DOES ADDING STRAW OR SAWDUST TO CATTLE EXCRETA REDUCE AMMONIA, NITROUS OXIDE AND METHANE EMISSIONS DURING STORAGE?

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ABSTRACT

Animal shelters are used to house dairy cows off-paddock over winter (non-lactation season) and strategically during the lactation season when soils are wet. Shelters generally include bedding material such as sawdust or straw. Adding these materials will change the manure properties which may result in reduced ammonia (NH_3), nitrous oxide (N_2O) and methane (CH_4) emissions during manure storage. All three gases contribute to greenhouse gas (GHG) emissions from agriculture. Consequently, addition of sawdust or straw may provide a GHG mitigation option for dairy farmers.

The objective of this study was to compare NH₃, N₂O and CH₄ emissions from stored manures with different amounts of bedding material added. We conducted a 7 month manure storage trial where dairy cow excreta (dung:urine 1:1.3) was amended with straw or sawdust at two different ratios. At the end of the 7 months' storage, manures were mixed to simulate the disturbance that occurs when storage facilities are emptied.

Addition of straw and sawdust significantly reduced NH₃ emissions, while sawdust significantly reduced CH₄ emissions. However, N₂O emissions were significantly increased with sawdust addition. Converting emissions of all three GHGs to a carbon dioxide equivalent (eCO₂) basis indicated sawdust or straw addition to excreta had no significant effect on total emissions during the 7 month storage period. When including emissions from manure measured over a two week period following mixing, eCO₂ was significantly greater from the low rate of sawdust compared to the excreta treatment, due to large N₂O emissions. We conclude that sawdust and straw applied at the rates used in this study are not mitigation options for GHG emissions from stored manure. The data also suggested another and more practical option for farmers aiming to reduce emissions during manure storage would be to empty storage facilities as soon as ground conditions allow land application.

INTRODUCTION

There is increasing use of animal shelters that house dairy cows off-paddock over winter (non-lactation season) and strategically during the lactation season when soils are wet. These are particularly common in Southland and South Otago,New Zealand due to local soil and climatic conditions. There is dearth of data on greenhouse gas (GHG) emissions and potential mitigation options associated with manure storage in New Zealand. Dairy farmers use a variety of bedding materials for housed wintering systems, including straw and sawdust. Both products are carbon (C) -based, thereby can potentially immobilise N excreted as urine by the

cows. Thus, this practice may lead to more organic N in manure and lower GHG emissions compared to systems where no C material is added. The hypothesis tested in this study was that GHG emissions from stored manure will be significantly reduced by addition of C-rich material (straw and sawdust).

METHODS

An outdoor trial, conducted using a mini-animal shelter facility at Ruakura, Waikato, was used to quantify N_2O , NH_3 and CH_4 emissions from stored manures that were amended with straw and sawdust in early July 2011. Fresh cattle excreta (dung and urine) was collected from a Waikato dairy farm and mixed with differing ratios of straw or sawdust to provide additional C. The ratio of excreta to straw or sawdust was chosen to approximate current bedding practice on two representative southern New Zealand farms. The straw was a mixture of barley and wheat at a ratio of 1:3 v/v; again, representing the mix used on farm for bedding. Characteristics of excreta and C materials are shown in Table 1, while treatments are shown in Table 2. On 6 July 2011 each treatment, replicated four times, was placed into a series of 0.5 m long upright plastic pipes, sealed at the base and buried, until level with the ground level.

Table 1. Characteristics of excreta and C materials used in storage trial.

Manure	рН	Total N (%, dry weight basis) ^A	Total C (%, dry weight basis)	C:N
Dung	6.4	3.10	41.5	13
Urine	8.4	0.47^{A}	< 0.1	
'Excreta' (dung:urine = 1:1.3 v/v)	8.4	6.37	39.2	6.2
Straw mixture (Barley and wheat)	6.9	0.61	44.6	73
Sawdust	4.3	0.18	49.8	272

^AUrine N content presented on a wet weight basis, i.e. g/100ml

Table 2. Treatments for the outdoor manure storage trial.

Treatment	Components in columns
Control	Excreta only, dung:urine = 1:1.3 v/v
Sawdust - high rate	Excreta: $sawdust = 0.3:1v/v$
Sawdust - low rate	Excreta: $sawdust = 1:1v/v$
Straw - high rate	Excreta:straw mixture = 2.9:1 v/v
Straw - low rate	Excreta:straw mixture = 6.6:1 v/v

Two sets of columns were established: one for gas measurements, where each treatment was replicated 4 times. Manure in the second series of columns was destructively sampled on seven occasions throughout the trial period. Three samples were include on each sampling date i.e 3 replicates, giving a total of 21 destructive sampling columns for each manure type. Gas sampling columns used a larger 150 mm diameter piping, while columns for destructive sampling used 50 mm diameter piping.

