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Effects of dairy shed effluent dry matter content on ammonia and nitrous oxide emissions from a pasture soil

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Abstract

Atmospheric emissions of nitrogen (N) from New Zealand dairy farms are significant but have the potential to be affected by manure management prior to land application. The current work examined whether reducing cattle manure dry matter (DM) from 0.16 high DM (HDM) to 0.06 low DM (LDM), to enhance infiltration and reduce ammonia (NH₃) emissions when applied to grassland, would affect nitrous oxide (N₂O) emissions. Pasture was cut, simulating grazing, and either amended with HDM (173 kg N/ha) or LDM manure (48 kg N/ha) or left unamended. Ammonia emissions from HDM manure were higher than from LDM manure, as a flux or as a percentage of total ammoniacal nitrogen (TAN, i.e. NH₃ + NH₄⁺) applied, due to more TAN being retained near the soil surface and the higher soil surface pH under HDM manure treatment. Cumulative N₂O emissions over 37 days from HDM plots were higher than from the control but not from the LDM plots. After 5 days, the daily N₂O emission rate was larger from HDM plots than from LDM and control plots. The N₂O fluxes from LDM and HDM treatments did not differ, either as a proportion of TAN applied or as a proportion of total-N applied. Increasing DM contributed to reductions in both oxygen (O₂) availability and relative gas diffusivity, and thus potentially N₂O production. Under the conditions of the current study, lower manure DM content reduced NH₃ emissions but did not increase cumulative losses of N₂O.

Introduction

Livestock production, a major source of the greenhouse gas nitrous oxide (N₂O), comprises 0.3–0.5 of total global N₂O emissions (Oenema *et al.*, 2005). Nitrous oxide may be emitted during the storage of manure and when the stored manure is applied to pastures, or from excreta deposited while animals graze pasture. In New Zealand, manure collected on dairy farms is stored in anaerobic lagoons from where N₂O emissions are assumed to be negligible (Ministry for the Environment, 2016), and hence N₂O emissions from manure occur after application to pastures. Manure management and its subsequent application to land are also significant sources of ammonia (NH₃) emissions to the atmosphere (Beusen *et al.*, 2008); for cattle manure it is assumed that 0.35 of manure nitrogen (N) is lost as NH₃ during storage, while 0.10 is assumed lost as NH₃ if manure is applied to soil (IPCC, 2006; Hansen *et al.*, 2008).

Treatment or management aimed at reducing the emissions of a pollutant may lead to higher emissions of other pollutants, an effect referred to as pollution swapping (Stevens and Quinton, 2009; Petersen and Sommer, 2011). For example, Amon *et al.* (2006) found that both separation and aeration of cattle slurry increased NH₃ emissions, but reduced N₂O emissions resulting from manure storage and field application. Conversely, an increasingly concentrated distribution of cattle slurry and co-fermented slurry was shown to reduce NH₃ emissions, but increase N₂O emissions (Wulf *et al.*, 2002). However, there were no differences in NH₃ losses from untreated and co-fermented slurry despite a higher pH of the latter, which was assigned to higher infiltration rates (Wulf *et al.*, 2002). The relative contributions of N₂O and NH₃ emissions from manure are also influenced by animal feeding regimes, manure management and soil conditions after land application (Sommer *et al.*, 2003; Chadwick *et al.*, 2011). There remains a need to better understand the processes responsible for N₂O and NH₃ emissions from manure applied to grazed pastures.

In New Zealand, there has been little research into practices that could reduce gaseous emissions after manure application to grassland, despite a 42% increase in manure collection between 1990 and 2011 (Ministry for the Environment, 2013). To improve management of liquid manure (slurry) the physical separation of the dry matter (DM) component of slurry could be introduced using devices such as screw presses, weeping walls or anaerobic settling ponds. Lowering the DM content of slurry is a practice with a known potential to reduce

NH₃ emissions due to faster infiltration of the slurry into soil when DM is removed or reduced (Sommer and Olesen, 1991). This practice may also affect N₂O emissions, which are driven by a complex balance between soil oxygen (O₂) demand and O₂ supply (Thomsen *et al.*, 2010), both of which are influenced by manure composition. For example, reducing liquid manure DM may reduce the potential blockage of soil pores (Bourdin *et al.*, 2014), which implies that removal of DM by separation could influence N₂O emissions by increasing the diffusive supply of O₂ to sites of manure carbon (C) and N turnover. Balaine *et al.* (2013) found a well-defined optimum relative gas diffusivity (Dp/Do; where Dp is the diffusion of oxygen through soil (cm²/s) and Do is the diffusion of oxygen through air (cm²/s)) for N₂O emissions across a wide range of soil bulk densities and water contents. However, the potential effects of applied manure on Dp/Do and ensuing N₂O emissions have not been studied.

The current study hypothesized that N₂O emissions from manure-amended grassland soil would be related to Dp/Do near the soil surface, and that Dp/Do would in turn be modified by the manure DM content. This was tested by applying cattle manure (50 t/ha) with either a low DM (LDM) or a high DM (HDM) concentration to grassland soil and determining the NH₃ and N₂O emissions that ensued, while also measuring Dp/Do.

