and the four grid points nearest to it were omitted, to provide an access area where an operator could change the NH_3 samplers without disturbing any urine-treated soil. This effectively defined an inner radius for the urine patch area (Fig. 1). In addition, at 1 m distance outside the perimeter of the 15 m circle, 24 further urine patch locations were marked, at equal distances of 4.2 m from each other, for the purpose of repeated soil sampling during the experiment. This soil sampling inevitably constituted a potential disturbance to the NH_3 emissions process. While the 24 disturbed urine patches are accounted for as sources in the computation of the emission rates, their placement at the perimeter of the circle ensured that they provided only a minor fraction of the NH_3 collected at the circle's centre. The major fraction originated from the 132 patches within the 15 m radius. One additional urine patch was created at 20 m distance from the circle's centre, still within the irrigated area, for the purpose of taking horizontal transects of soil samples across a urine patch. This single patch is not accounted for in the emission rate computations, but the error from this is considered negligible.

Plot area, urine patch number and N content were all designed to provide a realistic simulation of the urine load created by about a dozen dairy cattle grazing an area of this size for about 24 h. This grazing time and stocking density are typical for rotational grazing practices on dairy farms in New Zealand.

4.3.2 Measurement schedule

Collection of NH_3 profiles began immediately after the urine application. The collection period must be long enough to collect measurable amounts, but short enough to provide meaningful time resolution. Daytime collection periods were 2 h long on the first 2 days and increased to 3 h and then 4 h on later days. Overnight, the samplers were left unchanged for

14 to 16 h. The long night-time collection periods provided increased analytical accuracy of the collected amounts of NH_3, but at the cost of, firstly, an increased risk of contamination of the background sampler when wind direction changed during the night, and secondly, poor resolution of the temporal evolution of the emission rates.

4.3.3 Ammonia electrode measurements

After collection, the oxalic acid and ammonium oxalate crystals were extracted from the NH_3 sampler with deionised water in a standardised fashion. The ammonium (NH_4^+) concentration in the extract solution was measured with an ion-specific electrode (ISE-10-10-00, HNU Systems, Newton, Massachusetts), after addition of 10 M NaOH to convert NH_4^+ ions to un-ionised NH_3 which could then be detected by the electrode to give a voltage reading proportional to the logarithm of NH_3 concentration. NH_4^+ standards prepared in very dilute aqueous oxalic acid were used to generate standard curves at the beginning of each set of analyses, and to check for any instrument drift, standards were also analysed at the end of each set of analyses.

4.3.4 Soil measurements

Soil temperature was measured at two depths (2 and 5 cm) in two replicates, using thermocouples. These were buried 1 m apart from each other, 6 m south of the wind profile mast, well within the irrigated area. Soil moisture, pH and the concentrations of three forms of mineral-N were determined from soil samples.

Soil samples were taken after the start of each NH_3 collection period (excluding the long overnight periods), in 6 replicates, from selected urine patch locations around the perimeter of the circle (Fig. 1). The sample size was marked by pushing a sharp-edged metal ring of 6.5 cm diameter to about 0.5 cm depth into the ground. The entire soil and herbage content inside the ring was then removed for laboratory analyses of soil pH, moisture and three forms of inorganic N content. Soil pH was determined using a flat-surface pH electrode (Broadley-James, Irvine, California). Soil moisture content was assessed using a gravimetric method. Analyses for ammonium-N (NH_4^+-N), nitrate-N (NO_3^--N) and nitrite-N (NO_2^--N) were performed on a twin-channel flow injection analyser (FS 3000, Alpkem, College Station, Texas).

4.4 Experiment 2: Cattle excreta in situ as NH_3 sources

4.4.1 Experiment schedule

The second experiment had been prepared to begin exactly one year after the first. Because of the Canterbury earthquake on 22 February, it had to be delayed by two weeks and was successfully completed in March 2011. For the first 3 days, 12 non-lactating cattle of an average liveweight (LW) of 470 kg were kept in a circle of 16 m radius to produce a sufficient amount of urine and dung as NH_3 emission sources. The cattle were fed twice daily with cut grass. The grass was laid out around the perimeter of the circle, to encourage the cattle to spread evenly across the area (Fig. 2).

Fig. 2 Circular area with 12 cattle, feeding on freshly-cut pasture laid out around the perimeter. The mast with NH_3 samplers at 5 heights marks the centre of the circle. The photo is taken from near the wind profile mast.

For the whole of the experiment's duration of 13 days, vertical NH_3 profiles were collected in the centre of the circle, and wind profiles, soil moisture and temperature were continuously recorded nearby. Night time collection periods were 14 to 16 h long, as in the first experiment. Daytime collection periods were chosen longer than in the first experiment because the emission sources were created over the course of three days and not within a short period prior to the start. During the cattle presence and the following two days, NH_3 collection periods were 4 h long. They were increased to 5 h for the next two days and then to a single daytime period, between 7 and 8 h long, for three days. The final collection period lasted 64 h (three nights and the two intervening days).

4.4.2 Quantification and analysis of feed intake

The cattle were provided with freshly-cut pasture *ad libitum*, twice daily, at 9:00 and 16:00 h. The offered feed was weighed. Feed samples were taken, dried, dry matter (DM) contents determined, and subsamples taken for chemical analysis. Prior to the morning feeding, the refused feed of the previous day was raked together and also weighed and its DM contents determined. DM digestibility was determined by near-infrared reflectance spectroscopy (NIRS).

Total carbon (C) and nitrogen (N) in the grass samples were obtained with an elemental analyser (Vario-Max CN, Elementar GmbH, Hanau, Germany). The samples were combusted at 900 °C in an oxygen atmosphere. This process converted any elemental C and N into CO_2, N_2 and NO_x. The NO_x was subsequently reduced to N_2. The CO_2 and N_2 gases were then passed through a thermal conductivity cell to determine their concentrations. The fractions of C and N (%) were calculated from these concentrations and the sample weights.

4.4.3 Ammonia measurements

Sample extraction from the NH_3 samplers and analysis with an ion-specific electrode followed exactly the same method as in Experiment 1. However, the subsequently computed NH_3 emission rates were unexpectedly high. A few NH_3 subsamples were then re-analysed by two different methods, on a Flow Injection Analyser (FIA) and on a clinical chemistry analyser (for which details are given below). Both these methods confirmed that the prepared NH_3 standards for the electrode were correct, and both indicated that the field-collected NH_3 concentrations were a factor 2 to 3 smaller than determined by the NH_3 electrode calibrated against these standards. The most likely explanation for the puzzling discrepancy between the electrode and the other methods is that the electrode is cross-sensitive to volatile amines. If the cattle and their dung emitted such amines, these would have been collected by the NH_3 samplers and then, in the extracted solution, would have biased the electrode reading as if additional NH_4^+ ions had been present. Such a bias could not have occurred in the first experiment, because there were no potential sources of volatile amines at the site.

To eliminate cross-sensitivity errors, subsamples from all NH_3 collections were re-analysed in a single batch on the clinical chemistry analyser (Daytona LT090, Randox Ltd., Crumlin, Co. Antrim, Northern Ireland). This instrument uses an enzymatic reaction to strip all NH_3 from the test solution and measures the difference in UV absorbance at 340 nm before and after the reaction. The precision of this method is specified by the manufacturer as 1 to 4 %

of the absolute reading (range-dependent). This is comparable to the 2.3 % relative error estimated for the NH_3 electrode. However, the detection limit is a factor 20 larger than for the electrode, which is likely to affect the accuracy of the samples collected at the upper heights towards the end of the experiment, and the upwind background samples throughout.

The NH_3 readings from the clinical analyser (CA) were well-correlated (R = +0.81) with those from the electrode for the 143 samples above the CA's detection limit. This is further support for the explanation of the mismatch between the two methods by the presence of amines in the samples, since Kellems et al. (1979) had observed that amine and NH_3 concentrations in manure samples were highly correlated with each other (R = 0.82 to 0.90), and both species were negatively correlated with storage time, indicating that they volatilised simultaneously. It was attempted to use the good correlation between electrode and CA measurements to predict CA results for the 25 samples below its detection limit (DL), and concluded that the most likely predictions were obtained by setting values "below DL" to "equal DL".

Prepared NH_3 standards were used to determine a correction factor of 0.9349 for the CA's sensitivity in the concentration range spanned by the collected samples. With this simple linear correction, the CA's readings provided the NH_3 concentration data for the subsequent computation of emission rates with the mass-budget method.

4.4.4 Soil, urine and dung measurements

In order to characterise the physical and chemical processes causing NH_3 emissions from the excreta, a few urine patches and dung pats were created for the purposes of measuring pH and taking samples for laboratory analyses. These urine patches and dung pats were placed outside the circular cattle area, near the wind profile mast. On each of four subsequent afternoons, for the first time when the cattle entered the circle and for the last time when they departed, one urine patch and two dung pats were created. Creating these in daily intervals served to represent the variability in the evolution of soil and weather conditions that the excreta produced by the cattle in the circle would have been subjected to, depending on their time of deposition. The urine had been collected at the Lincoln University dairy farm (not from the cattle in the circle) and was poured with the same method as in the first experiment. The dung was collected inside the circle, from selected pats that appeared freshest, and then applied at the target location by filling a ring of 25 cm diameter that was placed on the ground, to a height of 3 to 5 cm. The ring was subsequently removed.

Of each daily pair of dung pats, one was designated for surface pH measurements (see below), the other for the removal of samples of the crust and the interior. Crust samples were taken daily, one from each of these four pats. Interior samples were taken from one pat per day, in triplicates, and the next pat the next day etc., so that effectively each pat was sampled every fourth day. Upon arrival in the lab, the dung skin and dung interior samples were frozen, then weighed and placed in a freeze-dryer (FD 5.5, Cuddon Ltd., Blenheim, NZ) for a period of 48 h. Their moisture content was determined by weighing again after the freeze-drying. The contents of NH_4^+-N, NO_3^--N and NO_2^--N were obtained with the same methods as for the soil samples in the first experiment, see 4.3.3. Total C and N of dung subsamples were obtained with the same elemental combustion method as for the grass samples, see previous section.

Soil samples from urine patches were not taken in this experiment because the locating of urine patches within the cattle area and the recording of their time of application would have required considerable effort (and the urine used outside the circle would not have represented the correct N concentrations). The dynamics of NH_3 volatilisation from urine-affected soil was considered to be well enough understood from the analysis of the first experiment.

