GREENHOUSE GAS EMISSIONS FROM SOLID DAIRY COW MANURE DURING STORAGE AND FOLLOWING APPLICATION TO LAND

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Abstract
We conducted a study to determine greenhouse gas (GHG) emissions (nitrous oxide, N_2O; methane, CH_4; and ammonia, NH_3, which is an indirect source of N_2O emissions) from storage and land application of dairy manures collected during winter housing of cows in southern New Zealand. Gaseous emissions during storage were determined at Ruakura following collection and transport of manures from three storage facilities on commercial dairy farms. These storage facilities were (i) the bunker of a wintering barn with a slatted-floor (termed 'bunker'), (ii) the floor of a deep litter barn (termed 'deep litter'), and (iii) the solid fraction of a weeping wall system (termed 'weeping wall'). Following the end of the wintering period (generally mid-late August), manure is typically stored on-farm for *ca* 4 months prior to land application in October-early November. Cumulative emissions for all three GHGs, expressed as a percentage of the initial total N or C, differed for the three manures. Cumulative NH_3 emissions were greatest for storage of weeping wall manure, at 5.7%, while cumulative N_2O emissions were greatest for deep litter manure, at 1.9%. The largest cumulative CH_4 emission, at 0.3% of the initial total C, was associated with weeping wall manure. Increasing the storage period to 7 months increased cumulative N_2O and CH_4 emissions by up to 2.8 and 37 times, respectively. The proportional increase in emissions depended on the type of manure stored.

Following land application of two manures (bunker and weeping wall) to grassland at three rates (1.5, 3.0 and 4.5 t dry weight (DW)/ha), GHG emissions were measured and emission factors (EF) determined. EFs for N_2O and CH_4 were negligible, at <0.1% of N or C applied for both manures. The low N_2O EF was primarily due to dry conditions at the time of application. In contrast, NH_3 emissions were 11 and 22% of N applied in the weeping wall and bunker manure treatments, respectively. The rate of manure application did not influence EFs for all three GHGs.

Introduction
In Otago and Southland, dairy cow numbers have increased over the past 10 years (2002-2012) by 69% and 95%, respectively (DairyNZ, 2012). This rate of increase surpasses the national rate of 25% over the same period, and is rapidly creating demand for winter grazing/standoff options to house non-lactating cows. In these regions it is common practice to winter non-lactating cows on forage crops such as swedes (*Brassica napus*) and kale (*Brassica oleracea*). High stocking densities combined with soils that are typically wet often causes severe soil structural damage which must subsequently be cultivated prior to re-sowing paddocks into grass. This wintering option can also lead to significant nitrate leaching

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losses, with recent research finding a 3-year average loss of 52 kg N/ha/year (Monaghan et al. 2013) and high rates of sediment nutrient loss in surface flow (Orchiston et al. 2013).

The use of animal confinement facilities for housing dairy cattle off-paddock provides an alternative option to wintering cows on forage crops in southern New Zealand. Animal confinement facilities are also used in other regions, particularly where soils can remain wet for extended periods (e.g. Northland). However, in regions such as Otago and Southland dry cows may be housed during the entire winter period. Manure deposited in confinement facilities over winter is managed in differing ways, including storage in bunkers beneath the slatted floors of barns (e.g. Herdhomes), on the floor of a deep litter barn, or in weeping wall type facilities. Following the end of the wintering period (generally mid-late August), the manure is typically stored on-farm for a further 2 months prior to land application in spring (October-early November).

Currently the national GHG inventory assumes all animals are grazed on pastoral systems throughout the year. The use of animal confinement facilities and stand-off pads to avoid winter forage crop grazing could be an effective GHG mitigation technology and contribute to the overall goal of reducing GHG emissions from agriculture in NZ. However, there is uncertainty about unintended consequences (or 'pollution swapping') from such farm systems. Such consequences include potential ammonia (NH_3), nitrous oxide (N_2O) and methane (CH_4) losses from the animal confinement facilities and during land application of effluent/manure.

The objective of the current study was (i) to quantify cumulative NH_3, N_2O and CH_4 emissions associated with the storage of manure collected from commercial farms in southern New Zealand, and (ii) to determine if GHG emission factors for land application of manure can be reduced when spread to land at low rates.