Materials and methods

Site description and treatments

The study was conducted at the Lincoln University dairy farm in the South Island of New Zealand (172°30'E, 43°38'S), where the soil (6% sand, 65% silt, 29% clay) is classified as a Wakanui silt loam (Udic Dystrachrept) (Kear *et al.*, 1967). The study site, with a soil pH of 6.0 (0–7.5 cm), was a perennial pasture with perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.), with <1% slope, on which cattle grazing was discontinued 2 months before the experiment started in order to avoid antecedent excreta effects. Pasture was cut, with foliage removed, to a height of 1–3 cm at initiation of the experiment. Cattle manure from the commercial dairy farm at Lincoln University, where cattle graze perennial ryegrass-white clover pasture throughout the entire year, was used. To simulate separation, manures were dried (see below) to determine proportion DM. Then one batch of untreated manure, at 0.06 (±0.01, *n* = 2) proportion DM, was adjusted to 0.16 (±0.01, *n* = 2) proportion DM, where error term equals standard error of the mean, by addition of solids obtained from the weeping-wall separation at the dairy milking parlour. Manure entering the weeping-wall comprised dung and urine deposited onto the concrete yard while cattle stood waiting to be milked, and water used to wash down the yard at the completion of milking. The experimental design was a randomized complete block consisting of three treatments: slurry at 0.06 DM (LDM), slurry at 0.16 DM (HDM) and a control (equal volume of water), replicated four times. The manure treatments were evenly applied to the 2 × 2 m² plots using a watering can, with spray rosette removed, at a rate equivalent to 5 mm of irrigation, corresponding to 48 and 173 kg N/ha for the LDM and HDM treatments, respectively.

Manure characterization

Manure sub-samples were centrifuged at 3500 rpm for 20 min and filtered (Advantec 5C, Advantec FMS Inc., Dublin, CA, USA). Total ammoniacal nitrogen (TAN), the sum of NH₃ +

ammonium (NH₄⁺), nitrate (NO₃⁻) and nitrite (NO₂⁻) concentrations of the manure were determined using standard colorimetric methods and an auto-analyser with detection limits for NO₃⁻-N of 0.10 mg/l, NO₂⁻ of 0.01 mg/l and TAN of 0.01 mg/l (Alpkem FS3000 twin channel analyser, EZkem Hood River, OR, USA, application notes P/N A002380 and P/N A002423). Appropriate controls and standards were used to check for colour interference. Total dissolved organic carbon (DOC) concentrations were measured on the filtered samples using a Shimadzu TOC-Analyser (TOC 5000A, Shimadzu, Australia). Total N and C in manure were determined by freeze-drying sub-samples followed by combustion under an oxygen atmosphere in an automated Dumas style elemental analyser linked to a 20–20 stable isotope ratio mass spectrometer (PDZ, Europa Scientific, Crewe, UK). Manure pH was measured with an Inlab Expert Pro pH electrode (Mettler Toledo, Switzerland) and a SevenEasy pH meter (Mettler Toledo, Switzerland). The DM concentrations of the manures were determined gravimetrically after a 24 h drying period at 103 °C.

Soil sampling and soil water composition

During the study, air temperature (1 m) and soil temperatures (surface and 10 cm depth) were measured at the site, while rainfall data were obtained from a nearby (<1000 m) weather station.

From day 1 to 5 the pH of the soil was determined in the field with a portable pH meter (Schott Instruments HandyLab, Mainz, Germany) and a flat-surface pH electrode (Mettler Toledo, Switzerland), with five measurements per plot. When dry, plots were moistened with a drop of deionized water to wet the surface before measuring pH.

Soil was sampled from within the 2 × 2 m² plots, avoiding the area inside the gas sampling chambers (as described below). Samples of the soil surface were collected by scraping the surface (0–0.2 cm) with a spatula, five random samples per plot, 2 h after slurry application, and then once per day for the first 5 days after application. Thereafter, soil surface samples were collected from the surface once a week. The samples were stored at –18 °C until analysis for TAN. At these same sampling sites, where the soil surface was sampled, further soil samples (0–7 cm) were collected by gently pressing a steel tube (7.3 cm internal diameter) into the soil. Each soil core was split into two fractions corresponding to 0–3.5 and 3.5–7.0 cm depth. Soil water content, NO₃⁻, NO₂⁻, DOC and TAN concentrations were determined as follows: soil water content was measured gravimetrically by drying for 24 h at 104 °C. Soil NO₃⁻, NO₂⁻ and TAN were extracted by mixing and shaking soil for 30 min with 2 M potassium chloride (KCl [10 KCl : 1 soil, w/w]); the KCl suspensions were centrifuged at 3200 rpm for 20 min and filtered through Whatman 42 filter paper. The filtered sample was used for determination of NO₃⁻, NO₂⁻ and TAN, using standard colorimetric techniques as noted above. Soil DOC determinations were performed using a 30-min cold water extraction (ratio of 1 g soil : 6 ml deionized water) followed by 20 min centrifugation (3500 rpm) and filtering (Advantec 5C, Advantec FMS Inc., Dublin, CA, USA) before analysis on a TOC analyser as described above.

Nitrous oxide emissions

The N₂O emissions were determined using a static chamber technique (Hutchinson and Mosier, 1981) at various times: (1) before slurry application on 4 May 2015, (2) for the first 4 days after

slurry application and (3) every second or third day for the remainder of the experiment; monitoring continued until 8 June 2015. Emissions of N₂O were determined at 10.00 h as this time has been shown to result in no bias when calculating daily emissions (van der Weerden *et al.*, 2013). Static chambers were formed by inserting circular (internal diameter 36 cm) stainless steel bases, containing an annular channel for establishing a water seal, 10 cm into the soil. One chamber was placed in each of the 12 plots. During N₂O emission measurements, a headspace cover with a rubber septum to enable gas sampling was lowered onto the base, creating a headspace 13 cm high. Water was placed in the annular channel to seal the chamber. Using a syringe, fitted with a stopcock and a hypodermic needle, a 10-ml gas sample was taken and transferred to an evacuated 6 ml Exetainer (Labco, High Wycombe, UK) at 0, 15 and 30 min after headspace closure.