Since a hard hydrophobic crust tends to form quite rapidly on dung pats, pH had to be measured in the field, using a portable pH electrode (HI 9025, Hanna Instruments, Woonsocket, Rhode Island). Measurements were made in the middle of each daytime NH_3 collection period on the surface of one dung pat from each creation day (the one not used for taking samples) and on the surface of each urine patch. Each such measurement consisted of five replicate readings, taken at different spots of the surface. The pH of the dung interior was determined less frequently, using the samples taken to the lab.

Soil temperature was measured at two depths (2 and 5 cm) in two replicates, near the wind profile mast, as in the first experiment. Soil moisture was monitored continuously with five water content reflectometers (CS-616, Campbell Scientific, Logan, Utah). These were buried horizontally, four of them at 2 cm depth, one under each urine patch, and one at 5 cm depth in urine-free soil. The soil moisture data were corrected for temperature in post-processing.

5 Results

5.1 Experiment 1: NH_3 emissions from a grid pattern of urine patches

The results from the first experiment were first described in the progress report by Laubach et al. (2010). Since then, they have been analysed in more depth in a recently submitted manuscript (Laubach et al. 2011). The following subsections give a brief overview of the main findings, relevant to the objectives stated in Section 3.

5.1.1 Site and weather conditions and fraction of volatilised nitrogen

The experiment was conducted 24 February to 5 March 2010 in a paddock located 1 km west of Lincoln University, New Zealand (43° 38.56' S, 172° 27.34' E, 11 m a.s.l.). The soil is classified as Eyre stony sandy loam (Hewitt 2010). An area of ca. 40 m by 70 m including the marked circle was irrigated repeatedly prior to the experiment, first on 12 Feb and last on 23 Feb, providing an estimated total of 40 mm. Only one light rain event occurred during the experiment, providing 2.5 mm, overnight from 25 to 26 Feb between 23:30 and 02:30 h (36 to 39 h after urine application). Soil temperature was 24 to 26 °C in the first 6 h after urine application, favouring rapid urea hydrolysis. Mean soil temperature during the first 6 d was 18 °C. With the MB method, 25.7 % (SE ±0.5 %) of the applied urine-N was found to have volatilised as NH_3 over the first 6 d.

5.1.2 Method comparisons

The ZINST method provided emission rate estimates that did not differ systematically from the MB method, with 50 % larger random error (Fig. 3). The BLS method underestimated the emission rate by 10 to 24 %, dependent on which measurement height was used (Fig. 4). This was caused by the requirement to specify mean wind speed and mean concentration as input parameters, instead of the measured mean horizontal flux, which leads to neglect of the "turbulent backflow" term. The details of this issue and its implications are discussed in Laubach (2011) and Laubach et al. (2011).

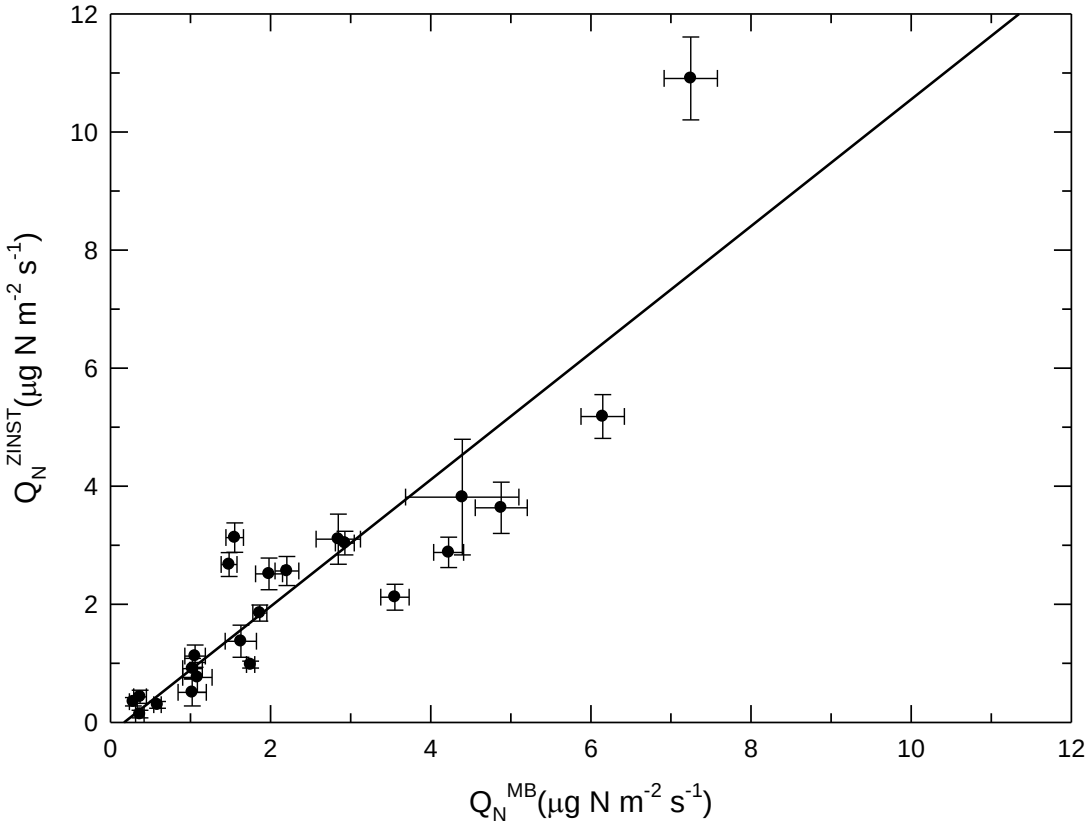

Fig. 3 NH_3 emission rates from ZINST method versus emission rate from MB method. Error bars indicate standard propagated measurement errors. The solid line represents linear regression (slope 1.07, intercept −0.18 µg N m^{-2} s^{-1}, R^2 = 0.78).

5.1.3 Evolution of NH_3 emissions from urine patches

The emission rates during the first 6 d are shown in Fig. 5. The largest emission rates occurred during the first 4 h after the urine application, about 7 µg N m^{-2} s^{-1}. Emissions dropped rapidly during the next two collection periods to about 2 µg N m^{-2} s^{-1}. From then, a steady decline had the emission rates roughly halving every 2 d. Such a pattern is expected from similar experiments (e.g. Beauchamp et al. 1978, Sherlock et al. 1995). Superimposed on the general decline are several short-lived increases in the emission rate. The second of these, over three consecutive daytime collection periods 2 d after urine application, may be in response to a light rain event during the preceding night (2.5 L m^{-2} in 3 h), indicated by dashed lines in Fig. 5. The others are restricted to afternoon collection periods, consistent

with the expectation that warming of the upper soil layers during the day leads to increased NH_3 volatilisation.

Fig. 6 shows the temporal changes in pH and three mineral-N species obtained from soil samples taken within the urine patches (means of 6 samples). The pH, which was 6.65 (±0.13) in urine-free topsoil, showed a maximum of 8.51 (±0.05) at 2 to 4 h after urine application and then declined more or less steadily throughout the experiment, except for a temporal increase from 7.9 to 8.4 after the nocturnal rain event. Background pH was first reached 6 d after urine application, and after a temporary increase back to 6.9, again after 8 d. With a pH below 7, NH_3 volatilisation is effectively suppressed (Sherlock and Goh 1985), which implies that the observed N loss during the first 6 d after urine application is probably very close to the total N loss from the urine patches.

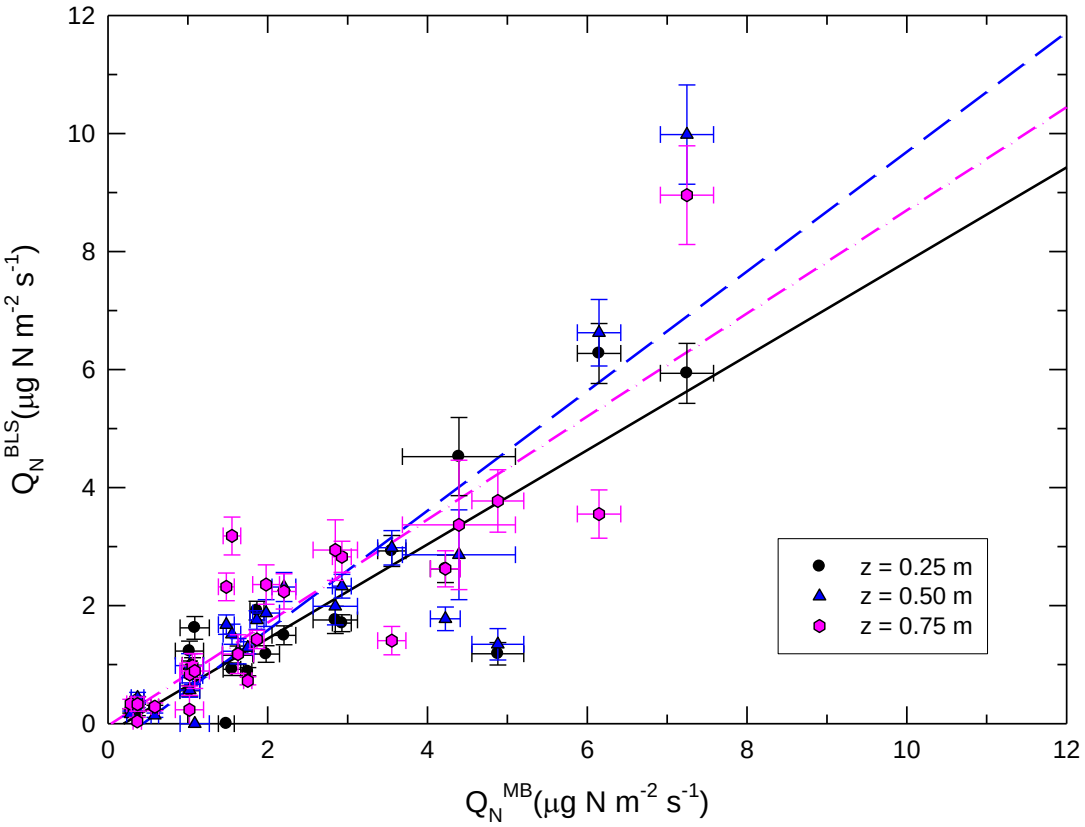

Fig. 4 NH_3 emission rates from BLS method, computed from NH_3 measurements at each of the lower three measurement heights separately, versus emission rate from MB method. Error bars indicate standard propagated measurement errors. Solid, long-dashed and dash-dotted lines represent linear regressions for $z = 0.25$, 0.50 and 0.75 m, respectively.

