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Ammonia emissions from cattle urine and dung excreted on pasture

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Abstract. Twelve cattle were kept for three days in a circular area of 16 m radius on short pasture and fed with freshly-cut pasture. Ammonia (NH_3) emissions from the urine and dung excreted by the cattle were measured with a micrometeorological mass-balance method, during the cattle presence and for 10 subsequent days. Daily-integrated emission rates peaked on Day 3 of the experiment (last day of cattle presence) and declined steadily for five days thereafter. Urine patches were the dominant sources for these emissions. On Day 9, a secondary emissions peak occurred, with dung pats likely to be the main sources. This interpretation is based on simultaneous observations of the pH evolution in urine patches and dung pats created next to the circular plot. Feed and dung samples were analysed to estimate the amounts of nitrogen (N) ingested and excreted. Total N volatilised as NH_3 was $19.8\,(\pm 0.9)\,\%$ of N intake and $22.4\,(\pm 1.3)\,\%$ of N excreted. The bimodal shape of the emissions time series allowed to infer separate estimates for volatilisation from urine and dung, respectively, with the result that urine accounted for $88.6\,(\pm 2.6)\,\%$ of the total NH_3 emissions. The emissions from urine represented $25.5\,(\pm 2.0)\,\%$ of the excreted urine-N, while the emissions from dung amounted to $11.6\,(\pm 2.7)\,\%$ of the deposited dung-N. Emissions from dung may have continued after Day 13 but were not resolved by the measurement technique. A simple resistance model shows that the magnitude of the emissions from dung is controlled by the resistance of the dung crust.

1 Introduction

Ammonia (NH_3) is generated at the soil surface, often in abundant quantities, shortly following the surface application of any source of ammoniacal-N (NH_x-N, combining NH_3-N and NH_4^+-N) that also induces an increase in soil-surface pH. Sources include urea and other ammoniacal fertilisers, ammoniacal wastes and ruminant urine (Sherlock et al., 1995). Such NH_3 is susceptible to volatilisation at rates which can vary extensively depending on the crop, cultural conditions, soil properties, dung or urine deposition rates and method of fertiliser application: e.g. for urea from 1.7 % to 56 % of the applied N (Ryden et al., 1987; Jarvis et al., 1989; Sherlock et al., 1989, 2008), or for slurry from 4 % to over 60 % (Sintermann et al., 2012). Ammonia volatilisation from agricultural soils is a dominant factor in the formation of atmospheric secondary aerosols due to its reaction with nitric and sulphuric acids in the atmosphere (Nemitz et al., 2009). These aerosols contribute to the formation of acid rain (Bobbink et al., 1992). Ammonia volatilisation decreases methane (CH_4) oxidation rates in soils (Mosier et al., 1997), and acts as an indirect source of nitrous oxide (N_2O) when the NH_3 is deposited downwind onto land surfaces (van der Eerden, 1982; Bobbink et al., 1992; Barthelmie and Pryor, 1998). As NH_3 is emitted, it is transported away from the soil surface by the wind both vertically and horizontally. These conditions are far removed from those typically experienced under laboratory conditions and consequently emissions under field conditions can differ substantially from NH_3 volatilisation losses measured in the laboratory (Fenn and Hossner, 1985).

Ammonia emissions can be measured under field conditions by micrometeorological methods. Laubach et al. (2012) compared several such methods to measure and model the NH_3 emissions from a circular plot of pasture soil, of 15 m radius, which had been treated with dairy cow urine deposited in a regular array of 132 "urine patches". The treatment rate used simulated the urine amounts and number of urination events expected from a dozen dairy cows grazing that area for 24 h (thereby simulating a grazing time and stocking density that are typical for rotational grazing practice on dairy farms in Canterbury, New Zealand). Laubach et al. (2012) concluded that of the tested methods, the mass-budget method was the most accurate. This method is applied in the experiment reported here, which represents a more realistic farming situation where the emissions from both urine and dung are measured as they are excreted by the cattle in situ. Similar experiments were conducted by Bussink (1992, 1994) in the Netherlands.

Apart from the practical challenges of handling live cattle around measurement equipment, an added difficulty of the in-situ approach is that neither the amounts of excreta deposited, nor their N contents, can be controlled. These can, however, be estimated, provided the feed intake of the cattle is known. In order to control, measure and chemically characterise the feed intake in this experiment, the cattle were prevented from grazing by mowing the pasture prior to the start, and offering them grass that had been freshly harvested nearby ("cut and carry"). While the provision of feed as such resembles feedlot practice rather than grazing, the experimental setup differed from true feedlots in several important aspects: the feed composition provided was equal to that in a grazing situation, the excreta were deposited on pasture soil with short herbage cover and left to their natural decomposition processes, and the cattle were removed after 3 d, leaving the excreta undisturbed after that time while NH_3 emissions were continuously measured until close to the resolution limit of the measurement method.

The results of this experiment therefore quantify the combined effect of NH_3 emissions from urine and dung, in conditions similar to a real rotational-grazing practice, and in weather conditions comparable to the experiment of Laubach et al. (2012). The observed emissions are further interpreted in the context of conversion processes in the dung, which were simultaneously investigated by analysing samples repeatedly taken from dung pats that had been created in a controlled fashion.

2   Materials and methods

2.1   Site and schedule

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 Temple-ton silt loam (N. Smith and P. Almond, Lincoln University, personal communication, 2011). A circle with 16 m radius was fenced as the experimental plot and the pasture mown to ca. 5 cm height. For the first three days, 12 non-lactating cattle with average live-weight of 470 kg were kept in the experimental plot. The stocking density represented by this setup (150 animals ha^{-1}) was typical for rotational grazing practice in New Zealand, but the cattle-presence period was 3 to 6 times longer than the feed supply in a real-world grazing situation would normally last. This longer period was chosen so that a sufficient amount of urine and dung was deposited to produce a well-resolvable NH_3 emission signal. Implications of the higher excreta density are discussed in Sect. 4.1.