For determination of gas sample N₂O concentrations, the samples were injected into a carrier stream of N₂ on a SRI-8610 gas chromatograph (GC, Torrance, CA, USA) equipped with a ⁶³Ni capture detector (Pye-Unicam, Cambridge, UK) and a Two Haysep-D packed Column (6' × 1/8") Di Vinyl Benzene-DVB. Detector and column temperatures were 310 and 20 °C, respectively. The GC was interfaced to a liquid autosampler (Gilson 222XL, Middleton, WI, USA) which had been modified for gas analysis by substituting a purpose-built double concentric injection needle (PDZ-Europa, Crewe, UK) for the default liquid level detector and needle. This enabled the entire gas sample to be flushed rapidly from the sealed Exetainer onto the GC column. Fluxes of N₂O, measured with the static chamber technique, were calculated using the linear regression approach in the free-ware HMR (Pedersen *et al.*, 2010), which provides a recommendation on best flux calculation method, as based on the concepts of Hutchinson and Mosier (1981).

Soil nitrous oxide concentration measurements

The concentration of N₂O in the soil air at 5, 10, 20 and 50 cm depth was determined at 3- to 7-day intervals using a simple and robust diffusion probe (Petersen, 2014). The diffusion probes were inserted prior to manure application and sufficiently far from soil sampling plots and gas chambers to avoid creating artefacts. The probes had a 10-ml diffusion cell with a 3-mm diameter opening covered by a 0.5 mm silicone membrane. At sampling, the diffusion cell was flushed with 10 ml N₂ containing 50 µl/l ethylene (C₂H₄) as a tracer; ethylene was removed immediately after sampling by flushing with nitrogen gas (N₂). Tracer recovery was used to calculate sample N₂O concentrations using the equations of Petersen (2014) with correction for dead volumes of connecting tubes and valves.

Ammonia emission estimates

Ammonia emissions during the first 5 days were calculated using the empirical model of Sherlock *et al.* (1994). For this, wind speed was measured at 1.2 m with a cup anemometer (Sensitive Anemometer No. T16108/2, Casella London Limited, London, UK) with a low stalling speed, and soil temperature at the soil surface was measured with a LM 35 CZ thermometer (R.S. Components, Corby, UK), with all data logged as 60 min averages (CR800, Campbell Scientific Ltd., Shepshed, UK). Since soil pH and TAN were determined at points in time at daily intervals, an average wind speed from 12 h prior to the soil measurements to 12 h after soil measurement was used. This approach assumes

that the averaged wind speed is representative of the 24 h period between soil samplings.

The equilibrium concentration of NH₃ in the gas phase (NH₃(g); µg NH₃-N/m³) immediately above the source was calculated using the soil temperature (K), soil surface pH and the TAN concentrations in the 0–0.2 cm depth as follows:

$$[\text{NH}_3]_{\text{solution}} = \frac{[\text{NH}_4^+ + \text{NH}_3]_{\text{solution}}}{1 + 10^{(0.09018 + 2729.92/T - \text{pH})}} \quad (1)$$

Then, using an empirical equation developed previously for the same grassland site as used in the current study (Sherlock *et al.*, 1994), the flux of NH₃ for a given plot was determined as follows:

$$F = 7.5 \times 10^{-5} [\text{NH}_3(\text{g})] \times u + 10.75 \quad (2)$$

where F is the flux of NH₃ from the plot (µg NH₃-N/m²/s), NH₃(g) is the equilibrium concentration of NH₃ in the gas phase immediately above the source, defined above and u is the average (defined above) wind speed (m/s) at 1.2 m. The ammonia equilibrium gas concentration (NH₃(g)) was calculated using previously determined equilibrium constants (Petersen *et al.*, 2014).

Air permeability and relative gas diffusivity

An *in-situ* method, similar to that described by Iversen *et al.* (2001), was used to measure the air permeability (AP) of the soil. The AP was measured on soil cores, taken by inserting 7.3 cm internal diameter stainless steel rings to a depth of 7.4 cm. These were collected on days 7 and 24, giving a total of 24 cores. To create a flow of air through the soil, a cylinder of dry compressed air was connected via a regulator to a variable flow meter (0–60 litres/min capacity). The regulator on the gas cylinder was manipulated until steady flows through the soil ring of 5, 10, 20, 30 and 50 litres/min were reached. The AP of the soil was calculated using the recommended method of Ball and Schjøning (2002) where AP (k_a) is calculated by solving Eqn (3) for k_a , and where q_v is the volumetric flow rate of air (L^3/T), ΔP_a is the pressure difference across the sample ($M/L/T^2$), A is the shape factor and h is the gas viscosity ($M/L/T$), where M , L and T are mass, length and time, respectively:

$$q_v = -[(k_a \Delta P_a A) / \eta] \quad (3)$$

Values of the shape factor A (L) are derived from cylinder dimensions and insertion depth according to Eqn (4) where D and H are cylinder diameter and insertion depth (L), respectively (Liang *et al.*, 1995):

$$A = D \left[0.4862 \left(\frac{D}{H} \right) - 0.0287 \left(\frac{D}{H} \right)^2 + 0.1106 \right] \quad (4)$$