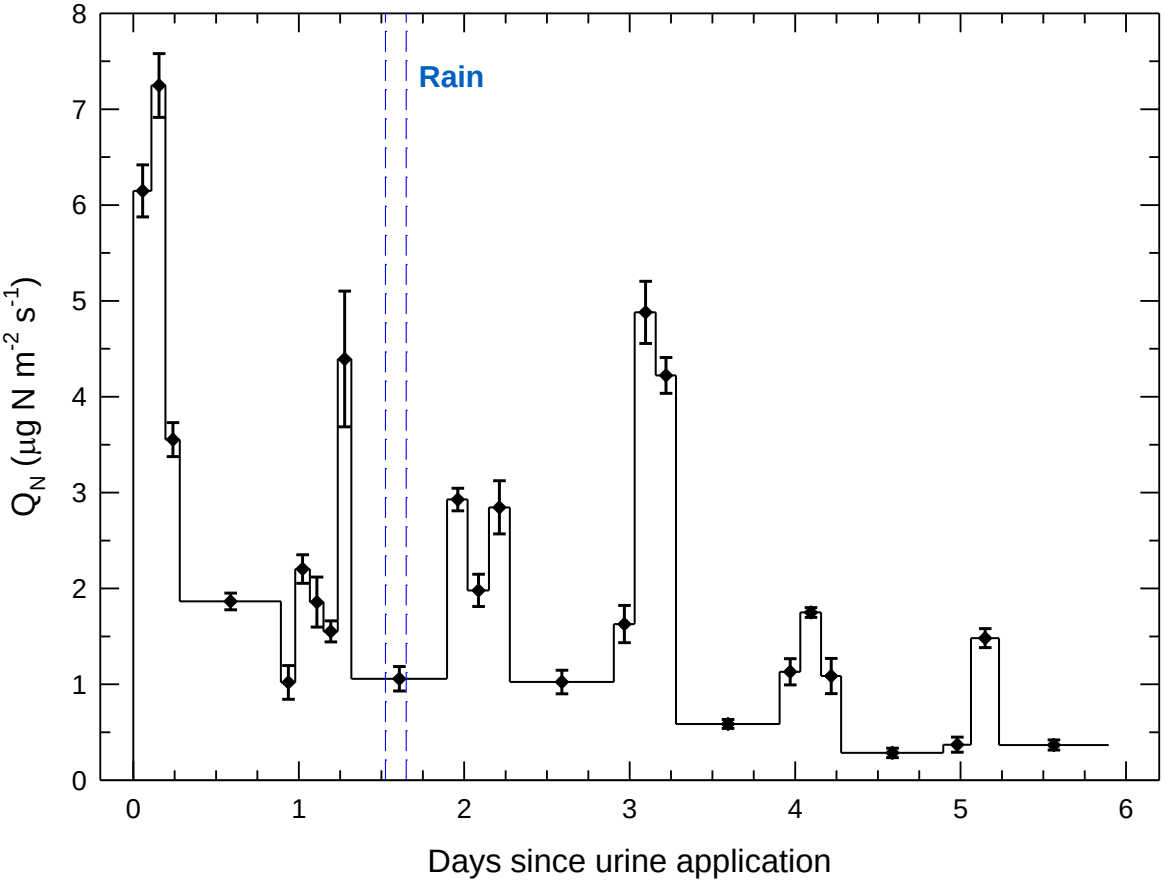

Fig. 5 NH_3 emission rates from urine patch pattern, determined with the MB method as a function of time since urine application. Error bars represent estimated measurement uncertainty and are placed at the mid-points of the collection periods, whose durations are indicated by horizontal sections of the solid line. The start and end of the only rain event are marked by vertical dashed lines.

Ammoniacal-N also peaked after 4 h, at 1226 (±129) µg N (g soil)$^{-1}$, and then generally declined, except for a second even higher but short-lived maximum after the rain. As the pH dropped below 7, NH_x-N stabilised at about 600 µg N (g soil)$^{-1}$. Nitrate-N, by contrast, rose steadily to a 100fold of its initial value of 2.5 (±0.4) µg N (g soil)$^{-1}$, indicating that some of the applied N underwent nitrification. NH_x-N was strongly correlated and NO_3^--N strongly anti-correlated to pH (Laubach et al. 2010), with squared correlation coefficients of 0.77 for both compounds. Nitrite-N was generally 1-2 magnitudes less abundant than NO_3^--N (and 2-3 magnitudes less than NH_x-N) and weakly positively correlated with pH (R^2 = 0.19), which is numerically caused by its maximum value also occurring in the first sampling period after the rain event. Apart from that temporary rise, NO_2^--N did not show a clear temporal pattern.

Comparison of Fig. 6 to Fig. 5 supports the interpretation that the general decrease of NH_3 emission rate over time follows a decrease in pH (Sherlock and Goh 1985). As pH declines, the amount of NH_x-N also declines, in part due to the loss from volatilisation and in part due to nitrification.

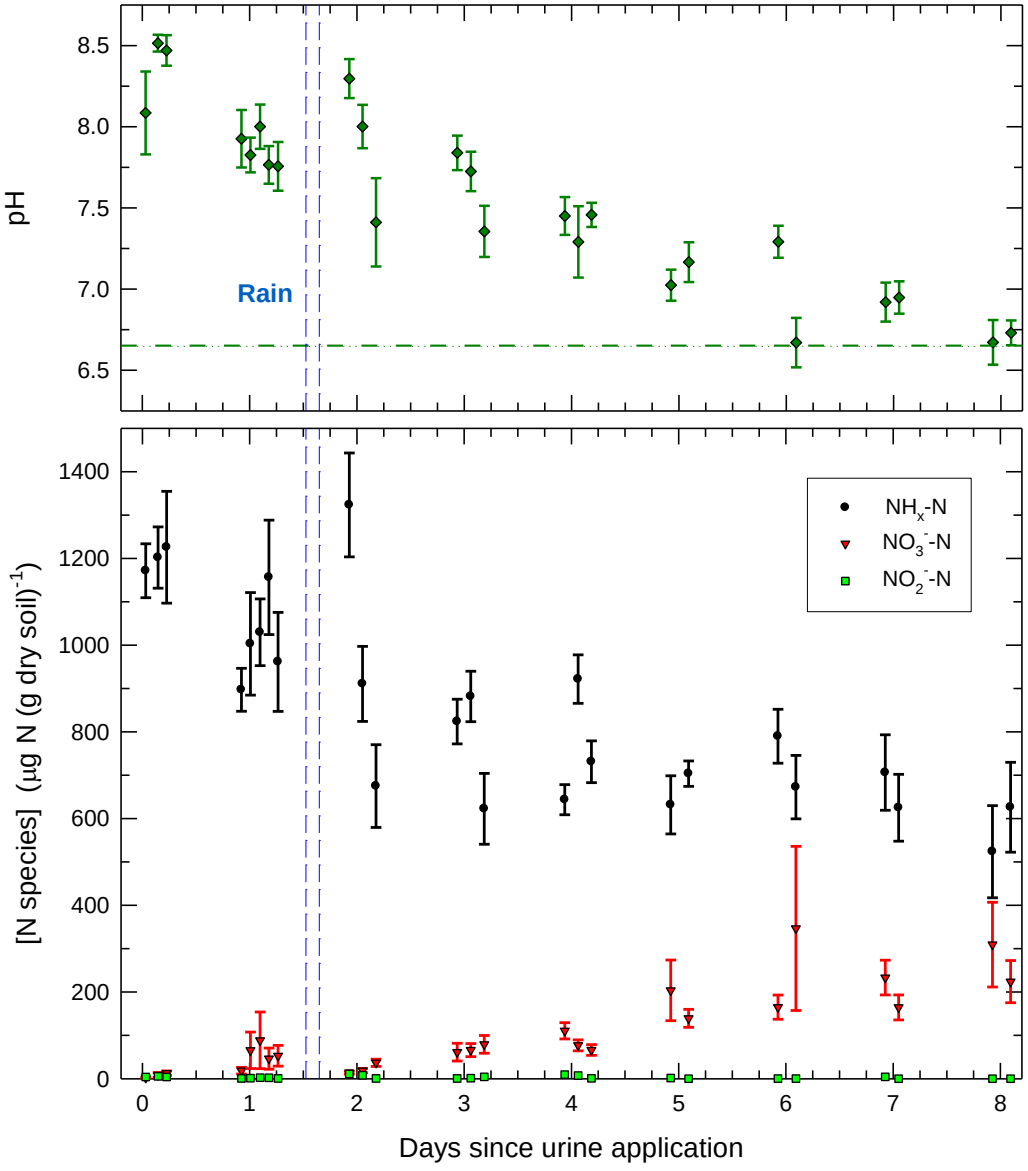

Fig. 6 Temporal evolution of pH (top panel) and mineral nitrogen species extracted from soil samples within urine patches (bottom panel). Error bars give standard errors of the mean of 6 replicates. The topsoil pH outside urine patches, of 6.65, is marked by a horizontal dash-dotted line in the top panel. The start and end of the only rain event are indicated by vertical dashed lines.

5.1.4 The role of patchiness and test of a resistance model

When the results of this experiment are subjected to the purely empirical approach of Sherlock et al. (1995), relating the observed NH_3 emission rates via linear regression to the product of wind speed and NH_3 equilibrium in solution, then one obtains a regression slope of about 5 % of the slope found by Sherlock et al. (1995) in an experiment with an evenly-spread urine circle as the NH_3 source (with $R^2 = 0.67$ somewhat lower than the value of 0.77 of Sherlock et al.). If one takes into account that the urine patches in the present experiment covered 5 % of the area of the circle, then the observed resistances are consistent between these experiments. Such a scaling of the emission rate by urine-covered area makes sense because the soil resistance dominates over the aerodynamic resistance (Laubach et al. 2011). To good approximation, the effect of patchiness can thus be captured simply by knowing the covered area fraction.