Materials and Methods

Manure storage trial
A small scale outdoor trial, under a poly-tunnel house (i.e. resembling an animal shelter) was conducted at Ruakura, Waikato to quantify N_2O, NH_3 and CH_4 emissions from stored manure. In late June 2011 manure was collected from two southern New Zealand dairy farms with barns that had been used to house cows over winter. Samples were air-freighted to Waikato, where subsamples were collected and sent to Analytical Research Laboratories (ARL) in Napier for analysis (Table 1). The manures were collected from:
1. the concrete bunker of an animal shelter with a slatted floor (termed 'bunker'),
2. the floor of a deep litter barn (termed 'deep litter')
3. the solid fraction of a weeping wall system (termed 'weeping wall')

Weeping wall facilities are typically used for collection of farm dairy effluent, generated from washdowns during milking. However, we collected manure from a commercial farm where the weeping wall was used for the sole purpose of storing non-diluted excreta scraped from a feeding apron adjacent to the litter barn. None of these storage facilities were stirred.

Table 1. Characteristics of the manures collected from the two dairy farms in southern NZ.

Manure	Total solids (g/kg wet weight)	pH	Ratio of excreta: straw or woodmix (v/v)[A]	Total N content (g/kg dry weight)	TAN[B] content (g N/kg dry weight)	Total C content (g/kg dry weight)	C:N ratio
bunker	193	7.4	4.3:1.0	17.6	6.6	336	19
weeping wall	115	7.6	n/a[C]	19.1	6.9	426	22
deep litter	224	8.2	0.2:1.0	15.6	3.2	433	28

[A] At the time of manure collection (on 28 June) this ratio was calculated from theoretical excreta inputs and farmer information on the quantity of straw/woodmix material used; [B] TAN = total ammoniacal-N ($NH_3 + NH_4^+$) content; [C] No carbon-rich material (straw or woodmix) added to weeping wall excreta.

Two sets of columns (0.5 m length) were established: one for gas measurements, where each treatment was replicated 4 times, and the second for destructive manure sampling on seven occasions, where each sampling date was replicated 3 times, giving a total of 21 destructive sampling columns for each manure type. For each destructive sampling, the entire contents of each column was removed and thoroughly mixed prior to sending to ARL, Napier, for physical and chemical analysis. Manure temperature was logged in one of the manures (weeping wall) at two depths (100 mm and 300 mm). Gas sampling columns were 150 mm diameter, while columns for destructive sampling were 50 mm diameter. All pipes were sealed at the base and buried, with the surface *ca* 150 mm above ground level.

Measurement of emissions commenced at the beginning of July 2011 (Fig. 1). Following the addition of the manure to the gas sampling columns, NH_3 emissions were measured on 25 occasions for a 24-hour period over 7 months, with nine of the measurements being made within the first month following trial establishment. Measurements were made by passing air at *ca* 12 air changes per minute through a column headspace, created by placing a lid on top of the column, and then through Dreshel bottles containing acid to trap the ammonia produced (Luo et al., 2004). The acid was analysed for ammonium-N colorimetrically using a Skalar segmented flow analyser. Nitrous oxide and CH_4 fluxes were measured using the standard closed chamber technique (de Klein et al., 2003), where headspace samples were collected at 0, 30 and 60 minute intervals and analysed by gas chromatography. Fluxes were determined on 24 occasions over a 7 month period, with an initial high frequency of measurements (8 in the first month) that reduced over time. The manures remained undisturbed for 7 months, with final gas and manure measurements made on 19 January 2012.

Gaseous fluxes were calculated and temporally integrated to provide cumulative losses over three durations (Fig. 1):-
1. 84 days (~3 months), assuming storage emptying in late September,
2. 112 days (~ 4 months), assuming storage emptying in late October,
3. 197 days (~ 7 months), assuming storage emptying in late January,

According to farmers with wintering barns, a 4 month storage period (based on early July as the beginning of storage, with late October emptying) is considered to be representative of typical manure storage periods in southern New Zealand.
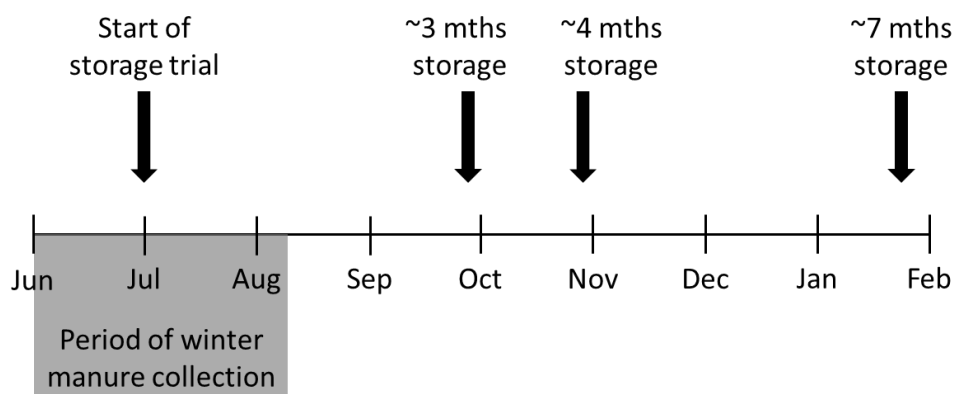
Figure 1: Schematic timeline of storage trial, started at the beginning of July (representative of period of winter manure collection), with cumulative GHG emissions calculated for 3, 4 and 7 months storage, assuming stores are emptied in late September, late October or late January.