Soil Dp/Do (0–7 cm) was determined using the method of Rolston and Moldrup (2002). In brief, a chamber containing a calibrated O₂ sensor (KE-25, Figaro Engineering Inc., Osaka, Japan) was purged with a gas mixture (0.9 argon [Ar] and 0.1 N₂) while the base of the soil core, of the same dimensions as described for AP, was isolated from the chamber. Then, after exposing the chamber to the soil surface, O₂ diffused through the soil core into the chamber, and over a period of 120–180 min

Table 1. Liquid manure characteristics

Treatment	DM (g/l)	TAN (mg N/l)	Total-N ^a (proportion)	Total-C ^a (proportion)	pH
LDM: low DM manure	51 (2.1)	16 (3.1)	0.019 (0.0009)	0.26 (0.015)	6.5 (0.11)
HDM: high DM manure	162 (7.9)	20 (3.8)	0.021 (0.0001)	0.31 (0.006)	7.7 (0.04)

Data are means with s.e.m. ($n=3$) in brackets, where DM and TAN are dry matter and total ammoniacal nitrogen, respectively.

^aMeasured on freeze-dried samples.

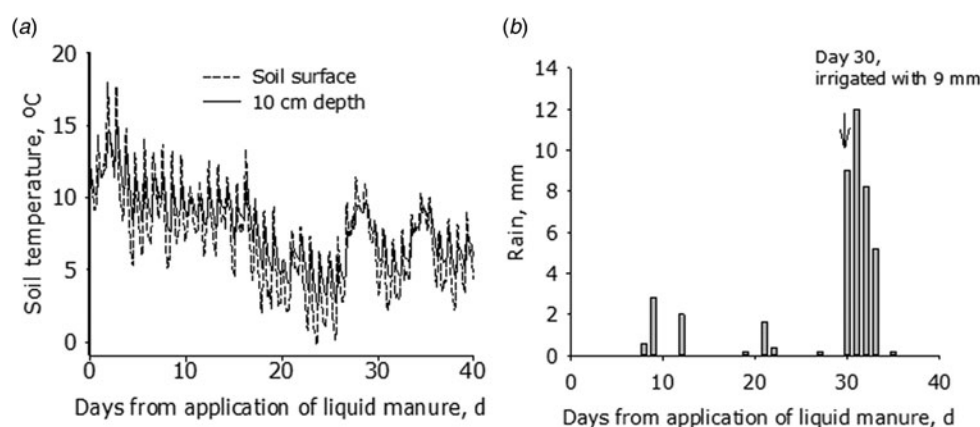


Fig. 1. Meteorological data over the course of the experiment from 4 May to 8 June 2015. (a) Soil temperature at the surface and 10 cm depth and (b) rainfall and irrigation.

the change in O_2 concentration was recorded as a function of time while assuming O_2 consumption was negligible (Moldrup *et al.*, 2000). A log-plot of the relative O_2 concentration *v.* time enabled D_p (O_2 diffusion coefficient in soil) to be calculated according to Rolston and Moldrup (2002). Diffusivity calculations were performed at 25 °C. The value of D_o (O_2 diffusion coefficient in air) at 25 °C was assumed to be 0.074 m²/h (Currie, 1960). Relative gas diffusivity was expressed as D_p/D_o .

Data analysis

Statistical analyses were performed using R (R Core Team, 2014). Differences between treatment means at $P \leq 0.05$ were assessed with one-way analysis of variance, and where differences were detected, Tukey's Honest Significant Difference test was applied. Measurements made at different times and depths were analysed separately in order to focus on effects of slurry application. Based on results from graphical tests for normality and homogeneity of variance, the N_2O -N flux and DOC data were \log_{10} transformed prior to analysis. Simple and multiple linear regression models were used to test for correlation between soil surface DOC or D_p/D_o and N_2O -N fluxes.

Results

Manure and soil characteristics

HDM manure contained three times as much DM as the LDM treatment (Table 1) and although there were no significant differences in the proportions of total C and N of the freeze-dried manure samples (Table 1), this resulted in higher N and C inputs. The TAN concentration of applied manures also did not vary statistically (Table 1). However, the manure pH was higher in the HDM treatment (Table 1; $P < 0.01$).

Soil surface temperatures were typical for the autumn season, with daily averages initially varying from 11 to 18 °C, and later declining to between 4 and 12 °C (Fig. 1). The late summer and autumn of 2015 was very dry, and only 7.8 mm of rain fell during the first 30 days of the study (Fig. 1). It was decided, therefore, to irrigate the plots with 9 mm on day 30, but several days with rain then followed with cumulative rainfall equalling 33.4 mm by day 37 (Fig. 1). Wind speeds ranged from 0.8 to 3.8 m/s.

Soil air-filled porosity and AP (Fig. 2) were not affected significantly by manure application. In contrast, soil gas diffusivity, D_p/D_o , at the soil surface (0–7 cm) had declined ($P < 0.05$) following the addition of both LDM (0.017) and HDM (0.015) manures, when compared with untreated soil (0.035), 7 days after manure application, with no difference due to manure DM levels. After 24 days, however, D_p/D_o did not differ significantly (0.034–0.036) between manure-treated and untreated soil (Fig. 2).

Initially the TAN concentrations (Fig. 3) of manure-amended soil were consistently higher at the soil surface than in the soil below ($P < 0.001$). The TAN concentrations then declined by day 5 following application but by day 18, concentrations at the surface had increased again in all treatments and peaked after 20–30 days; thereafter, the concentration declined. This trend was similar for both manure treatments, but in plots receiving HDM manure the concentration of TAN at the start and after 20–30 days was 10 and 3 times higher, respectively, at the surface than in plots receiving LDM manure and the control ($P < 0.001$). There were no differences in the sub-surface TAN concentrations between the LDM-treated and control plots over this period (Fig. 3).