The resistance model of Laubach et al. (2011) accounts for both the soil and the aerodynamic resistances and includes the area scaling factor in the description of the soil transport. The soil resistance is expressed as a linear function of an "effective depth" at which gaseous and dissolved NH_3 are in equilibrium. If this effective depth was known, the NH_3 emission rate could be predicted by the model. In the present experiment, the model was used in reverse, using measured emission rates and computing the effective depth. This depth was found to be of the order of 0.2 cm, which is one magnitude smaller than two independent estimates of urine penetration depth, one from a dye penetration experiment and the other from N budget considerations of a single urine patch (Laubach et al. 2011). As one would expect the effective depth somewhere in the upper half of the urine-penetrated soil layer, it is concluded that the model gives correct magnitude estimates for the soil resistance.

5.2 Experiment 2: NH_3 emissions from cattle excreta in situ

With respect to NH_3 volatilisation dynamics, the second experiment showed two main differences from the first experiment: the inclusion of dung as an additional N source, and the continuous application of animal excreta over a period of 3 days, rather than quasi-instantaneously (i.e. within 0.5 h). The start of the experiment is in the following defined by the time when the cattle entered the fenced circle, at 16:05 h on 8 March 2011. The cattle departed at 16:20 h on 11 March, 3.01 d later. Measurements ceased in the morning of 21 March, at 12.75 d.

5.2.1 Site and weather conditions

The experiment was conducted in a paddock located 3 km south of Lincoln University, New Zealand (43° 40.45' S, 172° 28.22' E, 4 m a.s.l.). The soil was classified as a Templeton silt loam (N. Smith and P. Almond, Lincoln University, pers. comm.).

Some rain had fallen prior to the experiment, on 5 and 6 March, and the soil dried from 0.17 to 0.10 m^3 H_2O $(m^3$ soil$)^{-1}$ during the first week of measurements (Fig. 7). Rain events that noticeably increased soil moisture occurred on three occasions. The first delivered 3 mm on the morning of 15 March, at 6.66 to 6.72 d after the start of the experiment. The second provided 1 mm on 19 March around noon, at 10.81 to 10.88 d, and the third delivered 5 mm intermittently during the daytime hours of 20 March, between 11.72 and 12.11 d. Only negligible soil moisture increase was observed when 0.3 mm of drizzle fell at 2.98 d, just before the cattle departed. Soil moisture measured under the urine test patches increased by 0.03 m^3 H_2O $(m^3$ soil$)^{-1}$ immediately after pouring and then gradually over several days approached background soil moisture again. Hence, soil moisture within urine patches was comparable to that on Days 3 to 6 of the first experiment, and drier than on Days 1 and 2.

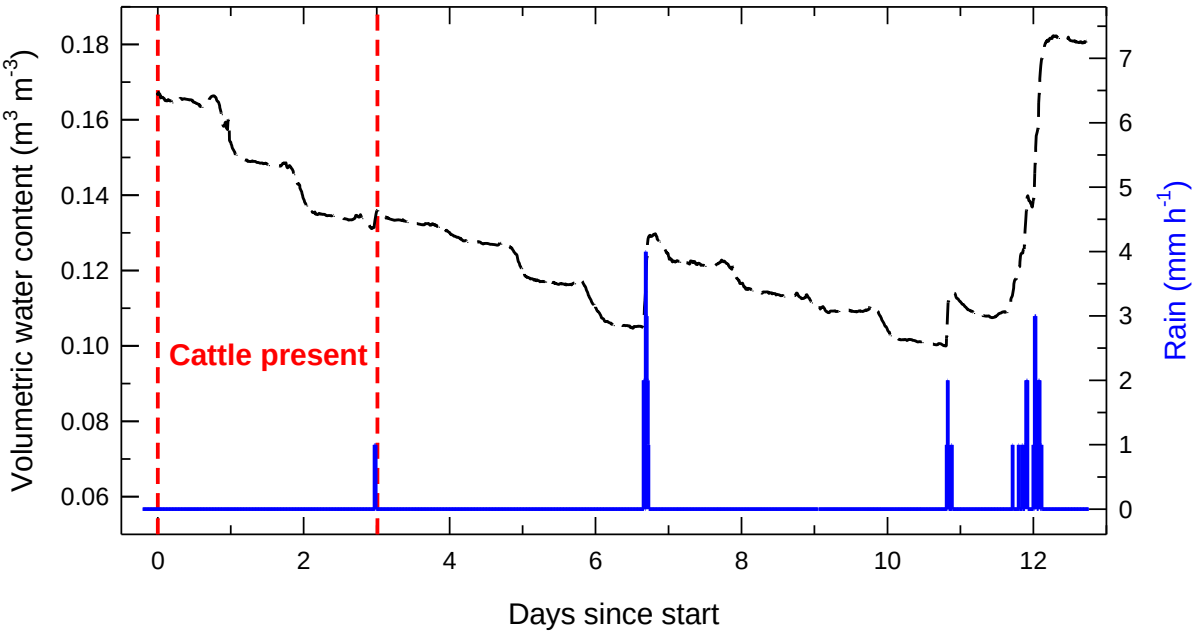

Fig. 7 Temporal evolution of soil moisture (black dashed line) and rainfall intensity (blue columns) during Experiment 2. The origin of the time axis is at 16:05 h on 8 March 2011, when the cattle entered the circular plot. The period of cattle presence is marked by vertical red dashed lines.

Soil temperature at 2 cm depth reached afternoon maxima of 31, 28 and 27 °C on the start day and the following two days, respectively, favouring rapid urea hydrolysis in the freshly deposited excreta. The day of the cattle departure and the next day were overcast and cooler, with soil temperature maxima of 20 °C. Peaks on the following four days were again above 25 °C. Nocturnal minima varied between 9 and 16 °C, and overall mean soil temperature of the 13 days of measurement was 18 °C, both at 2 cm and 5 cm. Temperatures were thus by and large similar to those in the first experiment.

5.2.2 Estimation of nitrogen deposited with the excreta

The total grass weight offered to the group of cattle on each of the 6 feeding occasions varied between 419 and 546 kg. The DM content was around 14 % in the mornings and 16 % in the afternoons (overall mean ± SE was 15.2 ± 0.5 %). This resulted in a total DM offered of 446 kg, of which 67 kg were refused. Each cattle thus consumed 10.53 (±0.35) kg DM per day on average. Nitrogen content as a fraction of DM was determined for each feeding occasion, as 2.59 (±0.07) % (mean ± SE). The total N intake throughout the 3-d period was thus 9.81 (±0.42) kg, representing 0.273 (±0.012) kg N d^{-1} $cattle^{-1}$. Some of this N intake was retained by the cattle in the form of liveweight (LW) gain, the balance was excreted as urine and dung (since the cattle were non-lactating). These N amounts are estimated in the following paragraphs and summarised in Table 1 (Section 5.3).

The amount of dung excreted can be estimated as DM intake times (100 % − digestibility). The DM digestibility of the pasture was 80.3 (±0.6) % (mean ± SE of 6 feeding occasions), which gives the total dung DM as 74.7 (±2.5) kg. The N content of dung DM is assumed to be in proportion to the N content in the feed DM, thus taken as 2.59 % of dung DM. (This fraction is corroborated by measurements of the initial N fractions in the four dung pats created on the start day and the following three afternoons, which ranged from 2.10 % to 2.88 %.) The deposited amount of dung-N was thus obtained as 1.93 (±0.08) kg.

It is estimated that each cattle gained on average 1.25 (±0.25) kg LW per day, based on reference tables for nutritional requirements (Agricultural Research Council 1980). For 12 cattle over 3 d, this amounts to 45 (±9) kg LW gain. The amount of N retained in the weight gain is assumed to be 2.5 (±0.25) % of that (default value used by the Helsinki Commission of the European Union), resulting in a total of 1.13 (±0.25) kg N retained. This represents 11.5 (±2.6) % of the N intake.

Subtracting dung-N and N retained from the total N intake provides an estimate of the total N amount deposited with urine, of 6.75 (±0.50) kg. This represents a daily per-capita excretion of 0.188 (±0.014) kg N d^{-1} $cattle^{-1}$. If one assumes the daily volume of urine voided as 40 L per cattle, the concentration of N in urine is obtained as 4.7 g L^{-1}, which is a realistic value.

The estimated amount of urine-N, of 6.75 kg, is 2.88 times the amount deposited in the first experiment. Combining urine-N and dung-N, the total amount of excreted N was 8.68 (±0.49) kg, 3.71 times the amount of N deposited in the first experiment. Urine accounted for 77.8 (±1.6) % and dung for 22.2 (±1.6) % of the excreted N.

5.2.3 Dung and urine distribution

The total number of dung pats created in the experimental circle was estimated, in order to corroborate the dung DM estimate in the previous section, and to test statistically whether the visual impression of a directionally homogeneous distribution is correct. (A similar exercise for urine patches was not possible because, once dried at the surface, their locations were not obvious.)

The experimental "circle" was confined by an outer fence with 21 posts, de-facto creating a polygon with 21 corners. This could be subdivided into 21 triangular pieces, each defined by two neighbouring fence posts and the centre point. Four of these triangles were marked to count dung pats within them, orientated at directions roughly 90 deg apart. Two operators did the counting independently and then compared results to estimate the counting error. When the difference between the two independent counts exceeded 4 pats, the operators did a joint recount to obtain a third estimate.

The numbers of dung pats in the four chosen segments were 23 (±2), 18 (±3), 19 (±2), and 27 (±2), respectively. The last segment had also the largest area, so on a per-area basis the relative variation between the segments was slightly smaller than on an absolute basis. Summing the four counts and scaling up to the whole circle results in a total of 445 (±23) dung pats. From this results a defecation frequency of 12.36 (±0.64) per cattle per day. This is very close to the mean of observations from 13 studies collated by Haynes and Williams (1993), which ranged from 10.5 to 16.1 defecations per cattle per day. The average amount of DM per dung pat was 74.7 kg divided by 445, giving 0.168 kg, and the average amount of dung-N per pat was 4.3 g. This is also compatible with the data reviewed by Haynes and Williams (1993), who give the typical annual output of dung-N as 23 kg per cattle: assuming 12 defecations per day, this is equivalent to 5.0 g N per defecation.

The frequency of urinations is typically 20 % smaller than the frequency of defecations, at 8.0 to 12.1 per cattle per day (Haynes and Williams 1993, White et al. 2001). From this we may infer that the total number of urine patches within the circle was probably between 300 and 400. This is roughly 2 to 3 times the number of patches used in the first experiment, and is also about the number that was aimed for when deciding on the number of cattle and the duration of their presence. The estimated range of 300 to 400 patches corresponds to an average amount of urine-N between 22 and 17 g per patch.