The cattle were excluded from an area of 1.4 m radius in the centre of the circle, where the NH_3 samplers were installed. Meteorological and soil measurements (details below) were conducted outside the circle, ca. 40 m E of the circle's centre.

The start of the experiment was defined as the time when the cattle entered the fenced circle, at 16:05 LT on 8 March 2011. The cattle departed at 16:20 LT on 11 March, 3.01 d later, and the NH_3 measurements were discontinued in the morning of 21 March, at 12.75 d.

2.2   Feed supply and analyses

The cattle were provided with freshly-cut pasture made up mainly from ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*). The feed originated from a paddock nearby. It was provided *ad libitum*, twice daily, at 9:00 LT and 16:00 LT. The feed was laid out around the perimeter of the plot, to encourage the cattle to spread evenly across the area – which they did, judging from casual observation of their behaviour as well as from the distribution of dung pats, inspected after the cattle had left.

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, any refused feed from the previous day was raked together and also weighed and its DM content 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 being 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.

2.3 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 to measure pH and take samples for laboratory analyses. These urine patches and dung pats were placed outside the circular cattle area, near the meteorological sensors. On each of four subsequent afternoons, firstly when the cattle entered the circle and finally when they departed, one urine patch and two dung pats were created. The daily intervals were intended 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 required had been collected at the Lincoln University dairy farm and was stored at 4 °C until needed. The urine patches were created with the method of Laubach et al. (2012): for each patch, 1.5 L urine was poured from a plastic bottle into a funnel with bendable tubing attached to the outlet. The tubing outlet was at 1.2 m above ground, and the urine ran out within 15 to 20 s, covering a soil area of about 0.25 m^2.

The dung was collected inside the experimental plot, 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, 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 crust and dung interior samples were frozen, then weighed and placed in a freeze-dryer (FD 5.5, Cuddon Ltd., Blenheim, NZ) for 48 h. After that they were re-weighed and their gravimetric moisture contents were determined. The amounts of ammonium-N (NH$_4^+$-N), nitrite-N (NO$_2^-$-N), nitrate-N (NO$_3^-$-N) were obtained with a twin-channel flow injection analyser (FS 3000, Alpkem, College Station, TX, USA). Total C and N of dung subsamples were obtained with the same elemental combustion method as for the grass samples.

Since a hard hydrophobic crust formed quite rapidly on the dung pats, their surface pH was measured in the field, using a portable pH electrode (HI 9025, Hanna Instruments, Woonsocket, RI, USA) with a flat-surface electrode (Broadley-James, Irvine, CA, USA). 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 also on the surface of each urine patch. Each measurement consisted of five replicate readings, taken at different locations on the surface. The pH of the dung interior was determined less frequently, using

the samples taken to the lab, with the same portable electrode as in the field.

2.4 Meteorological and soil measurements

Wind speed was measured by five cup anemometers (A101M, Vector Instruments, Rhyl, Co. Clwyd, UK) with matched calibrations. They were installed at five sampling heights, 0.25, 0.50, 0.75, 1.25 and 2.10 m above the ground on a mast 40 m E of the circle's centre. Rainfall was recorded by a tipping-bucket rain gauge (Ogawa Seiki, Tokyo, Japan) with a resolution of 0.167 mm. Soil temperature was measured by thermocouples buried at two depths (2 and 5 cm), in two replicates, near the wind profile mast. Soil moisture was monitored continuously with five water content reflectometers (CS-616, Campbell Scientific, Logan, UT, USA). These were buried horizontally, four of them at 2 cm depth, one under each urine test patch, and one at 5 cm depth in urine-free soil. The soil moisture data were corrected for temperature in post-processing. All meteorological variables were recorded by a datalogger (CR-3000, Campbell Scientific, Logan, UT, USA), as 10-min averages.

2.5 Ammonia collection and mass-budget method

NH$_3$ emission rates were determined with the micrometeorological mass-budget method (Beauchamp et al., 1978; Denmead, 1995). In the centre of the fenced circle, vertical profiles of the horizontal NH$_3$ flux were measured with "Leuning samplers" (Leuning et al., 1985). These devices have a vertical rotation axis that allows them to point into the wind and respond quickly to wind direction changes, similar to a wind vane. As air passes continuously through a sampler, the NH$_3$ content of that air is completely removed by reaction with a solid oxalic acid coat. This coat must be applied to a complex array of internal surfaces prior to sampling. At the end of the sampling period, the sampler needs to be exchanged for an identical one in order to continue collection, while the reaction product, (NH$_4$)$_2$C$_2$O$_4$ (ammonium oxalate), is retrieved in the lab by a discharging procedure (described in Laubach et al., 2012) and converted to NH$_x$ in aqueous solution.

NH$_3$ samplers were installed at the same five heights as the cup anemometers. A simple mass budget is constructed in the atmospheric surface layer, for the vertical plane that contains the measurement mast and is aligned with the wind direction. In this mass budget, all the NH$_3$ gas carried horizontally past the mast (in the centre of the source area) must originate from surface sources along the radius of the circular plot upwind of the mast, except for a background contribution carried by the air entering the circle at its perimeter. This background contribution is assumed height-constant. To quantify it, a sixth sampler was installed at 2.10 m height ca. 50 m away from the circle's centre. To ensure in practice that this sampler operated in upwind air, it was mounted

on one of four masts that had been placed to the NW, NE, SE and SW, whichever suited best the anticipated wind direction. Further details concerning the evaluation of the NH_3 profiles and subsequent computation of the NH_3 emission rate are given in Laubach et al. (2012) and in the Supplement.

Nighttime NH_3 collection periods were 14 to 16 h long. During the cattle presence and the following two days, day-time collection periods lasted 4 h. They were increased to 5 h for the next two days and then to a single day-time period, between 7 and 8 h long, for three days. The final collection period lasted 64 h (three nights and the two intervening days).