In the surface layer of the control ($P < 0.001$) and LDM treatment ($P < 0.05$), soil NO_3^- concentrations were higher than in the sub-surface ($P < 0.001$). In both of these treatments, the concentration of NO_3^- in the surface layer increased after *ca.* 10 days, peaking by day 25, and then declined to background levels by

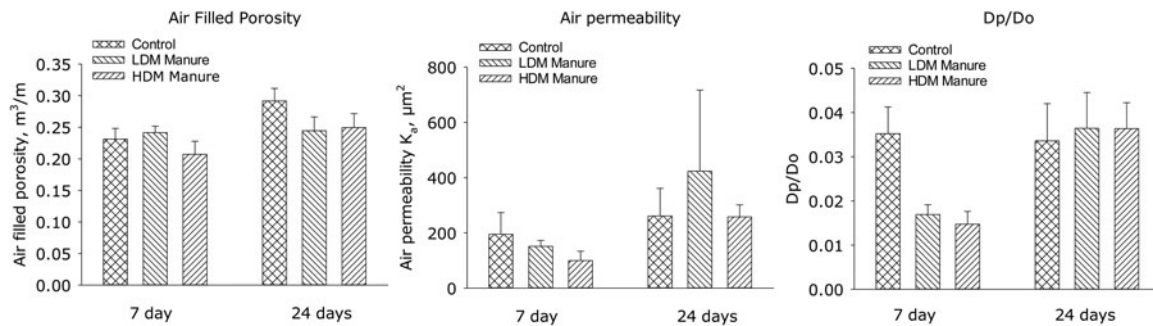


Fig. 2. Air-filled porosity, air permeability and relative gas diffusivity (D_p/D_o) in the soil surface (0–7 cm) as affected by liquid manure application (error bars: s.e., $n = 4$).

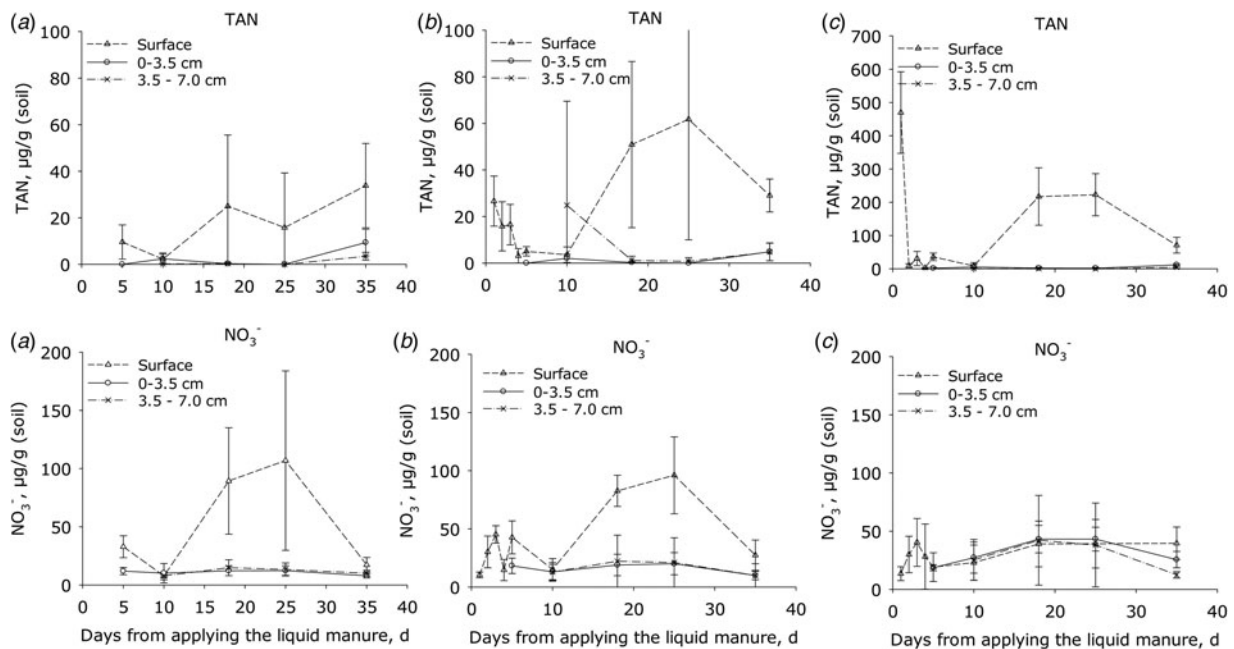


Fig. 3. Concentrations of total ammoniacal nitrogen ($TAN = NH_4^+ + NH_3$) and nitrate (NO_3^-) in surface soil samples. (a) Control plots, (b) plots amended with LDM manure and (c) plots amended with HDM manure. Notice that the Y axis scale is larger for the upper right diagram (C; TAN) than in the two other diagrams in the line (error bars: s.e.m., $n = 4$).

day 35. In contrast, the plot amended with HDM manure showed no significant differences in NO_3^- concentrations when comparing surface or sub-surface concentrations (Fig. 3). The surface NO_2^- concentrations ranged from 0 to $0.6 \mu\text{g/g}$ in the control and LDM plots. After 3 days, the NO_2^- concentrations were 2–4 $\mu\text{g/g}$ in the HDM plots (data not shown), higher ($P < 0.005$) than in LDM plots.