The observed dung pat counts are fully compatible with a random distribution across the circle (see Appendix). Hence, no directional bias is expected for the NH_3 emission results.

5.2.4 Ammonia emissions

The evolution of NH_3-N emission rates, for all collection periods, is shown in Fig. 8, along with the mean N excretion rates, estimated as the difference of N intake and N retained (Section 5.2.2). While the cattle were present and the amount of excreta was rising, emission rates generally increased. Superimposed on this general trend were strong variations between large daytime emissions and smaller night time emissions (night time periods are recognisable by their longer duration). These variations are in response to the diurnal temperature cycle and are similar to those observed in the first experiment (Fig. 5). Absolute emission rates peaked at 35 and 34 g N h^{-1} on the first and third day, respectively, equivalent to per-area emissions of 12.6 and 12.0 µg N m^{-2} s^{-1}, which is about twice the maximum emission rates of the first experiment. After the cattle had departed, emission rates continued to increase for another day (until d = 4). For the next 6 days, volatilisation rates generally decreased, as could be expected from the first experiment. The residual emission rate over the final collection period, from 10.07 d to 12.75 d, was only 0.65 g N h^{-1}, one magnitude less than emission rates of the first week.

The total amount of NH_3-N volatilised, over the 12.75 d of measurements, was 1.94 kg N, with a cumulative propagated standard error of 0.02 kg N. This represents 19.8 (±0.9) % of the cattle's N intake and 22.4 (±1.3) % of the N excreted (propagated SE in parentheses). The latter value is 87 % of the fraction of volatilised N found in the first experiment with urine only.

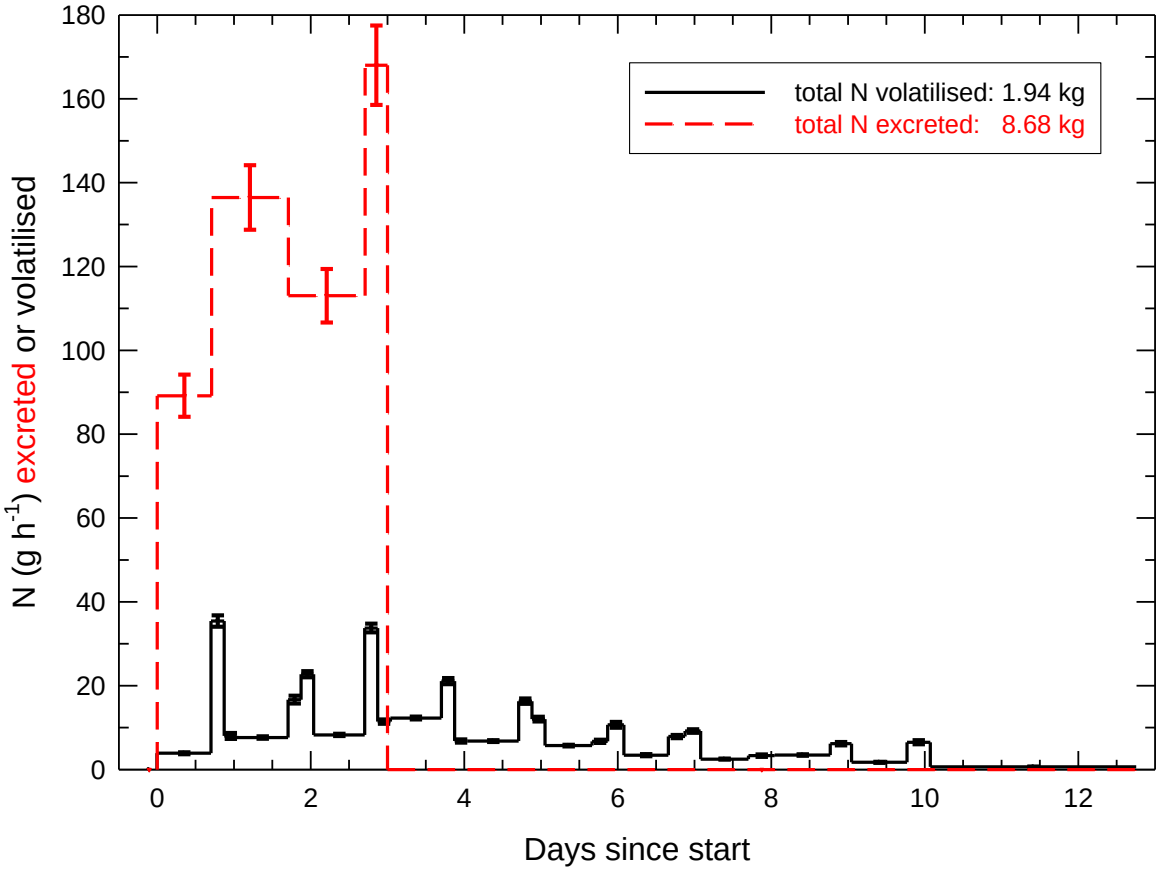

Fig. 8 Temporal evolution of nitrogen excreted by 12 cattle during their 3-day presence, estimated as the difference of N intake and N retained (red dashed), and NH_3-N emission rates, determined with the MB method (black solid). Error bars for the latter represent estimated measurement uncertainty and are placed at the mid-times of the NH_3 collection periods, whose lengths are marked by the horizontally-constant parts of the connecting solid line.

5.2.5 Evolution of pH in urine patches and dung pats

Fig. 9 shows the evolution of the pH at the urine patch and dung pat surfaces and inside the dung pats, with separate symbols for each individual patch or pat (created on successive days). For each urine patch, the maximum pH, between 8.5 and 9.0, occurred one day after its creation, indicating the completion of urea hydrolysis. After that, the pH decreased steadily while NH_3 volatilisation rates were high (Fig. 8). Six days after the start, the pH had fallen to below 7.7 for all patches. By this time, the NH_3 emission rate had dropped below 10 g N h^{-1},

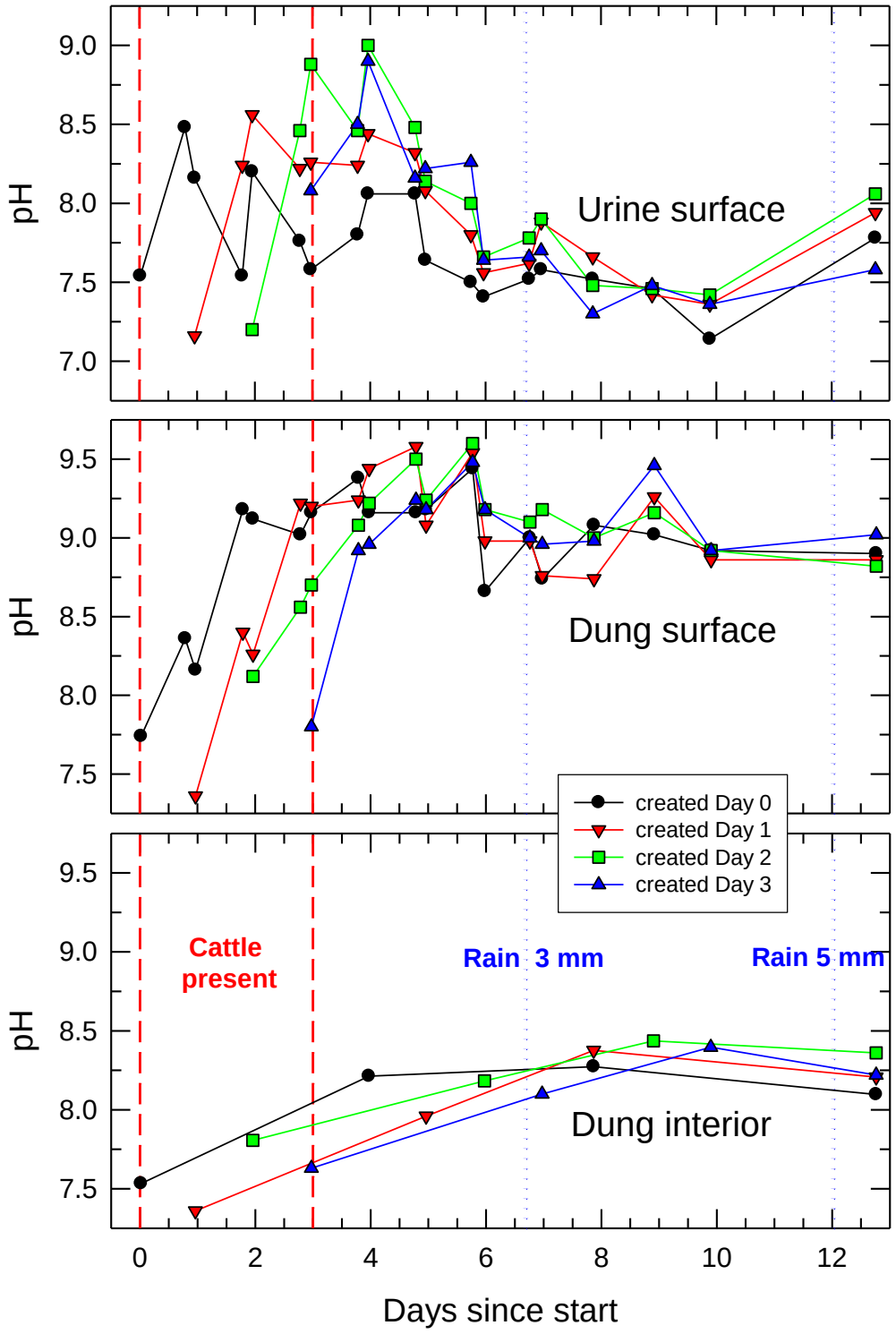

Fig. 9 Temporal evolution of pH on urine patch surfaces (top panel), dung pat surfaces (middle) and inside dung pats (bottom). The period of cattle presence is marked by vertical red dashed lines, and the times of the two rain events with more than 1 mm yield by blue dotted lines.

and 79 % of all observed emissions had occurred. The main trends for urine pH and NH_3 emissions are thus correlated, as could be expected from the results of the first experiment and the fact that 77.8 % of the N excreted by the cattle was in the urine.

The two major rain events, with 3 mm and 5 mm yield, caused temporary increases in urine pH and seemed to synchronise the timing of subsequent pH evolution (Fig. 9, top panel). It is unclear, though, whether the rain events had any significant impact on the NH_3 emissions.