Cumulative NH_3, CH_4 and N_2O emissions were calculated as a percentage of the initial total N or C content of the manure by integrating flux measurements over the trial duration. It should be noted that, in the case of the bunker and deep litter collection systems, manures contained straw and/or sawdust. The weeping wall manure was assumed to consist of 100% excreta; the high dry matter content measured (Table 1) was likely due to a large proportion of the urine being removed through the weeping wall slats.

Land application trial
The study site was located on the AgResearch Invermay Research Station sheep farm approximately 20 km from Dunedin (700 mm mean annual rainfall). The soil was an imperfectly-drained Warepa deep silt loam (Mottled Fragic Pallic soil; Hewitt 2010). An enclosure area (12 × 18 m) within a selected paddock was established one month prior to the start of the trial, to exclude stock and allow sufficient time for N_2O emissions from previously-deposited urine and dung during grazing to return to background levels. The soil fertility was: pH 6.3, Olsen P 22 µg/ml, K 0.64 milli-equivalent (me)/100 g, SO_4-S 12 µg/mL, Mg 2.56 me/100 g, Ca 8.2 me/100 g, Organic C 5.7 %, Organic Matter 9.8%, Total N 0.43%, NH_4-N 5 µg/mL and NO_3-N <1 µg/mL. The pasture was an established (20+ years) perennial ryegrass (*Lolium perenne)* and white clover (*Trifolium repens*) based sward.

'Bunker' and 'weeping wall' manures were collected on 17 October 2012 from two commercial farms in southern New Zealand and stored at 4ºC prior to application. Seven treatments were laid down in a randomised block design. The manures were chosen for their different total solids content (Table 2), with the bunker manure having straw added while the weeping wall manure was 100% excreta, with a portion of the liquid seeping out through the weeping wall slats and into the FDE pond.   On 20 November each manure type was applied to pasture plots in a way that simulated what occurs on a commercial farm, i.e. the manure was captured on the grass sward above the soil surface. Three rates of manure were applied (Table 3) and a control treatment (no manure) included. Plots of 0.8 x 1.5 m were treated, providing sufficient area for both static chamber bases (250 mm internal diameter) for N_2O and CH_4 measurements and soil sampling plots (1 m^2); where each treatment was replicated 4 times. A separate area adjacent to the N_2O/CH_4 plots and soil sampling plots was used for NH_3 measurements, which required a network of airlines and aspirated chambers for passing air across the surface of treated plots: each treatment was replicated 6 times.

Table 2: Characteristics of manures based on samples collected on the day of application.

Manure	Total Solids (g/kg wet weight)	pH	VFA[A], total (g/kg dry weight)	Total N content (g/kg dry weight)	TAN[B] content (g N/kg dry weight)	Total C content (g/kg dry weight)	C:N ratio
Bunker	177	7.8	11.8	23.7	10.9	439	19
Weeping wall	147	7.3	41.5	25.2	6.9	437	17

[A] VFA = volatile fatty acids

[B] TAN = total ammoniacal-N ($NH_3 + NH_4^+$) content

Table 3. Treatments and N and C application rates.

Treatment details	Rate of manure applied (t fresh wt/ha)	Total N applied (kg N/ha)	TAN[A] applied (kg N/ha)	Total C applied (kg C/ha)
Control				
Bunker @ 1.5 t DW/ha	8.5	34	16.4	659
Bunker @ 3.0 t DW/ha	16.9	68	32.7	1315
Bunker @ 4.5 t DW/ha	25.4	102	49.1	1968
Weeping wall @ 1.5 t DW/ha	10.2	38	10.4	614
Weeping wall @ 3.0 t DW/ha	20.4	76	20.7	1239
Weeping wall @ 4.5 t DW/ha	30.6	114	31.1	1860

[A] TAN = total ammoniacal-N ($NH_3 + NH_4^+$) content

Methods for gas sampling and analysis were the same as those used for the manure storage trial (described above), where static chambers were used for measuring N_2O and CH_4 fluxes over a 14 week period while aspirated chambers were employed for measuring NH_3 emissions over a 3 week period. Emissions were integrated over the duration of the trial to estimate cumulative emissions over the measurement period. Emission factors were then calculated following standard protocols (de Klein et al., 2003).