On day 10, DOC concentration at the soil surface was higher in the HDM treatment than in either the LDM or the control treatments ($P < 0.001$), which did not differ from each other (Fig. 4). Soil depth affected DOC ($P = 0.001$) in manure-treated plots (Fig. 4).

The pH of LDM and HDM manures were 6.5 and 7.7, respectively, prior to manure application (Table 1). Soil surface pH of the untreated plots was 6.5 during the course of the experiment. The pH of the HDM soil immediately after manure application was 7.8 and this declined to 6.7 during the first 5 days after manure application. The pH values at the soil surface in the LDM-treated plots were initially 6.3 and increased on day two to 6.7 and remained at 6.6 thereafter.

Ammonia and nitrous oxide fluxes

The calculated cumulative NH_3 emissions from the HDM treatment (49 g N/ha; s.e. 2.5, $n = 4$) were higher than those from the LDM plots (10 g N/ha; s.e. 1.7, $n = 4$) when expressed either as a flux ($P < 0.01$) or as a proportion of TAN applied ($P < 0.01$) with mean NH_3 fluxes corresponding to 0.050 and 0.012 of TAN applied, respectively. As a proportion of total-N applied, the cumulative NH_3 emissions were 0.0003 and 0.0002 of total-N applied in the HDM and LDM treatments, respectively (Fig. 5).

The cumulative N_2O emissions from the HDM plots were higher than from the control ($P = 0.01$), but not from the LDM plots, with no difference in the cumulative N_2O emissions when comparing LDM plots with control plots (Fig. 5). After 5 days the daily N_2O emission rate was larger from HDM plots than from LDM and control plots. Cumulative N_2O emissions from control, LDM and HDM plots equalled 25 g N/ha (s.e. 11, $n = 4$), 61 g N/ha (s.e. 19, $n = 4$) and 147 g N/ha (s.e. 34, $n = 4$), respectively. The cumulative N_2O emissions from the LDM and HDM plots did not differ significantly when expressed as a

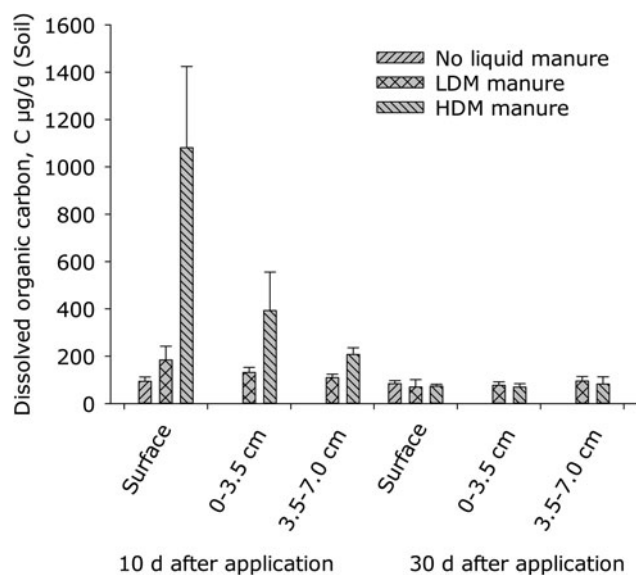


Fig. 4. Dissolved organic carbon (DOC) at day 10 and day 30 after application of slurry (error bars: s.e.m., $n = 4$). Surface refers to 0–0.2 cm depth. Control values at 0–3.5 cm and 3.5–7.0 cm are not presented.

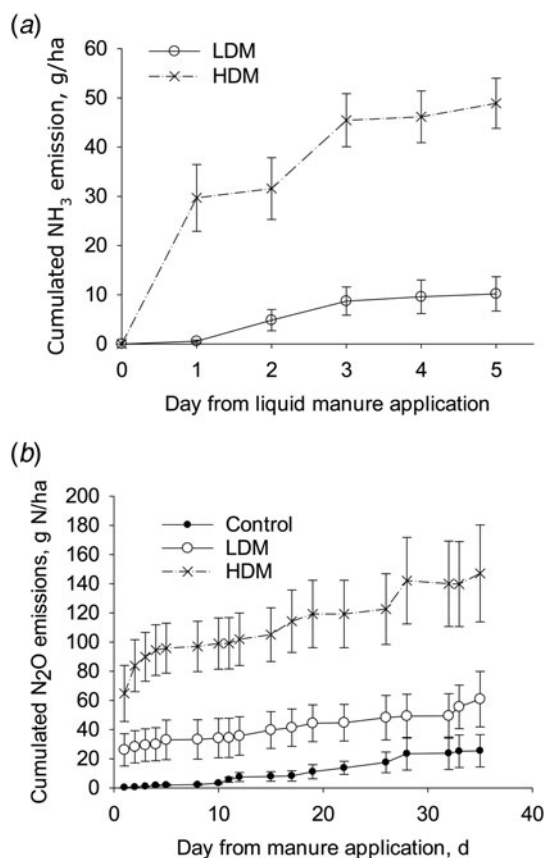


Fig. 5. Cumulative NH₃ emissions (a) and cumulative N₂O emissions (b) from LDM manure or HDM manure treatments (error bars: s.d., $n = 4$).

proportion of either TAN or total-N applied. In the LDM and HDM treatments these values corresponded to 0.08 and 0.15 of TAN applied or 0.00094 and 0.00072 of total-N applied, respectively.