Initial pH values at the dung pat surfaces were between 7 and 8, as at the urine patch surfaces (Fig. 9, middle panel). They then rose more slowly than in the urine and peaked 3 to 4 d after the dung pat's creation, at a consistent value of 9.5 (±0.1). After that, the dung surface pH decreased slowly and steadily, except that all pats showed a secondary peak, 8 d after the start for the oldest pat and 9 d after the start for the others (representing ages of 6 to 8 d for them). Dung surface pH at the end of the experiment was still consistent between pats and surprisingly high, at 8.8 (±0.2).

For each dung pat, the interior pH (Fig. 9, bottom panel) was consistently lower than the surface pH, and it rose more slowly, peaking about 7 d after the pat's creation (the exact timing is somewhat uncertain because samples from the same pat were only taken every 3 or 4 d). All four pats were sampled at the end of the experiment and showed an interior pH of 8.4 (±0.2), still markedly above neutral. This would suggest, firstly, that the lower rates of volatilisation observed towards the end of the experiment originated mainly from dung, and secondly, that after 12.75 d there were still considerable amounts of NH_4^+ present in the dung, providing potential for further NH_3 volatilisation, albeit at a slow rate.

5.2.6 Moisture, mineral N and pH of dung samples

The dung interior samples contained 66 to 89 % water on a mass basis (mean ± SE of 48 samples: 82.7 ± 0.6 %), and moisture did not show a trend over time, which means there was plenty of dung solution available throughout. The water content of the dung crust samples showed no clear trend either. It was significantly lower than in the interior but also more variable, from 8 to 82 % (mean ± SE of 37 samples: 49.7 ± 2.8 %), where the variability may partly stem from incomplete separation of dung interior material sticking to the crust sample. The crust was clearly physically different from the interior material. It felt solid, was about 1 mm thick, would break under pressure and could be cut with a sharp knife. After harvesting a sample, new crust would form underneath within a day or so.

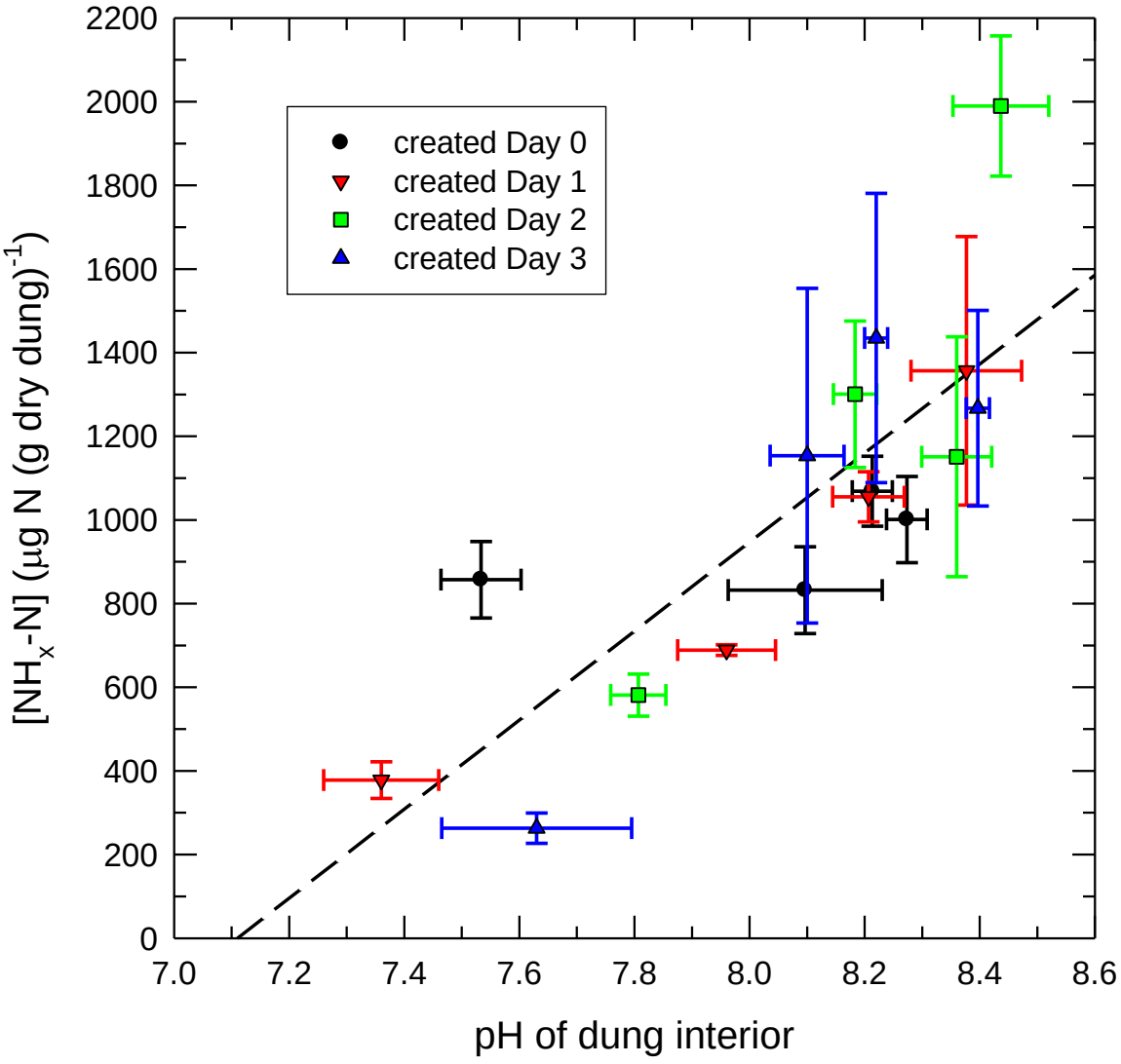

Fig. 10 NH_x-N concentration in samples from the dung interior versus pH of the same samples. The different dung pats are identified by different colours and symbols, the same as in the bottom panel of Fig. 9. Error bars mark standard errors of the mean of 3 replicates. The dashed line represents linear regression ($R^2 = 0.66$).

Nitrate-N and nitrite-N of the dung interior were not significantly correlated to pH measured in the same samples ($R^2 = 0.08$ for either species, not shown). Ammoniacal-N was significantly correlated to pH (Fig. 10, $R^2 = 0.66$), almost as strongly as it was in the urine-patch soil samples in the first experiment (where $R^2 = 0.77$, Section 5.1.3). Such a high correlation between pH and [NH_x-N] in dung was also reported by Kirchmann and Lundvall (1998). The regression line in Fig. 10 has a slope of 1064 µg N (g dry dung)$^{-1}$ per pH unit

and predicts vanishing [NH_x-N] at a pH of 7.1, i.e. for near-neutral solution. Thus, dung-interior pH and [NH_x-N] rose in parallel over the first week after deposition and then decreased only slowly (Fig. 9, bottom panel). Together with the high moisture contents, these data suggest that the dung pats contained all necessary ingredients to build up considerable NH_3 volatilisation potential.

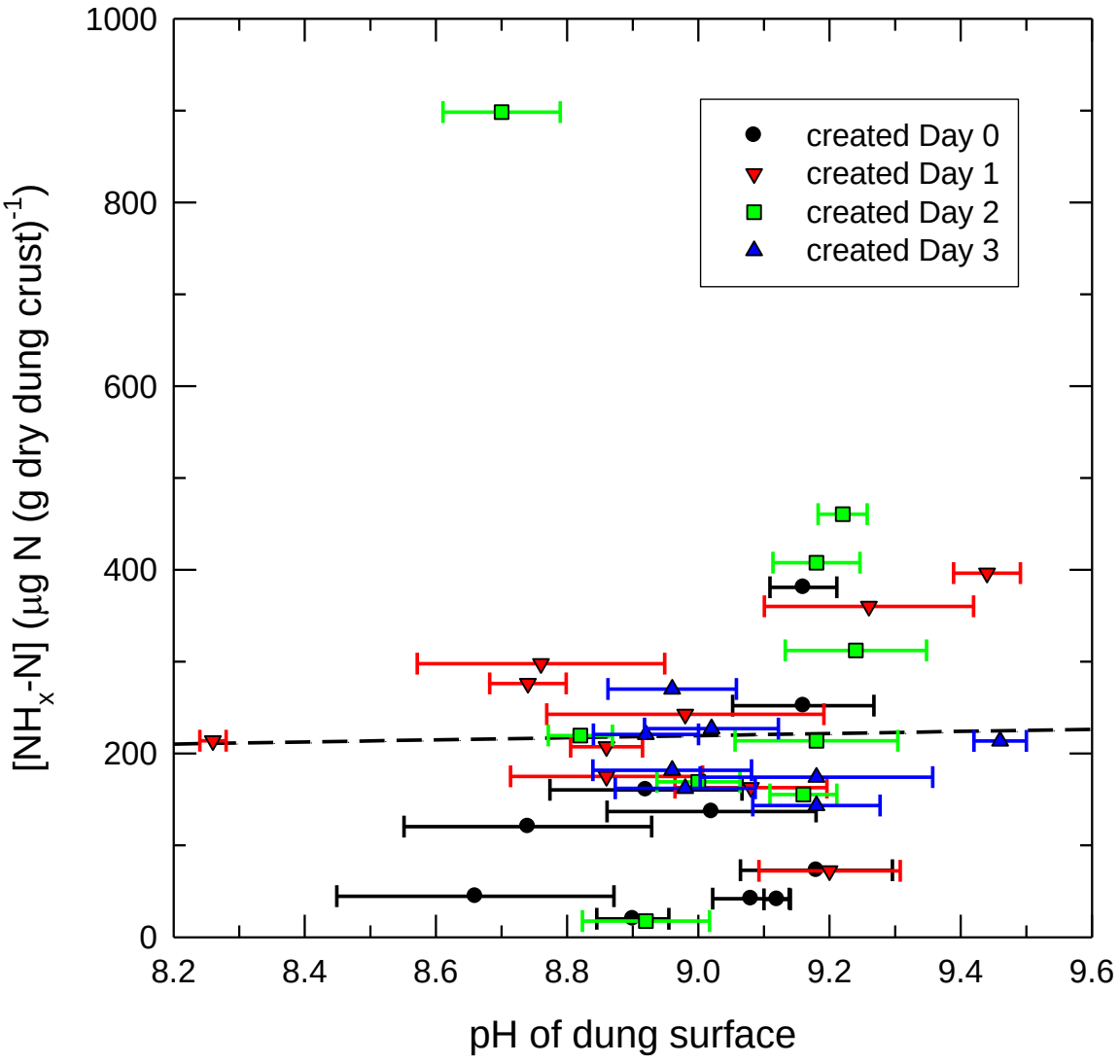

Fig. 11 NH_x-N concentration of dung crust samples versus pH on the dung surface. The different dung pats are identified by different colours and symbols, the same as in the middle panel of Fig. 9. Error bars for pH mark standard errors of the mean of 5 replicates. The dashed line represents linear regression (R^2 = 0.0003).