2.6 Ammonia analysis

Solutions extracted from the NH_3 samplers were initially analysed with an ion-specific electrode (ISE-10-10-00, HNU Systems, Newton, MA, USA), as in Laubach et al. (2012). 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, the same as for the dung analyses) and on a clinical chemistry analyser (Daytona LT090, Randox Ltd., Crumlin, Co. Antrim, Northern Ireland). 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 by a factor 2 to 3 smaller than deter-mined by the NH_3 electrode calibrated against these stan-dards. From considerations detailed in the Appendix, it was concluded that the electrode was strongly sensitive to the presence of volatile amines, which were probably eructated by the cattle.

Subsamples from all NH_3 collections were thus re-analysed in a single batch on the clinical chemistry analyser (CCA). 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 (Laubach et al., 2012). 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.

As an additional check, two selected samples were anal-ysed for their total Kjeldahl nitrogen content (Hill Laborato-ries, Hamilton, New Zealand).

3 Results

3.1 Soil and weather conditions

Some rain fell prior to the experiment, on 5 and 6 March, and the soil dried from 0.17 to 0.10 $m^3 H_2O (m^3 soil)^{-1}$ dur-ing the first week of measurements (Fig. 1). Only a negligible
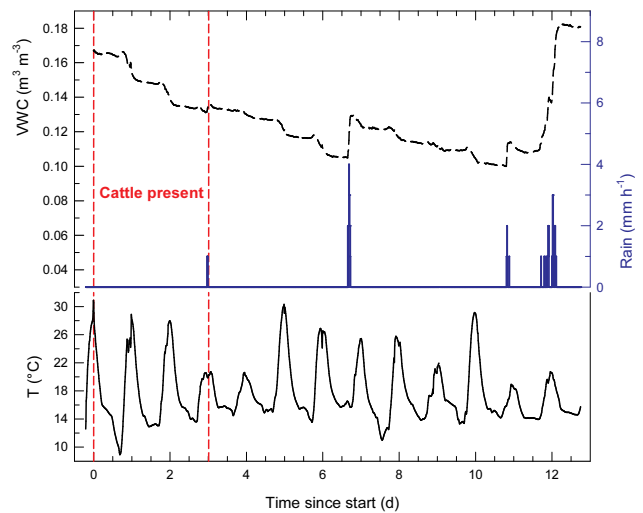

Fig. 1. Temporal evolution of volumetric water content (top) and soil temperature (bottom) at 2 cm depth, as well as rainfall intensity (centre). The origin of the time axis is at 16:05 LT on 8 March 2011, when the cattle entered the circular plot.

soil moisture increase was observed when 0.3 mm of drizzle fell at 2.98 d, just before the cattle departed. Rain events that noticeably increased soil moisture occurred on three occa-sions: 3 mm at 6.66 to 6.72 d after the start of the experiment, 1 mm at 10.81 to 10.88 d, and 5 mm intermittently between 11.72 and 12.11 d. Soil moisture measured under the urine test patches increased by 0.03 $m^3 H_2O (m^3 soil)^{-1}$ immedi-ately after their creation and gradually decreased towards background soil moisture over several days.

Soil temperature at 2 cm depth reached afternoon max-ima 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 tempera-ture 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.

3.2 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 morn-ings and 16 % in the afternoons (overall mean $\pm$ SE was 15.2 $\pm$ 0.5 %). This resulted in a total DM offered of 446 kg, of which 67 kg were refused. Each animal consumed 10.53 ($\pm$ 0.35) kg DM per day on average. Nitrogen content as a fraction of DM was determined for each feeding oc-casion, as 2.59 ($\pm$ 0.07) % (mean $\pm$ SE). The total N intake throughout the 3-d period was thus 9.81 ($\pm$ 0.42) kg, repre-senting 0.273 ($\pm$ 0.012) kg N d^{-1} animal^{-1}. Some of this N intake was retained by the cattle in the form of liveweight

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

N budget component	N amount (kg)	Fraction of N intake (%)	Fraction of N excreted (%)	Fraction of dung-N (%)	Fraction of urine-N (%)
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)		
volatilised from dung*	0.22 (0.05)	2.3 (0.5)	2.6 (0.6)	11.6 (2.7)	
volatilised from urine*	1.72 (0.05)	17.5 (0.9)	19.8 (1.3)		25.5 (2.0)

* 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 Sect. "Discussion").

(LW) gain, the balance was excreted as urine and dung (since the cattle were non-lactating). These N amounts are estimated as follows, and summarised in Table 1.

The amount of dung excreted can be estimated as a fraction of DM intake, where the fraction equals 100 % minus digestibility. The DM digestibility of the pasture was 80.3 ($\pm$ 0.6) % (mean $\pm$ SE of 6 feeding occasions), which gives the total dung DM as 74.7 ($\pm$ 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 %.) Hence, the deposited amount of dung-N was 1.93 ($\pm$ 0.08) kg.

It is estimated that each animal gained on average 1.25 ($\pm$ 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 ($\pm$ 9) kg LW gain. The amount of N retained in the weight gain is assumed to be 2.5 ($\pm$ 0.25) % of that (default value used by the Helsinki Commission of the European Union), resulting in a total of 1.13 ($\pm$ 0.25) kg N retained. This represents 11.5 ($\pm$ 2.6) % of the N intake.

Subtracting dung-N and N retained from the total N intake provides an estimate of the N amount deposited with urine, of 6.75 ($\pm$ 0.50) kg. This represents a daily per-capita excretion of 0.188 ($\pm$ 0.014) kg N d^{-1} animal^{-1}. Combining urine-N and dung-N, the total amount of excreted N was 8.68 ($\pm$ 0.49) kg, equivalent to an average application density of 111 kg ha^{-1}. Urine accounted for 77.8 ($\pm$ 1.6) % and dung for 22.2 ($\pm$ 1.6) % of the excreted N.