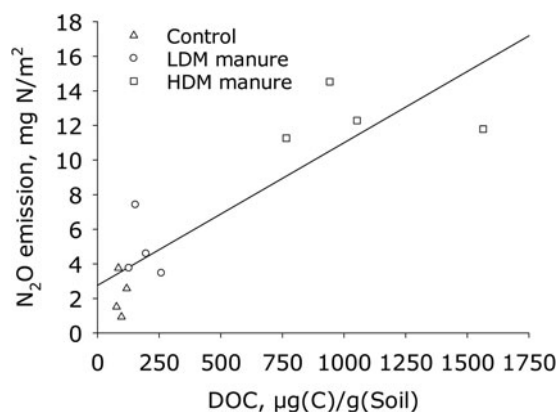


Fig. 6. Cumulative N₂O emissions v. DOC at the surface 10 days after application of manure (A) and v. mean Dp/Do ($n = 3$), measured 7 days after application of manure. Regression equation: $y = 0.0041x + 1.4$; $R^2 = 0.75$.

Linear regression showed that mean DOC (10 days) explained the variability in the cumulative N₂O emissions ($R^2 = 0.75$) and multiple linear regression analysis showed that N₂O emission was significantly ($P < 0.05$) related to DOC measured on 10 days (Fig. 6). Log N₂O fluxes were not linearly related to log (Dp/Do).

Discussion

The DM concentration in the LDM manure was comparable with previous studies (Bourdin *et al.*, 2014; Fangueiro *et al.*, 2015), while for HDM manure the level was relatively high and may be compared with that of the fibre fraction of slurry separated with a filter press (Møller *et al.*, 2000); however, it was lower than the 0.25–0.40 DM typically achieved by screw presses (DairyNZ, 2013).

Concentrations of TAN (15.8–19.9 mg/l) in the manure were low when compared with an earlier study using pig slurry applied to the same pasture (Sherlock *et al.*, 2002) and when compared with the study that derived Eqn (2) following ruminant urine application to pasture (Sherlock *et al.*, 1994). A meta-analysis showed that concentrations of TAN in New Zealand dairy shed manure vary markedly from 36 to 1400 mg/l, potentially reflecting seasonal changes in pasture quality and farm management practices and thus the manures applied in the current study are at the lower end of this range.

The initial decline in soil TAN concentration after application of manure (day 0 to 10) is a common observation and is attributed to volatilization of NH₃ and microbial immobilization, probably using volatile fatty acids as an easily digestible carbon source (Kirchmann and Lundvall, 1993). Given the relatively low NH₃ losses it is possible immobilization was also responsible for the initial decline in TAN. However, the changes in soil pH and NH₄⁺ concentration were also consistent with occurrence of NH₃ volatilization and the initial decline in TAN. The increase in surface layer TAN after day 10 probably resulted from mineralization of manure N but, due to the low pH of the surface soil (<7.0) by this time, emissions of NH₃ would have been relatively low.

There was a notable lack of NO₃⁻ accumulation in the surface layer of the HDM manure treatment. Since the temporal dynamics of TAN accumulation and removal were comparable with the treatment with LDM manure, it suggests that nitrification took place in both treatments at the soil surface but that there was a

denitrification sink for NO_3^- at the soil surface in the HDM manure treatment. Past studies have documented that O_2 disappears rapidly (Petersen *et al.*, 1996; Markfoged *et al.*, 2011) and coupled nitrification–denitrification develops around manure–soil interfaces (Petersen *et al.*, 1991, 1992), which may also result in release of N_2O (Nielsen and Revsbech, 1998).

Ammonia emissions as a proportion of N applied were low when compared with previous studies. For example, losses of NH_3 from slurry have been recorded to range from 0.04 to over 0.60 (Sintermann *et al.*, 2012), while losses from urine and dung reportedly accounted for 0.26 (± 0.020) and 0.12 (± 0.027) of the deposited urine-N and dung-N deposited, respectively (Laubach *et al.*, 2013). These relatively low emissions can be attributed to differences in substrate supply, the relatively low soil pH, relatively low soil temperatures (10–15 °C) and low-wind speeds (0.8–3.8 m/s) that occurred (Søgaard *et al.*, 2002) and because the dry soil would have enhanced the infiltration of liquid from the manure (Sommer and Jacobsen, 1999). Cumulative emissions of NH_3 from plots amended with LDM manure were lower than in HDM plots due to either the rate of TAN applied in the LDM treatment tending to be lower, the lower manure pH of the LDM treatment, or possibly because liquid from the LDM manure better infiltrated into the soil as shown by the lower initial TAN concentration in the surface layer (Braschkat *et al.*, 1997). Conversely, the HDM manure contained a high amount of water in the surface following the first 2–3 days due to the capacity of organic matter in manure to retain water (Petersen *et al.*, 2003). The initial decline in NH_3 emission rates from manure-amended plots coincided with declining TAN concentrations and a decline in pH at the surface.

The NH_3 flux method used is an indirect method based on soil measurements and facilitates a clear understanding of the dynamics, key variables and their interactions driving NH_3 emissions (e.g. TAN, soil pH and depth). It is a simply applied protocol that can be followed easily. However, limitations and bias may arise if data required for the indirect method are not collected with sufficient frequency to account for potential nocturnal (e.g. wind) or diel (e.g. soil temperature) trends. With adequate data sets, however, the indirect method used in the current study is capable of determining low NH_3 fluxes as derived here. Ideally, field experiments could also be performed for verification of indirect flux measurement and to further compare the NH_3 flux method with measured emissions under differing N substrates.