The question then is to what extent this potential volatilisation actually occurred, and to what extent it was inhibited by other processes. It seems that the dung crust plays a crucial role in this, by reducing direct contact between NH_x-containing solution in the interior and the gas phase, i.e. the surrounding air. Such contact is necessary for equilibration of gaseous NH_3 between the liquid phase and the gas phase. Without that step, volatilisation cannot proceed. Two observations support the hypothesis that the dung crust inhibited NH_3 exchange. Firstly, the dung crust samples contained far less (about 1/5) NH_x per dry matter than the dung interior, on average 220 (±26) µg N g^{-1} compared to 1024 (±73) µg N g^{-1}. Secondly, [NH_x-N] of the dung crust did not correlate to pH (Fig. 11), although this may in part be due to the fact that the pH was not measured in the collected samples but at 5 different random spots on the dung surface.

5.2.7 Separation of urine and dung emissions

The results of the previous section suggest that the volatilisation from urine, which tends to be rapid, and the volatilisation from dung, which is partly inhibited by the dung crust, may be separated in time. A crude attempt to verify this is made in Fig. 12. There, the daily N loss fractions due to NH_3 volatilisation are shown, relative to N excreted. That way, the day-night variability, which is a main feature in Fig. 8, is averaged out and the day-to-day evolution is emphasised. In Fig. 12, the daily N losses increase during the first 3 d, while excreta were added to the experimental plot, and then decrease during the following 5 d. This pattern is unambiguously explained by the dominance of volatilisation from urine, which provided the major part of all deposited N. On Days 9 and 10 of the experiment, though, the NH_3 volatilisation is larger than on Day 8.

This secondary maximum of the NH_3 loss trajectory occurs at the same time that the pH of the dung interior reaches its overall maximum, and the pH of the dung surface attains a secondary maximum (Fig. 9). It thus appears plausible that the secondary maximum of NH_3 emissions on Day 9 is caused by volatilisation from dung, and that dung emissions also provide the dominant contribution to N loss thereafter. Similar bimodal curves of NH_3 emissions over time were obtained by Jarvis et al. (1989) in experiments on grazed paddocks, and by Kellems et al. (1979) in laboratory experiments with various mixtures of cattle urine and dung, where the larger and earlier peak increased with increasing urine content and the smaller and later peak with increasing dung content. Sugimoto et al. (1992) measured NH_3 volatilisation rates from dung and found that they peaked after 15 d when wet and after 20 d

when dry, during cooler conditions than in the present experiment. This also supports the interpretation that a peak in dung emissions at about 9 d in our experiment is plausible.

In Fig. 12, the transition between the NH_3 emissions mainly from urine and those mainly from dung is indicated by a vertical dashed line at 8 d since start. In reality there is an overlap of the two modes, but for a crude approximation this overlap is ignored here and it is assumed that all emissions before this time originate from urine and all emissions thereafter from dung. The former amount to 1.72 kg N and the latter to 0.22 kg N. The uncertainty is estimated as 0.05 kg N for either, to account for the crude separation method. Relative to the total N excreted, the emissions from urine and dung represent 19.8 % and 2.6 %, respectively. Relative to the amounts of urine-N and dung-N, of 6.75 kg and 1.93 kg, respectively, they represent loss rates of 25.5 (±2.0) % from urine and 11.6 (±2.7) % from dung. The value for urine agrees excellently with that from the first experiment, under similar weather conditions.

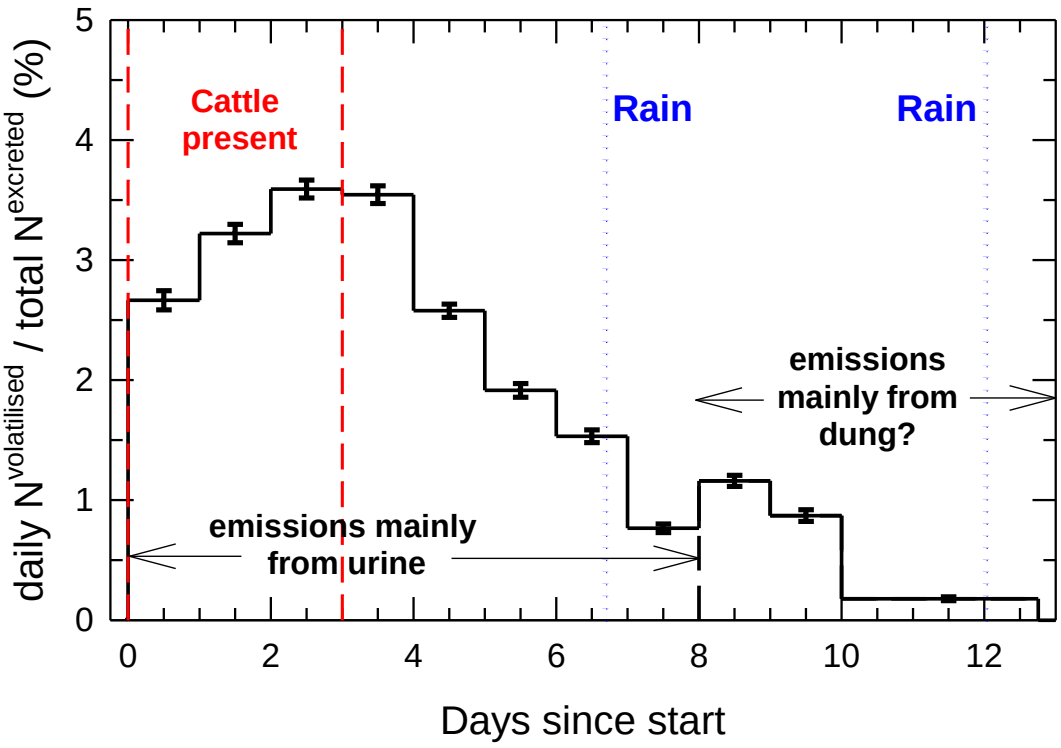

Fig. 12 Day-to-day evolution of N loss fraction due to volatilisation, relative to the amount of N excreted by 12 cattle over the first 3 days (their presence is marked by vertical red dashed lines). The vertical black dashed line at 8 days since start indicates the time when N loss rates cease to be dominated by volatilisation from urine, and emissions from dung probably begin to constitute the major fraction. The times of the two rain events with more than 1 mm yield are marked by blue dotted lines.

Table 1 Amounts of nitrogen fed, deposited and volatilised, as well as their ratios, from the two experiments. Uncertainties (in parentheses) are propagated standard errors.

Experiment	Nitrogen budget component	N amount (kg)	Fraction of N intake (%)	Fraction of N excreted (%)	Fraction of dung-N (%)	Fraction of urine-N (%)
Cattle 3 days (Mar 2011)	intake	9.81 (0.42)	100			
	retained	1.13 (0.25)	11.5 (2.6)			
	excreted	8.68 (0.49)	88.5 (2.6)	100		
	in dung	1.93 (0.08)	19.7 (0.8)	22.2 (1.6)	100	
	in urine	6.75 (0.50)	68.8 (2.7)	77.8 (1.6)		100
	volatilised as NH_3	1.94 (0.02)	19.8 (0.9)	22.4 (1.3)		
	volat. from dung*	0.22 (0.05)	2.3 (0.5)	2.6 (0.6)	11.6 (2.7)	
	volat. from urine*	1.72 (0.05)	17.5 (0.9)	19.8 (1.3)		25.5 (2.0)
Urine-patch pattern (Feb 2010)	in urine	2.34 (0.01)				100
	volat. from urine	0.60 (0.01)				25.7 (0.5)

* The urine-dung split was not measured, but inferred by plausibility arguments from the temporal evolution of the volatilisation rates and the pH observations (see 5.2.5 and 5.2.7).

5.3 Summary and discussion of nitrogen budgets

Table 1 summarises the observed components of the nitrogen budget for both experiments, as given in previous sections. The table also includes the inferred split between the volatilisation rates from urine and dung in Experiment 2. Even though the provided values for this split are somewhat speculative, there is no doubt that the absolute amounts of N volatilised from urine are typically about one magnitude larger than those volatilised from dung. This is the result of two effects. Firstly, the larger fraction of excreted N is usually found in the urine, and this fraction increases with increasing digestibility of the feed. Secondly, the volatilisation process itself is more rapid and more extensive from urine patches than from dung pats, because in the urine both urea and liquid are abundant and urea hydrolysis can begin immediately, creating NH_4^+ ions and causing the pH rise that is the main driver of

volatilisation (Sherlock and Goh 1985), while in the dung this is not the case. Still, the second experiment has shown that over time the pH in the dung interior does rise to values above 8 and this rise is correlated with a rise in [NH_x-N], creating conditions conducive to volatilisation. To some degree this volatilisation seems to occur, though it may be slowed down by the presence of the dung crust, inhibiting gaseous exchange between dung interior and the ambient air. In effect, the fractional loss of N from dung is only about half of that from urine. The fractional loss from urine was found to be about one quarter of the deposited N, in both experiments. This high consistency suggests that this loss rate is probably representative for warm late-summer conditions in NZ.

5.4 Relevance of results for NZ's N_2O inventory

In the first experiment, after 6 d the pH in the urine patches had dropped to less than 7, hence the observed fractional N loss until then is considered to be the total volatilisation loss. This value, of 25.7 (±0.5) %, is at the upper end of the results of Sherlock and Goh (1984), which ranged from 12.2 to 24.6 %, but is typical for the warm summer conditions of this experiment. The mean soil temperature for the first four days, when the bulk of the emissions occurred, was about 19 °C, compared to an annual average for NZ of about 12 °C. Mean soil temperature, N loss from urine and its timing in the second experiment were similar to those in the first.