On each gas sampling day, two soil cores were taken (75 mm deep, 25 mm diameter) for measurement of gravimetric soil water content. In addition, four soil cores were taken at weekly intervals for soil mineral N and gravimetric soil water content analysis. The soil samples were thoroughly mixed before subsamples were taken for the various analyses. For soil mineral N analysis (i.e. ammonium-N, NH_4^+-N, and nitrate-N plus nitrite-N, NO_3^--N + NO_2^--N), 15 g of fresh soil was extracted for 1 hour in 100 mL of 2 *M* KCl. Samples were filtered using glass-fibre filter papers (110 mm) and extracts frozen until analysis for nitrate (plus nitrite) and ammonium using a modified hydrazine reduction and a salicylate/dichloroisocyanurate method, respectively (Blakemore *et al.* 1987). Gravimetric

soil moisture content was determined by drying soil at 105˚C for 24 hours. Volumetric water contents were calculated by multiplying gravimetric water content by the average bulk density representative of the trial area. Water-filled pore space (WFPS) was calculated by dividing volumetric water content by total porosity, where total porosity was calculated as 1−(bulk density/particle density). Hourly and daily rainfall was logged by an electronic rain gauge installed at the trial site; hourly soil temperature (50 mm depth) was logged for the duration of the trial.

Statistics
Cumulative emissions and emission factors were statistically analysed by conducting an ANOVA, where data required a log-transformation prior to statistical analysis to normalise residuals; back-transformed means are presented here.

Results

Manure storage trial
There was little difference in temperatures between the depths; monthly mean temperatures are therefore reported. The mean temperature in July and August was 10°C, and slowly increased by 2-3°C per month, reaching a monthly mean of 21°C in January and February.

The rate of NH_3 volatilisation was initially high for all three manures, ranging between 40 and 43 µg NH_3-N/g oven dry manure/day (Fig. 2). Emissions declined over a four month period for the bunker and weeping wall manures, while the decline was more rapid (in the first month) for the deep litter manure.

Nitrous oxide emissions from the deep litter were virtually zero for the first 2 weeks of the trial. Thereafter, emissions increased dramatically, peaking at 10 µg N_2O-N/g oven dry manure/day by 1 September (Fig. 3). Emissions then declined rapidly to near zero for the duration of the trial. Increases in N_2O emissions from the bunker and weeping wall manures occurred later, at approximately 8 and 11 weeks, respectively. Emissions from the bunker manure peaked at 3.8 µg N_2O-N/g oven dry manure/day 2 months following the start of the trial, then gradually declined to near zero.
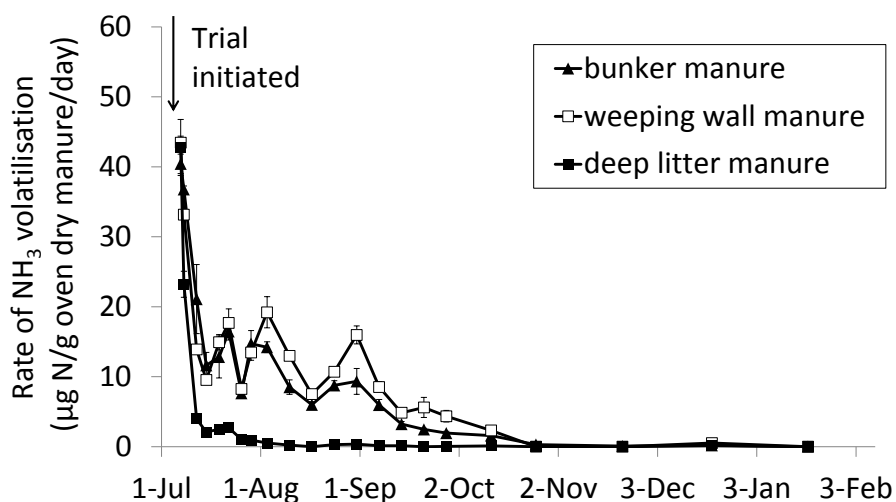