The cumulative emissions of N_2O from the manure-amended plots, as a proportion of total N applied, were also low when compared with results of a meta-analysis examining N_2O emissions from dairy manure applied to grassland (van der Weerden *et al.*, 2016). These relatively low cumulative emissions are probably due to the manure being applied to a relatively dry soil (Luo *et al.*, 2008); however, they will also be a function of the shorter duration of the current study. Initial N_2O emissions were higher from manure-amended compared with control plots. This is in accordance with the higher inorganic-N and DOC availability in manure-amended soil, and in particular the higher DOC availability in HDM manure represented a sink for O_2 that could support O_2 limited conditions even close to the soil surface. Soil gas diffusivity also changed for a period, as indicated by Dp/Do, and this would also restrict supply of O_2 to manure–soil interfaces (Balaine *et al.*, 2013; Baral *et al.*, 2016). The higher daily N_2O emissions, after day 5, from the HDM plots, were thus due to total TAN and DOC concentrations being higher than in the control and LDM plots.

There was a strong relationship between DOC and accumulated N_2O across all treatments, suggesting that under the conditions of the current study, where manure was applied to grassland during a dry autumn, the O_2 demand associated with heterotrophic processes was a driver for N_2O production. Petersen *et al.* (1996) found that around 0.90 of degradable organic matter in manure was metabolized with O_2 as the electron acceptor, and only 0.10 via denitrification when cattle manure was applied to a sandy loam soil at field capacity. This ratio could be shifted even more towards aerobic decomposition in drier soil (Baral *et al.*, 2016). Relative gas diffusivity, Dp/Do, on days 7 or 24 did not explain the variability in the N_2O emissions from the LDM and HDM manures, which was in contrast to previous studies with either NO_3^- , urea, or ruminant urine application (Balaine *et al.*, 2013, 2016; Owens *et al.*, 2016, 2017). Baral *et al.* (2016) also found a relationship between Dp/Do and N_2O emissions, but showed there was a dynamic interaction between O_2 consuming processes and O_2 supply. In accordance with this, Petersen *et al.* (2013) found different relationships between N_2O emission and Dp/Do depending on C input in four crop rotations, and proposed that this was due to a higher O_2 demand associated with higher C inputs. It is possible that the measurements of Dp/Do by day 7 did not represent the potential dynamic range in Dp/Do during the initial phase of the experiment – for example if highly labile C had been consuming O_2 in the first days of the experiment, it would mean that O_2 limitation supporting N_2O emissions could occur at a higher Dp/Do value.

Identifying pathways of N_2O production was beyond the scope of the current study; however, the lower soil NO_3^- concentration under the HDM treatment, together with the positive relationship between DOC and accumulated N_2O emissions and the lower Dp/Do in both LDM and HDM treatments after 7 days, indicate that denitrification was a dominant source of N_2O . This may not have been the case by day 24, when there was no treatment effect on Dp/Do. However, it is well-known that organic matter applied with manure can enhance N_2O production (Chadwick *et al.*, 2011). Baral *et al.* (2016), using ^{15}N -labelling, also found that denitrification was the main source of N_2O from surface-applied cattle manure independent of soil water content. A recent study under wet conditions concluded that denitrification was the main N_2O source in grassland soil following surface application of cattle manure (Van Nguyen *et al.*, 2017).

It is recognized that NH_3 emissions are affected by TAN (Huijsmans *et al.*, 2003) and by the manure DM content (Sommer and Olesen, 1991). While manipulating TAN can alter NH_3 emissions, so too can manipulation of the manure DM content, due to changes in the water retention capacity of manure at varying DM contents altering infiltration of TAN into soil. When manipulating manure to mitigate NH_3 emissions, pollution swapping must also be considered. The lower NH_3 emissions associated with the reduced DM content in LDM manure did not result in higher N_2O emissions in the current study, which is in contrast to an Irish study where DM was adjusted before application of manure to grassland (Bourdin *et al.*, 2014). In the study by Bourdin *et al.* (2014), higher NH_3 emissions reduced significantly the residual N available for N_2O production in the soil. However, pollution swapping did not occur if slurry was applied in spring when plant demand for N was higher. Soil moisture, driven by seasonal rainfall, also strongly influenced N_2O emissions in the study by Bourdin *et al.* (2014) and thus soil moisture may be a strong determinant of the potential for pollution swapping. This indicates that not only manure specifications

but also the environmental conditions at the application site must be considered to prevent pollution swapping.

The current study was of a relatively short-term duration (37 days) and while the majority of NH_3 emissions will have occurred over this period there may be trade-offs between removing DM from dairy manure that would otherwise be applied and improvements in both pasture nutrient availability and soil quality (organic C amendments). An answer to this is beyond the scope of the current study but the potential impacts of DM separation over the long term are unknown and need to be addressed in future work. The current study was performed at a plot scale and so *in situ* manure management, involving manure DM separation, needs to be assessed at the farm scale with respect to gaseous N losses. Furthermore, future manure management studies should assess the influence of DM separation across a wider range of embodied TAN.

In summary, cumulative N_2O emissions from livestock manure applied to grassland on well-drained soils were lower with a lower DM content in the manure if the emissions are considered simply as a gross flux (g/ha). This was probably due to a lower DOC concentration in the soil amended with the lower DM animal manure. However, when expressed as a proportion of TAN or total-N applied cumulative N_2O , emissions did not differ with treatment. In the current study, where the soil was relatively dry, the N_2O emissions were not related to gas diffusivity of the soil, 7 days after manure application, however, soil gas diffusivity did vary with treatment, declining with manure application at 7 days. Applying dairy shed manure to a dry soil, with the DM reduced in order to reduce NH_3 emissions, did not cause pollution swapping in the form of increased N_2O emissions in this instance.

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