3.3 Ammonia emissions

The evolution of NH_3-N emission rates is shown in Fig. 2, along with the mean N excretion rates, estimated as the
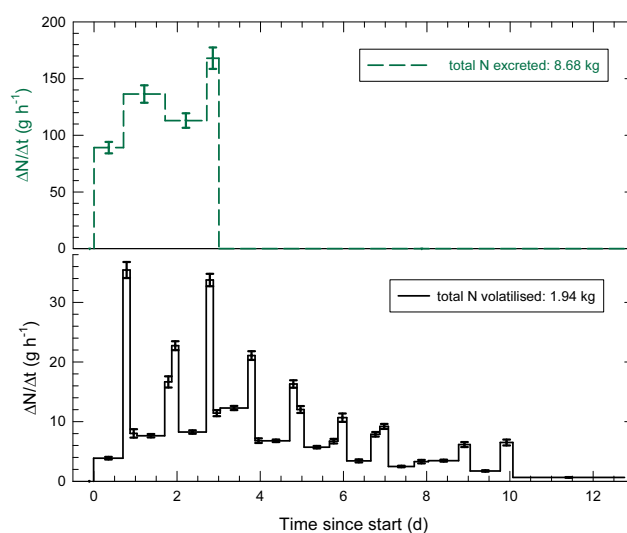

Fig. 2. Temporal evolution of N excretion rate of 12 cattle during their 3-day presence, estimated as the difference of N intake and N retained (top), and NH_3-N volatilisation rate (bottom). Error bars for the latter represent estimated measurement uncertainty and are placed at the mid-times of the NH_3 collection periods, whose lengths are marked by the horizontally constant parts of the connecting solid line.

difference of N intake and N retained. 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 nighttime emissions (nighttime periods are recognisable by their longer duration). These variations are in response to the diurnal temperature cycle and are similar to those observed by Laubach et al. (2012). 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 $12.0 \mu g \, N \, m^{-2} \, s^{-1}$. After the cattle had departed, emission rates stayed high for another day. For the remaining 9 days, volatilisation rates generally decreased. 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 was 1.94 kg N, with a cumulative propagated standard error of 0.02 kg N, computed as described in Laubach et al. (2012). This represents $19.8 \, (\pm 0.9) \, \%$ of the cattle's N intake and $22.4 \, (\pm 1.3) \, \%$ of the N excreted (Table 1). Expressed per area, the N loss was $24.7 \, kg \, ha^{-1}$.

3.4 Evolution of pH in urine patches and dung pats

Figure 3 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 soil surface 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. 2). Six days after the start, the pH had fallen to below 7.7 for all patches. The two major rainfall events, with 3 mm and 5 mm yield, caused temporary increases in urine patch surface pH and synchronised the subsequent pH evolution for all four patches. 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. 3, 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 $9.5 \, (\pm 0.1)$. 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 elevated, at $8.8 \, (\pm 0.2)$, and consistent between pats.

For each dung pat, the interior pH (Fig. 3, 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 $8.4 \, (\pm 0.2)$, still markedly above neutral.

3.5 Moisture and mineral N of dung samples

The dung-interior samples contained 66 to 89 % water on a mass basis (mean $\pm$ SE of 48 samples: $82.7 \pm 0.6 \, \%$), 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 $\pm$ SE of 37 samples was
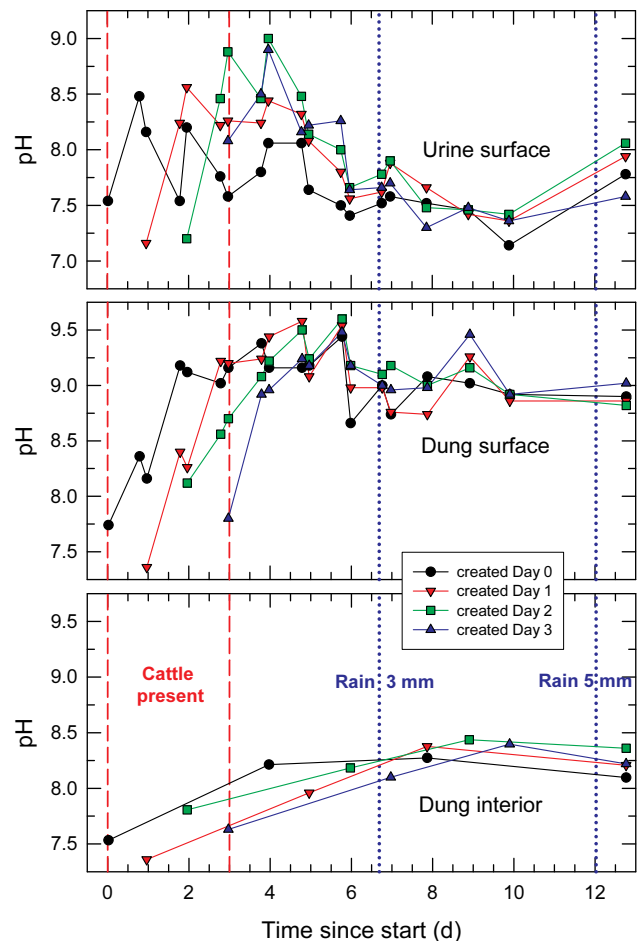

Fig. 3. Temporal evolution of pH on urine patch surfaces (top panel), dung pat surfaces (middle) and inside dung pats (bottom). The period of cattle presence is indicated by vertical dashed lines, and the two rain events with more than 1 mm yield are marked by dotted lines.

$49.7 \pm 2.8 \, \%$). The variability may partly stem from incomplete separation of dung interior material sticking to the crust sample.

The NH_x-N content of the dung interior was significantly correlated to pH measured in the same samples (Fig. 4a), while $[NO_2^- \text{-N}]$ and $[NO_3^- \text{-N}]$ of the dung interior were not significantly correlated to pH ($R^2 = 0.08$ for either species, not shown). For the dung crusts, neither $[NH_x \text{-N}]$ (Fig. 4b) nor $[NO_2^- \text{-N}]$ nor $[NO_3^- \text{-N}]$ correlated to pH.