Figure 2. Rates of NH_3 volatilisation (µg NH_3-N/g oven dry manure/day) from the stored bunker, weeping and deep litter manures. Error bars indicate ± SEM (n=4).
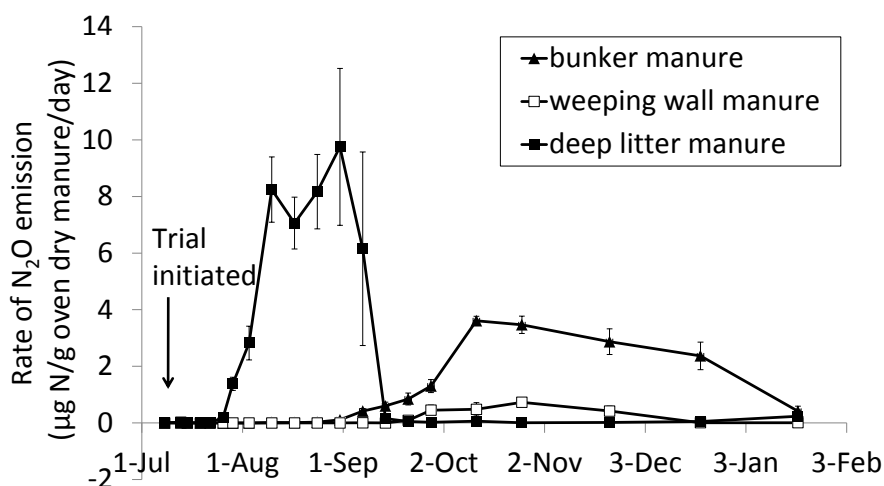
Figure 3. Rates of N₂O emissions (μg N_2O-N/g oven dry manure/day) from the stored bunker, weeping and deep litter manures. Error bars indicate ± SEM (n=4).
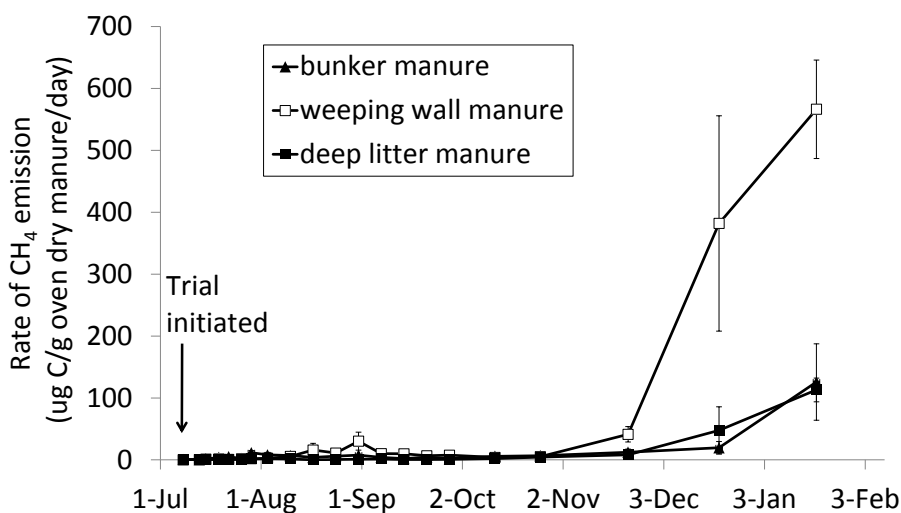

Figure 4. Rates of CH₄ emissions (μg CH_4-C/g oven dry manure/day) from the stored bunker, weeping and deep litter manures. Error bars indicate ± SEM (n=4).

Methane emissions were relatively low for the first 4 months of storage. Emissions then increased for all three manures, with the largest increase observed for the weeping wall manure, peaking at 566 μg CH_4-C/g oven dry manure/day in late January (Fig. 4).

Estimates of cumulative NH_3, N_2O and CH_4 emissions are shown in Table 4. Cumulative NH_3 emissions were significantly ($P < 0.003$) lower from the deep litter manure compared to the bunker and weeping wall manures regardless of storage duration. By 7 months, NH_3 emissions reached 5.2-5.7 % of the initial N contents for the bunker and weeping wall manures. Methane emissions were significantly greater ($P < 0.05$) from the weeping wall manure compared to the bunker and deep litter manures for all storage durations assessed. However, all three manures showed an increase in CH_4 emissions over time (Fig. 4), with the weeping wall manure emitting 5.1% of the initial C content as CH_4 by 7 months. In contrast,

N_2O emissions were greatest from the deep litter manure (1.9% of initial total N content), with cumulative emissions occurring in the first three months. By late January (7 months' storage), emissions from the bunker manure were similar to the deep litter manure, while the weeping wall manure produced significantly less N_2O ($P < 0.001$).

Table 4: Cumulative NH_3, N_2O and CH_4 emissions (% of initial total N or C) from the stored bunker, weeping and deep litter manures.