If, in the first experiment, temperature was reduced by 7 K and all other parameters were unchanged, then the resulting Q_N would be reduced in three ways: by a factor 0.59 on average due to changed equilibrium between $[NH_4^+]_{aq}$ and$[NH_3]_{aq}$, by a factor 0.76 on average due to changed equilibrium between $[NH_3]_{aq}$ and $[NH_3]_g$ (i.e. $C_{N,w}$), and by a factor 0.96 due to reduced D_g. Combining these effects, only 43 % of the original Q_N would result. This figure is misleading, however, because a temperature reduction would also slow the urea hydrolysis after urine deposition, and consequently the temporal evolution of the pH would follow a different trajectory, peaking later and lower but also declining to background values more slowly (Sherlock and Goh 1984). The cumulative N loss would still be expected to decrease with decreasing temperature, but not by as much as the combination of the three direct temperature effects on volatilisation suggests.

In the second experiment, the NH_3 volatilisation loss was determined from a distribution of excreta that was representative for cattle grazing highly digestible pasture, as is widespread

farming practice in NZ. The N loss from this combination of urine and dung, expressed as the fraction of N deposited, was 22.4 (±1.3) %, which is in relative terms 13 % less than from urine only in the first experiment. This was because the N loss fraction from dung, estimated at 11.6 (±2.7) %, was less than half the N loss fraction from urine. Again, this value can be taken as an upper limit for NZ, typical for the warmest part of the year, based on the same considerations of temperature effects as above. These considerations hold for dung, too, because the essential steps for NH_3 volatilisation are the same as in urine-treated soil, namely: urea hydrolysis, NH_3 formation in the liquid phase, equilibrium transition into the gas phase, and diffusion through a porous medium into the atmosphere. Total volatilisation rates are reduced because some of these steps are interfered with by other processes in the dung, but a positive correlation of NH_3 emissions with temperature can still be expected.

When Sherlock et al. (2008) reviewed results from 18 experiments in NZ, they found the fraction of applied N that volatilised from urine to be 16.0 (±3.6) % (mean ± SE). The results of the present experiments are fully compatible with these earlier experiments when the temperature dependence is taken into account. The review of Sherlock et al. (2008) also showed that NH_3 volatilisation from dung is generally found to be much less than from urine, with reported N losses averaging just 1.5 % from studies in England (Ryden et al. 1987) and Finland (Saarijärvi et al. 2006) and 4.5 % from chamber studies carried out on dung in New Zealand (Sugimoto et al. 1992). Again, the present results are compatible with these figures.

6 Conclusions

In two experiments, one with a regular urine-patch pattern deposited onto pasture, the other with cattle excreta in-situ, the observed NH_3 emission rates were consistent with each other, and also with emission rates found elsewhere in similar weather conditions. Expressed as fractions of deposited nitrogen, the N losses were 25.7 (±0.5) % from the urine-patch pattern, and 22.4 (±1.3) % from the cattle excreta. As both experiments were conducted at the warmest time of the year, the emission rates were at the upper end of the range that can occur in NZ. Taking the positive correlation between temperature and volatilisation rate into account, the observed emission rates are compatible with an annually-averaged emissions factor $Frac_{GASM}$ of 10 %, for urine and dung combined.

The comparison of micrometeorological methods in the first experiment showed that the ZINST method agreed well with the MB method. The MB method has the better precision,

here giving the cumulative emissions over 6 d with 2 % relative error, compared to 3 % for the ZINST method. As the latter requires fewer NH_3 samplers, it is well-suited to be used for comparative studies of different treatments. The BLS method underestimated the emission rate by 10 to 24 % (dependent on which measurement height was used), because of the requirement to specify mean wind speed and mean concentration as input parameters, instead of the measured mean horizontal flux. This underestimate is an issue specific to the use of the Leuning samplers and would not arise in experiments where wind speed and NH_3 concentration were measured with separate instruments.

The simple multiple-resistance model for emissions from urine patches (Laubach et al. 2011) offers the potential to replace, at tolerable reduction of precision, any direct measurements of the NH_3 emission rates by estimates obtained from repeated sampling of a suite of soil parameters within the urine-affected area. The modelled NH_3 source depths were of the correct magnitude, but it also became apparent that for good accuracy of emission rates it would be necessary to characterise the vertical distribution of the applied N accurately.

Finally, a somewhat unexpected, practical conclusion from the second experiment is that the NH_3 electrode is not a suitable instrument to analyse samples from sites where dung pats or animals are present, because of its cross-sensitivity to amines.

7 Recommendations

Sherlock et al. (2008) recommended that NZ uses a country-specific emission factor $Frac_{GASM}$ of 0.1 in its greenhouse gas emissions inventory. The NH_3 emission rates in the two present experiments are in good agreement with previous results reviewed by Sherlock et al. (2008), hence their recommendation is upheld.

For further refinement of the inventory, it may be considered to implement separate emission factors for urine and dung, the former somewhat greater than 0.1 and the latter less than 0.1. Such a split may not be practical on its own merits. However, if NZ decided in the future to account for the direct N_2O emissions from urine and dung separately, instead of using a single factor $EF3_{PR\&P}$, then doing the same for the indirect emission pathways from excreta would provide consistency. In that case, it would probably be straightforward to implement such a split because the required activity data would be the same for direct (N_2O) and indirect (NH_3) emissions.

One aspect that is still not very well understood is the role of soil moisture in the volatilisation process, in particular when short-term changes occur, due to precipitation or irrigation. It is recommended to fund more research in this area. To this end, the ZINST method, applied to side-by-side comparisons of irrigated and non-irrigated plots, could be combined with soil sampling and resistance modelling as tested in this project.

8 Acknowledgements

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Appendix – Directional distribution of dung in Experiment 2

It is to be tested whether the observed variation in dung pat numbers between 4 (of 21) triangular segments is consistent with a "random" distribution, i.e. equal chance for any location within the fenced area to be defecated on. For this test it is assumed that each of the selected segments represents 4.9 % of the total area (in practice, they varied from 4.7 to 5.2 % except for the smallest, which was only 2.2 % of the area). The 445 defecations are treated as independent repetitions of a chance experiment. The probability of one defecation to be inside a certain test segment, p, is thus $p = 0.049$, and to be outside of it is $1 - p = 0.951$. The probability for finding a certain number, m, of a total of $M = 445$ dung pats inside the segment can be computed with the binomial distribution:

$$P(m) = p^m \ (1-p)^{M-m} \ M!/[m!\ (M-m)!]$$

where "!" is the faculty symbol, i.e. $m! = 1 * 2 *...* (m-1) * m$.

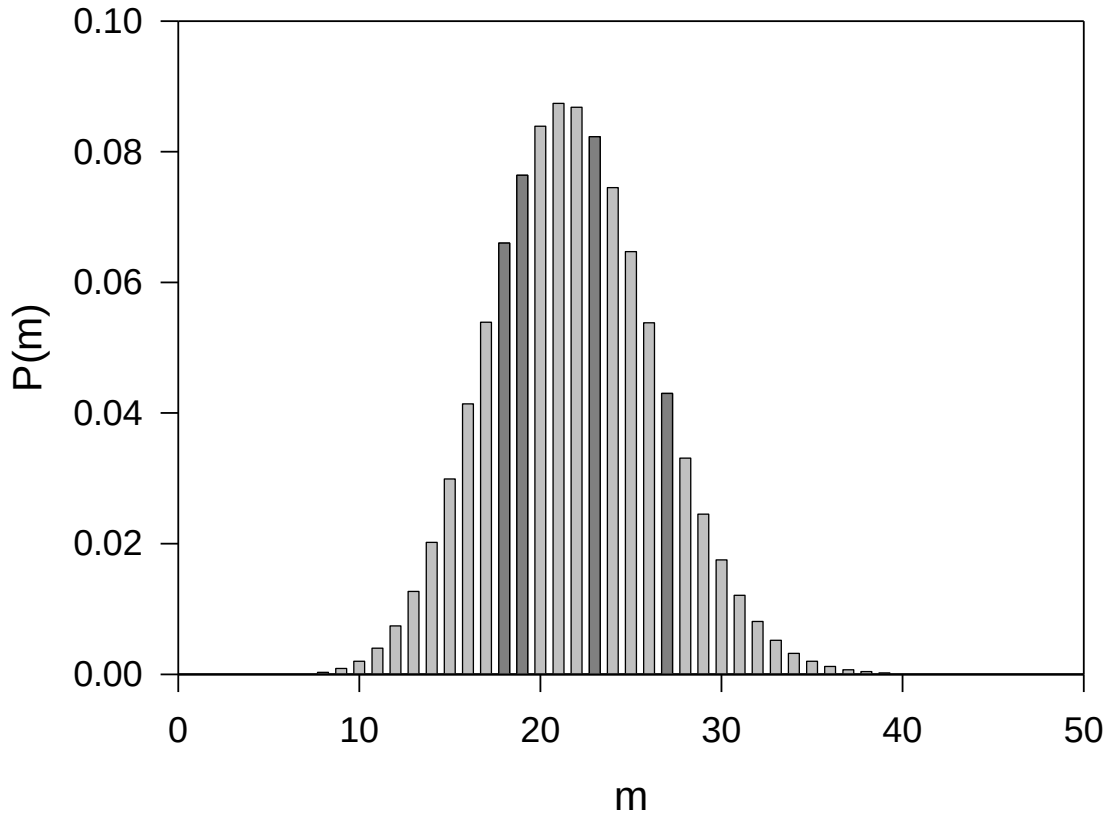

Fig. A1 Probability distribution for m dung pats (of a total of 445) to be found in a given segment that covers 4.9 % of the total area. Darker columns mark the dung pat numbers that were actually observed.

This distribution is shown in Fig. A1. The most likely count is 21 dung pats in a segment. The probability to find ±10 % of that number, i.e. 19 to 23 pats, is 41.7 %, and the probability to find ±20 % of that number, i.e. 17 to 25 pats, is 67.6 %. Two of the four counts fall into the ±10 % region, and three of the four into the ±20 % region. Hence, the observed distribution of the four counts is as close to the statistical prediction as possible. This gives strong support to the hypothesis that the dung pat distribution was random. Since both dung and urine distributions are closely coupled to the time of cattle presence (White et al. 2001), we infer that the urine distribution was spatially random, too. It then follows that there is a high likelihood for the ammonia emissions from the dung and urine deposited in the fenced area to be statistically uniformly distributed.