4 Discussion

4.1 Ammonia loss fractions

The extent of NH_3 volatilisation from dung tends to be much less than from urine with reported N loss fractions from dung averaging just 1.5 % from studies in England (Ryden et al.,
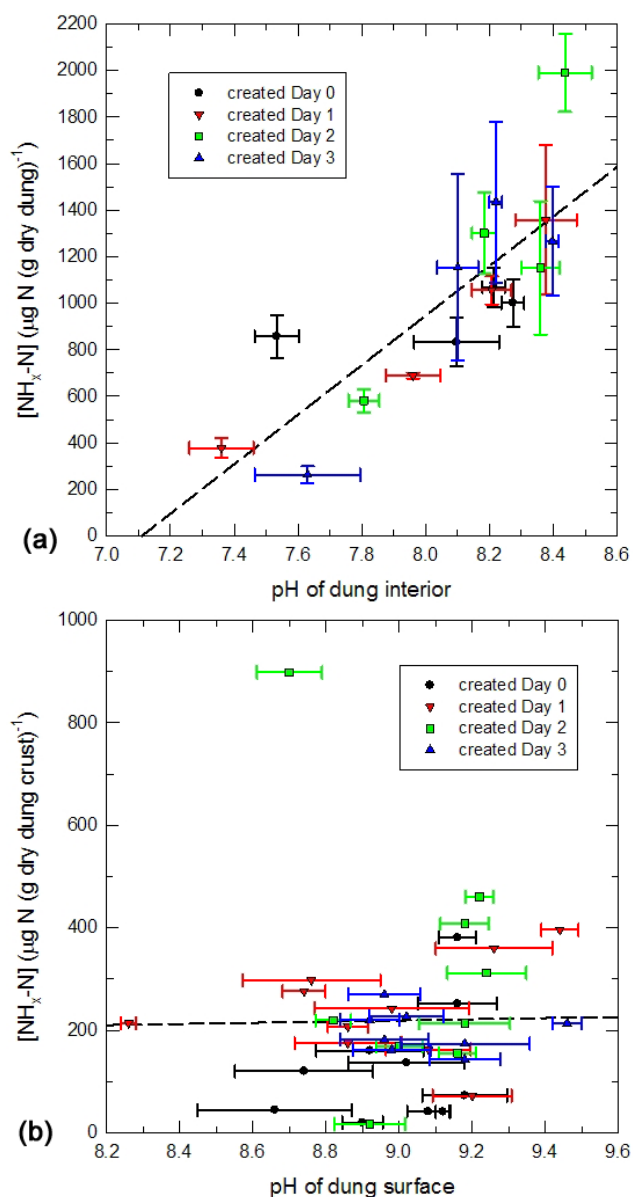
Fig. 4. (a) NH_x-N concentration in samples from the dung interior versus pH of the same samples. The different dung pats are identified by different symbols (same as in Fig. 3). Error bars mark standard errors of the mean of 3 replicates. The dashed line represents linear regression ($R^2 = 0.66$). **(b)** Same for NH_x-N concentration of dung-crust samples versus pH on the dung surface (mean of 5 replicates). The linear regression has $R^2 = 0.0003$.

1987) and Finland (Saarijärvi et al., 2006) and 4.5 % from chamber studies carried out in New Zealand (Sugimoto et al., 1992). The proportion of total urinary-N volatilised as NH_3-N is typically 10 to 40 %, with the higher values during warm summer conditions and the lower values in the cooler seasons (Ball et al., 1979; Whitehead et al., 1989; Whitehead and Raistrick, 1991, 1992; Bol et al., 2004). In New Zealand, Sherlock and Goh (1984) measured NH_3-N emis-

sions for urine-treated plots of 22.2 %, 24.6 %, and 12.2 % of total urinary-N in summer, autumn, and winter, respectively. The total N losses from urine and dung combined are therefore most likely of order 10 to 30 %. The present result of 22.4 % N loss falls into this range, yet the range of reported measurements is even wider, from 3 to 52 % (Petersen et al., 1998).

Past experiments similar to the present one were undertaken by Bussink (1992, 1994), with cattle grazing circular plots repeatedly over the course of a year, and fertilisation of the pasture following each grazing occasion. There, the N loss fractions for summertime grazing events were of order 15 % only, and in the cooler seasons they were less than 10 %. The N excretion rate (urine and dung combined) reported by Bussink (1992, 1994) was typically 40 to 80 kg ha^{-1}, roughly half of that in the present experiment. The excreta density in the latter was higher because of the unrealistically long period of animal presence. A consequence of this was an increased probability for urine and dung being co-deposited in the same location, which could have increased the rate of urea hydrolysis because of the interaction of urinary urea and faecal urease. This probability can be estimated from the respective number of urinations and defecations and the average dung pat size. An approximate count of dung pats, after the cattle had departed, gave $N = 445 \, (\pm 23)$. Dung pat size was not measured and is guessed as $a = 0.1 \, m^2$. Given the fenced surface area $A = 785 \, m^2$, the dung cover fraction was thus $p = Na/A = 0.057$. This is the probability for a single urination to occur in a defecation's location (regardless of the timing of both events). For cattle, urination counts are typically about 80 % of defecation counts (Haynes and Williams, 1993; White et al., 2001), which gives an estimated total of 356 urinations. Using the binomial probability distribution, it results that the most likely number of urine patches being co-located with a dung pat was 20. The occurrence of 20 co-locations would imply that 5.6 % of all urine-N and 4.5 % of all dung-N was potentially subject to interaction with each other. However, even if such interaction altered the volatilisation rate considerably (e.g. doubled it), the effect of that on the total N volatilised would still be small (of order 5 %).