	NH_3			N_2O			CH_4		
Storage period (mths)	3	4	7	3	4	7	3	4	7
Bunker	4.90	5.11	5.20	0.12	0.60	1.71	0.15	0.22	0.99
Weeping wall	5.35	5.67	5.67	0.01	0.09	0.20	0.21	0.27	5.10
Deep litter	1.15	1.16	1.16	1.93	1.93	1.93	0.01	0.02	0.74
P-value	0.003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.003	0.003

Emissions following land application of manures
During the week prior to manure application, 26 mm of rain was recorded, resulting in a high initial WFPS at the time of application (89%). No rain was recorded during the four days following manure application, while only 9 mm of rain fell over the next 5 days. This resulted in WFPS declining to between 37% and 65% by 3 weeks following the treatment application. Soil mineral N content in the manure-treated plots did not differ markedly from that measured in the control treatment throughout the trial (data not shown). Soil NH_4-N contents ranged from 0.10 to 0.69 mg N/kg dry soil for all treatments over the course of the trial, while soil NO_3-N ranged from 0 to 0.08 mg N/kg dry soil (data not shown).

Nitrous oxide emissions were extremely low for the duration of the trial, with fluxes never greater than 0.01 mg N_2O-N/m^2/hr. Methane fluxes were initially very high (up to 1.7 mg CH_4-C/m^2/hr from weeping wall manure), but declined rapidly over the next three days; thereafter negative emissions were measured (i.e. the soil and manure appeared to be a sink for CH_4), although the magnitude of these fluxes were low. Ammonia emissions were greatest immediately following manure application, with 76% and 69% of the cumulative loss occurring in the first 24 hours, from the bunker and weeping wall manures, respectively.

Nitrous oxide EFs ranged from -0.03 to 0.03% of the total N applied, with no significant differences ($P > 0.05$) in EFs due to manure type and application rate (Table 5). When presented on the basis of TAN applied, EFs ranged from -0.06% to +0.05% of TAN applied, again with manure type and application rate showing no significant differences ($P > 0.05$).

While CH_4 EFs were extremely low, weeping wall manure resulted in a significantly greater ($P = 0.011$) EF of 0.01% of applied C compared to the very small negative value for bunker manure (-0.003%; Table 5). Emission factors were not influenced by manure application rate ($P > 0.05$).

Manure type had a significant effect on NH_3 EFs, with emissions from the bunker manure being 21.6% of the total N applied, which was significantly greater ($P < 0.001$) than the 10.9% loss measured from the weeping wall manure (Table 5). Presenting the emissions as a percentage of the TAN applied showed that differences in losses remained significant ($P <$

0.001), at 46.9 and 39.8% of the TAN applied in bunker and weeping wall manure, respectively. The rate of manure applied did not influence the NH_3 emission factor ($P > 0.05$).

Table 5: Nitrous oxide, methane and ammonia emission factors for bunker and weeping wall manures applied at three rates to pasture. Negative values suggest sink activity.

Treatment (manure type and rate)	N_2O (% of N applied)	N_2O (% of TAN applied)	CH_4 (% of C applied)	NH_3 (% of N applied)	NH_3 (% of TAN applied)
Bunker @ 1.5 t DW/ha	-0.031	-0.064	-0.008	20.8	45.3
Bunker @ 3.0 t DW/ha	0.015	0.034	-0.002	21.5	46.7
Bunker @ 4.5 t DW/ha	0.022	0.046	-0.001	22.4	48.8
Weeping wall @ 1.5 t DW/ha	0.009	0.034	0.000	10.4	38.0
Weeping wall @ 3.0 t DW/ha	0.029	0.106	0.012	10.7	39.2
Weeping wall @ 4.5 t DW/ha	-0.002	-0.008	0.017	11.6	42.2
Statistics: effect of rate					
F-stat (Rate)	P = 0.187	P = 0.164	P = 0.294	P = 0.128	P = 0.163
Mean of manure type					
Bunker	0.005	0.011	-0.003	21.6	46.9
Weeping wall	0.009	0.032	0.011	10.9	39.8
Statistics: effect of manure type					
F-stat (Manure type)	P = 0.662	P = 0.742	P = 0.011	P < 0.001	P < 0.001

Discussion

Manure storage trial

The initially high rates of NH_3 emission observed from all three manures was probably due to a high rate of urea hydrolysis and ammonia volatilisation in response to the physical disturbance caused during their transfer into storage containers. The lower NH_3 emission from the deep litter manure was probably due to the lower ammoniacal-N content of this manure and the higher manure C:N ratio compared with either bunker or weeping wall manures (Table 1) as a result of woodmix included in this manure. Results from the destructive sampling of manures showed that ammoniacal-N remained low throughout the trial (data not presented). A higher C:N ratio in the deep litter manure will increase the likelihood of NH_3 being immobilised into the organic N pool. The C:N ratios for the remaining two manures were very similar, at 19 and 22 (Table 1), which may explain the similar cumulative NH_3 losses from these two materials (Table 4).