Bussink (1994) showed for his data that on an annual basis, the amount of N lost as NH_3 increased more than linearly with increasing amount of N applied. Hence, the higher N application rate in the present experiment may have been a cause for the N volatilisation rate to be higher than in Bussink's studies. However, when Laubach et al. (2012) mimicked a realistic urine application pattern for grazing cattle, the NH_3 loss amounted to 25.7 (± 0.5) % of the applied urine-N, similar to the present experiment, while the application rate had been equivalent to 30 kg ha^{-1} only. This suggests that the N application rate may be less important than other factors in controlling N loss rates. Incidentally, in the figure of Bussink (1994) showing the dependence of annual N loss on N application, the slope for high amounts of applied N approaches 0.22, predicting that 22 % of any

N applied in addition to already high N levels would be volatilised. The present results are compatible with this finding.

4.2 Contributions of urine and dung to ammonia volatilisation

In the present experiment, the daily N losses increased during the first 3 d, while excreta were being voided onto the experimental plot, and then decreased during the following 5 d. This pattern was 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 was larger than on Day 8 (Fig. 5). This secondary maximum in the NH_3 loss trajectory occurred at the same time that the pH of the dung interior reached its overall maximum, and the pH of the dung surface attained a secondary maximum (Fig. 3). It thus appears plausible that the secondary maximum in NH_3 emissions on Day 9 was caused by volatilisation from dung, and that dung emissions also provided 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 supports the interpretation that a peak in dung emissions at about 9 d in the current experiment was plausible. It also suggests that volatilisation from dung probably continued at low levels after 13 d, but sampling ceased then because the collected NH_3 amounts approached the resolution limit of the method.

In Fig. 5, the transition between the NH_3 emissions mainly from urine to those mainly from dung is indicated by a vertical dashed line at 8 d. In reality there is an overlap of the two modes, but for budgeting purposes this 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, with an uncertainty estimated as 0.05 kg N for either, to account for the crude separation method. This implies that $88.6\,(\pm 2.6)\,\%$ of the volatilised N originated from urine, an even larger fraction than the urine fraction of the deposited N ($77.8\,\%$). Relative to the total N excreted, the emissions from urine and dung represent $19.8\,\%$ and $2.6\,\%$, respectively (Table 1). Relative to the amounts of urine-N and dung-N, of 6.75 kg and 1.93 kg, respectively, they represent loss rates of $25.5\,(\pm 2.0)\,\%$ from urine and $11.6\,(\pm 2.7)\,\%$ from dung. The value for urine agrees with that from Laubach et al. (2012), obtained in similar weather conditions. The value for dung exceeds the numbers cited at the start of Sect. 4.1,
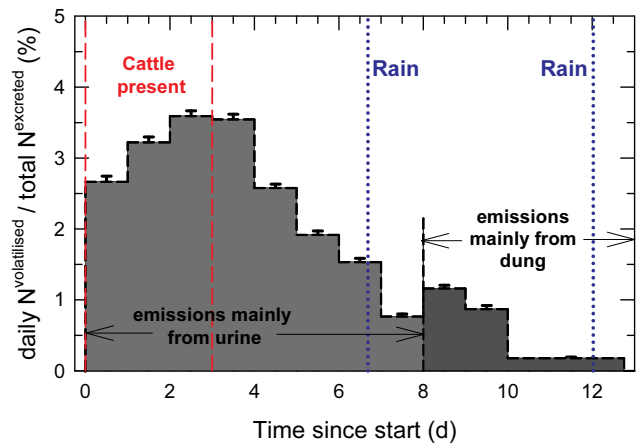

Fig. 5. Day-to-day evolution of N loss fraction due to volatilisation, relative to the amount of N excreted by 12 cattle over the first 3 days. The vertical dashed line at 8 d marks when N loss rates cease to be dominated by volatilisation from urine, and emissions from dung probably begin to constitute the major fraction. The times of the two rain events with more than 1 mm yield are marked by dotted lines.

but may still be an underestimate because it potentially excludes emissions after 13 d. Nevertheless, it is less than half the loss rate for urine, hence for refined NH_3 inventories it may be justified to define different emission factors for urine and dung.

Even though the urine–dung split inferred here is only based on plausibility arguments, there is no doubt that the absolute amounts of N volatilised from urine are typically one magnitude larger than those from dung. After 6 d, the soil surface pH had fallen to below 7.7 for all urine patches. By this time, the area-integrated NH_3 emission rate had dropped to less than $10\,g\,N\,h^{-1}$ (Fig. 2), and $79\,\%$ of all observed emissions had occurred. The main trends for urine patch surface pH and NH_3 emissions are thus correlated, as has been shown previously (Laubach et al., 2012).

4.3 Processes controlling the volatilisation from urine and dung

The essential steps for NH_3 volatilisation from dung are the same as in urine-treated soil, namely: an elevation in the pH of the volatilisation surface, NH_4^+ formation in the liquid phase, equilibrium transition of that NH_4^+ into NH_3 in the gas phase, and its diffusion through a porous medium into the atmosphere.

In the case of urine, the elevation in soil surface pH and the formation of NH_4^+ is a direct consequence of the hydrolysis of the urea contained in the urine (Sherlock and Goh, 1985). At summer temperatures, hydrolysis tends to be nearly complete within a few hours, leading to rapid pH rise and high volatilisation rate in the first couple of days. The same is true for surface-applied slurry (Spirig et al., 2010), where the urea

Table 2. Estimation of variables required for a resistance-model description of the NH_3 volatilisation from dung pats, analogous to that for urine-treated soil patches by Laubach et al. (2012), for Days 6 to 13.

Model variable	Obtained range	Input variables	Method, or Equation in Laubach et al. (2012)
dung temperature	16.0 to 28.5 °C	soil temperature	extrapolated to surface ratio of inputs
$[NH_x\text{-}N]_{aq}$	207 to 396 µg mL^{-1}	$[NH_x\text{-}N]$ in dry dung, $[H_2O]$ in dung	(6), (7)
$C_{N,w}$ (gaseous equilibrium $[NH_3\text{-}N]$ within dung)	4.3 to 24.0 mg m^{-3}	pH of dung interior, dung temperature, $[NH_x\text{-}N]_{aq}$	
r_a (aerodynamic resistance from ground to height z)	11 to 117 s m^{-1} [a, b]	wind speed, stability parameter	(9)
r_b (laminar boundary-layer resistance)	9 to 44 s m^{-1} [a]	friction velocity	(12)
$C_{N,s}$ (mean gaseous $[NH_3\text{-}N]$ at the soil/dung surface)	23 to 224 µg m^{-3}	C_N (concentration at height z), Q_N (emission rate of $NH_3\text{-}N$), r_a, r_b	(16)
r_s (dung crust resistance)	94 to 960 s m^{-1} [c]	$C_{N,w}$, $C_{N,s}$, Q_N	(22)
tortuosity of dung	0.05 to 0.47 [d]	r_s	(18)

[a] Depends on roughness length, assumed as 0.02 m.
[b] Increases with height (maximum range given).
[c] Depends on dung cover fraction, assumed as 0.057.
[d] Depends on dung crust thickness, assumed as 1 mm.

hydrolysis is often already completed at the time of application. As volatilisation proceeds, a subsequent reduction in surface pH occurs as a consequence of the chemical transformation of NH_4^+ to NH_3 with the accompanying release of a proton into the soil solution. This re-acidifies the soil surface and after some time a surface soil pH arises which is inadequate to sustain further NH_3 volatilisation (Sherlock and Goh, 1985). In the present experiment, that time was approximately 8 d.

In the case of dung pats, the initial rise in dung-surface pH is not due to urea hydrolysis since dung contains little or no urea (Ryden et al., 1987; Kirchmann and Lundvall, 1998). Instead the rise in pH is readily explained by the transformation of the bicarbonate ion, HCO_3^-, into CO_2 (Sommer and Sherlock, 1996). In contrast to the transformation of NH_4^+ to NH_3, which releases a proton, the transformation of HCO_3^- into CO_2 releases a hydroxyl ion (OH^-) into the dung pat thereby increasing its pH. Despite a lack of urea hydrolysis, dung contains some NH_x. In the dung interior, its concentration ranged from 263 to 1990 µg N (g dry dung)$^{-1}$ (Fig. 4a), with a mean of 1024 µg N (g dry dung)$^{-1}$. The latter value represented only 4 % of the total N content of the dung, and the estimated N release from dung over 13 d was 3 times larger, which means new NH_x must have been formed in the dung on a time scale of days, rather than hours, comparable to the time scale of the volatilisation process. A complete model of the dynamics of volatilisation from dung (not derived in this study) must therefore include the chemistry of NH_x formation.

In the dung interior, $[NH_x\text{-}N]$ was positively correlated to pH ($R^2 = 0.66$, Fig. 4a), almost as strongly as it was

in the urine-patch soil samples of Laubach et al. (2012), where $R^2 = 0.77$. Such a high correlation between pH and $[NH_x\text{-}N]$ in dung was also reported by Kirchmann and Lundvall (1998). The regression line in Fig. 4a has a slope of 1064 µg N (g dry dung)$^{-1}$ per pH unit and predicts vanishing $[NH_x\text{-}N]$ at a pH of 7.1, i.e. for near-neutral solution. Together with the high moisture content, these data suggest that the dung pats contained all necessary ingredients to build up considerable NH_3 volatilisation potential. The actual volatilisation rate was controlled by the permeability of the solid dung crust, discussed next.

4.4 Resistance of the dung crust to NH_3 exchange

Laubach et al. (2012) employed a simple resistance model to understand the dynamics of NH_3 volatilisation from urine-treated soil. Considering a dung pat as a porous medium, similar to the topsoil layer, the same physical principles can be applied to describe its exchange of matter with the atmosphere. To be meaningful, this approach is restricted here to the time period when emissions from urine did not overwhelm emissions from dung, i.e. from Day 6 onwards when dung pH exceeded urine pH (Fig. 3).

The model comprises three sequences of steps (Table 2). The first task is to compute the gaseous equilibrium NH_3 concentration in the dung interior, from pH, temperature, and aqueous $[NH_x\text{-}N]$ in the dung. The pH was measured in triplicate (Fig. 3). Dung temperature was estimated by extrapolating the soil temperatures from two depths towards the surface. The value of $[NH_x\text{-}N]_{aq}$ was taken as the ratio of NH_x and H_2O contents of the dung samples. This assumes that all NH_x found in the dry samples had previously been dissolved

in the moisture content of the dung, which may be an over-estimate. The resulting gaseous equilibrium $[NH_3\text{-}N]$ ranges from 4300 to $24\,000\,\mu g\,m^{-3}$, typically with 20 % uncertainty (assuming 1 K temperature error and including sampling errors of the other inputs).

The second task is to compute the atmospheric resistance and then use it, together with the measured NH_3 emission rate and NH_3 concentrations in the air, to infer the spatial average of $[NH_3\text{-}N]_g$ at the soil (and dung) surface. The atmospheric resistance consists of an aerodynamic (turbulent) part, r_a, and a laminar-boundary-layer part, r_b. Both depend on roughness length, derived as 2 cm from the wind profiles, and both decrease with increasing wind speed. Here, typical values found for $r_a + r_b$ were 50 to $80\,s\,m^{-1}$, and the resulting $[NH_3\text{-}N]_g$ at the soil surface ranged from 23 to $224\,\mu g\,m^{-3}$.

The third task is to use the measured NH_3 emission rate and the concentration difference between inside and outside of the dung crust to derive a dung crust resistance, r_s. For this to be accurate, it would be necessary that NH_3 emissions from urine had ceased. As this is not strictly true, the result should be interpreted as a magnitude estimate only. Further, the equilibrium concentration needs to be scaled with the area fraction within the circle covered by dung pats, which was estimated in Sect. 4.1 as $p = 0.057$. Multiplying the equilibrium concentration from above by p gives 240 to $1400\,\mu g\,m^{-3}$, which is a factor 3 to 12 larger than $[NH_3\text{-}N]_g$ at the soil surface. With this, r_s is obtained as 94 to $960\,s\,m^{-1}$. This is the same magnitude as the value of $119\,s\,m^{-1}$ found by Olesen and Sommer (1993) for the resistance of a thin surface crust on slurry tanks.