The large N_2O loss observed from the deep litter manure, which began in late July three weeks after manure placement and lasted 6 weeks (Fig. 3), was likely due to enhanced mineralisation and nitrification of organic N within the aerated zone of the manure producing nitrate, which will have diffused to anaerobic zones. With ample C substrate supply, nitrate will have rapidly denitrified through to N_2O and N_2 in these anaerobic areas. Results from the destructive sampling indicated an increase in nitrate-N content in the manure during the period when N_2O emissions were highest, supporting the suggestion that nitrification activity was high. This manure also had the highest dry matter content (Table 1), which may have aided oxygenation and gas diffusion through the manure, aiding both mineralisation and nitrification activity. The depth of the aerated zone in the surface crust of manure appears to regulate nitrate production and N_2O emissions, with these processes and losses increasing with increased depths of aeration (Aguerre et al., 2012). While the bunker manure had a dry matter content that was only a little lower than for the deep litter manure, N_2O emissions were lower and also were initiated about one month later (Fig. 3). This may have been due to insufficient labile C being available for denitrifying bacteria. In contrast, the lower dry matter contents, and therefore presumably more anaerobic conditions, within the weeping wall manure may have completely reduced the rate of nitrification, and/or denitrifying bacteria may have reduced nitrate through to N_2, resulting in lower N_2O losses (Fig. 3).

Methanogenesis in manures and slurries occurs under anaerobic conditions when there is a C supply, with CH_4 production increasing with increasing temperatures. Methane emissions were not detected until more than 4 months after the manure storage trial was initiated (Fig. 4). Weeping wall manure produced the largest CH_4 losses, presumably due to this manure being the most anoxic, with a moisture content of 88% (Table 1). Methane was only detected once the mean monthly manure temperature reached *ca* 18 °C, with CH_4 emissions increasing with increasing manure temperatures. The similar amount of CH_4 produced from the deep litter and bunker manures was presumably due to the similar aeration status of these manures, with both having approximately 80% moisture content during the entire storage trial period (*ca* 7 months).

Emissions following land application
The manure treatments were applied to the pasture sward to simulate commercial application of material with high total solids content. Consequently, in this trial there was little contact between the manure and the soil due to no rain during the four days following application, resulting in manure drying out while located on top of the sward. Rainfall that occurred 5 days later caused the manure to drop down to the soil surface. Unless rainfall or irrigation within several days of application is able to transport manure through the sward to the soil surface, where the microbial processes occur, it is likely that the biologically-regulated production of gases would be low. Consequently, N_2O production, a biologically driven soil process, was low in this study, resulting in very low emissions being measured. We observed a poor relationship between soil WFPS and N_2O emissions (data not shown).

Nitrous oxide EFs were less than 0.1% of applied total N from all treatments. Overseas research has shown that N_2O emissions from manure applied to land ranged from <0.1 to 3.0% (Chadwick et al., 2011; Webb and Misselbrook, 2004). This signifies the values observed in the current study are at the low end of the spectrum. N_2O emission factors are highly dependent on environmental conditions, manure composition and placement. Soil conditions (pH, drainage, texture, soil moisture) will also influence the degree of N_2O production when manures do infiltrate into the soil.

Chadwick et al. (2011) suggested that N_2O emission factors for land-applied manures may be better expressed on the basis of the inorganic N content of the manure, which is primarily in the form of ammonium and ammonia i.e. TAN, rather than on the basis of total N applied, as this represents the readily available N content. This may provide a more useful way of expressing emission factors, as mineralisation of organic N may make a minor contribution to short to medium term N_2O emissions. The lack of a significant difference in EFs between manures was maintained when presenting the results on the basis of TAN applied. The rate of manure application showed no effect on EF values. However, this was probably partly influenced by the low rate of N_2O emission affecting the ability to detect differences in emissions between the different rates of manure applied.

In contrast to N_2O, CH_4 emissions occurred rapidly following manure application, then declined to zero within 3-6 days. This is most likely due to trapped CH_4 produced during manure storage being released following land application (Rodhe et al., 2006; Sommer et al., 1996). It is also possible that CH_4 production ceased following land application due to the sensitivity of methanogens to oxygen (Chadwick et al., 2011). The immediate release of CH_4 following manure application was also observed by Chadwick et al (2000), with >90% of the total loss occurring in the first 24 hours.