Since r_s was 2 to 20 times larger than $r_a + r_b$, the dung crust provided the dominant resistance to volatilisation. Assuming a typical thickness of about 1 mm, the tortuosity of the dung crust can be estimated from r_s. This gives the following values for Days 6, 7, 8, 9, 10, and 13, respectively: 0.21, 0.47, 0.11, 0.14, 0.08, and 0.05. All but the second value are within the range obtained for the soil in the experiment of Laubach et al. (2012), suggesting that the dung crust can indeed be modelled as a porous medium similar to soil. The drop in tortuosity over the last days corresponds with wetting by rain, which provides a plausible mechanism by reducing the air-filled pore space in the dung crust.

It is thus possible to understand the dynamics of the dung volatilisation with the resistance model. For the present experiment, the values in Table 2 should be taken as order-of-magnitude indications, given the various sources of uncertainty for some of the required parameters.

5   Concluding remarks

In two experiments, one with a regular urine-patch pattern deposited onto pasture (Laubach et al., 2012), the other with cattle excreta in situ, the observed NH_3 emis-sion 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 likely to occur in New Zealand.

The second experiment, reported here, also investigated some aspects of the dung processes that were different to those in urine patches. Over time the pH in the dung interior increased above 8 and was positively correlated with $[NH_x\text{-}N]$, creating conditions conducive to volatilisation. To some degree this volatilisation occurs, though it is slowed down by the presence of the dung crust, providing a resistance to gaseous exchange between dung interior and the ambient air that is about one magnitude larger than the atmospheric resistances. In effect, the fractional loss of N from dung is less than half that from urine. Here, quantification of separate volatilisation rates for urine and dung was only by inference from the bimodal shape of the emissions time series; yet this inferred result is fully corroborated by the literature cited in Sects. 4.1. and 4.2.

Appendix A

Sensitivity of ammonia electrode to volatile amines

As mentioned in Sect. 2.6, the NH_3 concentrations in the extracted solutions measured with the NH_3 electrode exceeded those measured with the CCA systematically by a factor 2 to 3. The CCA results appeared plausible and were confirmed by comparison to those obtained using an FIA. This suggests that the electrode measurements were subject to an unanticipated analytical artefact, possibly interference by other basic compounds. Volatile amines (VA) are plausible candidates for this, as they are known to be emitted from animal husbandry (Schade and Crutzen, 1995). Indeed, the independent N analysis of two samples (Hill Laboratories, Hamilton, New Zealand) found that total Kjeldahl-N exceeded $NH_x\text{-}N$ significantly, by 20 % and 100 %, respectively. Evidently, some non-NH_x-N compounds must have been present, which may have been VA. If the cattle or their dung emitted VA, these would have been collected by the NH_3 samplers and then, in the extracted solution, could have biased the electrode reading just as if additional NH_4^+ ions had been present. Such a bias could not have occurred in earlier experiments with urea fertiliser and urine patches (Sherlock et al., 1995; Laubach et al., 2012), because there were no potential sources of VA at the respective sites.

According to Schade and Crutzen (1995), trimethylamine (TMA) is the dominant VA component emitted. Kuhn et al. (2011) investigated the co-emissions of TMA and NH_3 from cattle-related sources. They found molar emission

ratios [TMA]/[NH$_3$] of 0.017 to 0.078 from rumen samples, while emission ratios for dung and slurry were 3 orders of magnitude smaller. These results suggest that cattle eructate significant amounts of TMA from their rumen contents, along the same pathway as for their CH$_4$ emissions. Dung, though, appears not to be a significant TMA source. Further, Kuhn et al. (2011) found TMA/NH$_3$ emission ratios of order 0.002 to 0.004 from hay and silage. It is unclear whether this result would apply to freshly-cut pasture. As most of the feed was eaten rather quickly in the present experiment, and refused feed was removed before offering the next round, it appears unlikely that the grass acted as a significant source of VA. It should be noted that the discrepancy between electrode and CCA was reduced after the cattle had left, but did not disappear completely: at the two uppermost heights (which measure the lowest concentrations), the ratio of electrode to CCA readings approached 1 from about Day 6, but at the lower three heights, it stayed closer to 2.

Here, it was not attempted to reproduce in detail the influence of TMA, or other VA, on measurements of known NH$_4^+$ concentrations with the electrode, since that was beyond the scope of the current study. The NH$_3$ electrode is essentially a modified pH electrode. It relies on the diffusion of NH$_3$ molecules present in the sample (which is previously made strongly basic with added OH$^-$) through a hydrophobic membrane to the electrode surface. It is known that the basicity levels of VA (CRC, 2007) are generally significantly greater than the basicity of NH$_3$, implying that even low VA concentrations, if present in the sample, could produce elevated electrode readings. For a crude estimate, it may be assumed that VA diffuse through the hydrophobic membrane like NH$_3$, and that their aqueous solubilities (i.e. Henry's Law coefficients) are comparable to NH$_3$. Then, a molar ratio of methylamine to NH$_x$-N of 0.05, or a molar TMA/NH$_3$ ratio of 0.02, respectively, would be sufficient to cause an error of a factor of 2 in the NH$_x$-N reading, thanks to the VA's greater basicity. Subsequent tests involving modest additions of trimethylamine hydrochloride (TMAHCl) to NH$_4^+$-N solutions of known concentration, made basic with added OH$^-$, did produce marked changes in electrode readings broadly consistent with the above estimates. Hence, it is likely that only small amounts of VA need to be trapped in the NH$_3$ sampler, along with the NH$_3$, for the results to be wildly inaccurate. Further investigation is needed to more fully validate this conjecture.

Supplementary material related to this article is available online at: http://www.biogeosciences.net/10/327/2013/bg-10-327-2013-supplement.pdf.

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