Manure type influenced CH_4 emission factors, with weeping wall manure emitting 0.01% of the applied total C which is significantly greater than that from the bunker manure. Whilst this is a very small amount of CH_4 production, the difference in emissions between the two manures probably relates to their volatile fatty acid (VFA) content, which was greater for the weeping wall manure (Table 2). Correlations have previously been noted between VFA content in manure and the CH_4 emitted following manure application (Kirchmann and Lundvall, 1993; Sommer et al., 1996). The bunker manure produced negative cumulative losses and associated emission factors, suggesting the soil and manure acted as a net sink for CH_4. Rodhe et al. (2006) also reported net sink activity following the application of cattle slurry to a grassland soil, with soil and slurry consuming 362 g CH_4-C ha^{-1} over a 7 week period.

Ammonia emissions from the applied manures, at 11 and 22% of the applied total N in weeping wall and bunker manures, respectively, were sufficiently large to be considered as a significant agronomic loss of N. While this may deposit onto land downwind, thereby providing additional N to agricultural systems, this atmospheric input is non-targeted and non-controlled, therefore may deposit in areas vulnerable to these inputs (e.g. sensitive low N ecosystems such as native forests). It is possible that the aspirated chamber method we employed for measuring NH_3 emissions, using *ca* 12 air changes per minute, may have enhanced convective emissions. However, when presented on the basis of TAN applied, losses were 47 and 40%, respectively, which are similar to those measured by others using windtunnel methodologies where lower air changes per minute were used. For instance, Chambers et al. (1997) measured a loss of 30% of the applied TAN when cattle farmyard manure (total solids content of 23.5%) was applied to grassland, while Misselbrook et al. (2002) conducted 21 field trials and measured a mean loss of 37% of applied TAN when slurry was surface broadcast onto grassland. Windtunnels are considered to be more reliable than aspirated chambers (Sherlock et al., 2008).

The higher NH_3 emission factor for the bunker manure is likely due to a combination of factors all relating to the manure characteristics. The bunker manure had a higher TAN content (10.9 vs. 6.9 g TAN/kg DW manure) and slightly higher pH (7.8 vs. 7.2; Table 2),

both of which favour NH_3 volatilisation. This manure also had a slightly higher dry matter content, which would reduce its infiltration into the soil, thereby increasing its susceptibility to NH_3 emissions (Pain et al., 1989; Sommer and Olesen, 1991). However, as the manures were applied to the sward surface and the NH_3 emissions were measured from covered plots (and therefore not exposed to rainfall), this third characteristic is unlikely to have influenced the results in our study.

For all three GHGs (N_2O, CH_4 and NH_3) considered in this study, lowering the rate of manure application to pasture had no effect on the emission factors.

We aim to use the results of this study in conjunction with overseas data to conduct a life cycle assessment of contrasting wintering systems, where systems that include animal confinement facilities will be compared to the more traditional grazing of winter forage crops.

From our study we conclude that farmers should aim to empty their manure storage facilities by *ca* October provided ground conditions are suitable and the N inputs meet pasture or crop requirements, thereby reducing any risk of N leaching losses.

Conclusion
Our small-scale manure storage study showed that NH_3 emissions are greatest from weeping wall solid manure and bunker manure, with between 5-6% of the initial total N content being lost to the atmosphere in the first 4 months of storage. In contrast, only *ca* 1% was lost from deep litter manure. While NH_3 emissions were complete within 3 months, N_2O and CH_4 emissions generally increased as storage duration increased from 3 to 7 months. Cumulative N_2O emissions were negligible from weeping wall manure, but greatest from deep litter manure at *ca* 2% of the initial total N after 7 months storage. Cumulative CH_4 emissions were low from all three manures for up to 4 months storage, but increased to 5% of the initial total C content in the weeping wall manure, and *ca* 1% for the two remaining manures.

The land application trial resulted in large NH_3 emissions, with up to 22% of the total N and up to 47% of the TAN being lost to the atmosphere. In contrast, the N_2O EFs were extremely low, at < 0.1%, primarily due to little/no contact between the manure and the soil surface. Methane emissions were also very low, suggesting land application of manure is a negligible CH_4 source. The rate of manure application to pasture (ranging from 1.5 to 4.5 t dry weight/ha, equivalent to ~10 to ~30 t fresh weight/ha) did not influence the emission factor for all three greenhouse gases.

We suggest farmers empty manure storage facilities in October to avoid increased GHG emission from these facilities in the summer period. However ground conditions need to be suitable for access and N inputs should not exceed pasture or crop requirements, thereby reducing any risk of N leaching losses.

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