Following the addition of the manure to the gas sampling columns, NH_3 volatilisation was measured on 25 occasions for a 24-hour period over $7\frac{1}{2}$ months, with nine of the measurements being made within the first month. Measurements were made by placing lids on the top of the columns and passing air through the lids and then through dreshel bottles containing an acidic ammonia gas trap (Luo et al., 2004). The acid was analysed colorimetrically for ammonium 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). Fluxes of N_2O and CH_4 were determined on 24 occasions over a $7\frac{1}{2}$ month period, with an initial high frequency of measurements (8 in the first month) that gradually decreased over time.

Columns containing manures for gas sampling remained undisturbed for 7 months, with the final measurements made in early February 2012. For the destructive sampling columns, three replicates of each treatment were emptied each month, with the entire contents mixed and sent to Analytical Research Laboratories for nutrient content analysis.

Gaseous fluxes were calculated and integrated over two time periods to provide cumulative losses over two durations: 1) 190 days of storage, and 2) 227 days. This latter duration includes the storage period and 2 weeks of emissions following manure mixing to simulate emptying of manure storage facilities. For N and C, cumulative emissions were calculated on the basis of µg per g oven dry manure. Losses were calculated as a percentage of the initial total N or C content of the excreta. GHG emissions were converted to a carbon dioxideequivalent (eCO₂) basis to provide a comprehensive assessment of the impact of sawdust and straw addition. N₂O and CH₄ have a global warming potential (GWP) of 298 and 25 times that of CO₂ over a 100 year time period (Forster et al., 2007). Ammonia is an indirect source of N₂O, where it is assumed that 1% of emitted NH₃ will be re-emitted as N₂O following downwind deposition. Using the GWP values, adjusting NH₃ emissions for its indirect contribution to GHG emissions and converting emissions to a molecular weight basis, the eCO₂ emissions for each manure treatment was calculated. The calculations were based on eCO₂ emissions from 1 tonne of excreta on a dry weight basis, containing 392 kg C/t dry weight excreta and 63.7 kg N/t dry weight excreta, with an equivalent C:N ratio of 6.2:1 (all values shown in Table 1 for the excreta made from mixing dung and urine at 1:1.3 v/v). This approach ensured all treatments could be compared to determine their potential for mitigating emissions from the excreta component.

Results were statistically analysed by ANOVA (Genstat 13), where cumulative emissions required a log transformation to determine differences between treatments.

RESULTS

Manure characteristics

Manure pH was affected over the storage period by the addition of sawdust, but not by straw (Fig. 1). The addition of sawdust to excreta had no initial effect on pH, which was 8.4 and similar to the untreated control. However, analysis of the manures used for the gas measurements after 7½ months storage showed that the high sawdust treatment had the lowest pH (6.1; data not shown). Data from the destructively sampled manures show pH declining over time in this high sawdust rate treatment (Fig. 1), with the pH measured on the last sample date (1 February) being 5.5. This agrees with the pH measured in the same treatment from the large cores at the end of the gas trial. The sawdust had a pH of 4.3 (Table 1). In contrast, the straw with a pH of 6.9 had little effect on the manure pH, which was initially 8.1, increasing slightly to 8.3 by the end of the trial. The destructive sampling also showed little change in pH in the straw treatment, thus agreeing with the measurements made from the large cores of the end of the trial (Fig. 1).

The initial ammoniacal N content of the manures ranged from 302 to 2244 mg NH₄-N/L, with levels declining in relation to increasing amounts of C (Fig. 2). During the 7 months of storage, ammoniacal N content generally declined by, on average, 28%. In contrast, the nitrate N content of the manures was very low at the start of the trial (4 mg/L in the control and 1-3 mg NO₃-N/L in the amended manures; Fig. 3) and remained very low in the control and straw-amended manure. However, a rapid increase in NO₃-N content was observed in the sawdust-amended manure during November-December presumably due to nitrification when temperatures increased to *ca* 18° C (data not shown). Nitrate levels by the end of the storage period were 133 and 235 mg NO₃-N/L for high sawdust and low sawdust manures, respectively. An increase in NO₃-N was more rapid in the low sawdust treatment, presumably due to nitrification activity being less limited by NH₄-N supply than in the high sawdust treatment, which had declined to <50 mg N/L by early November (Fig. 2).

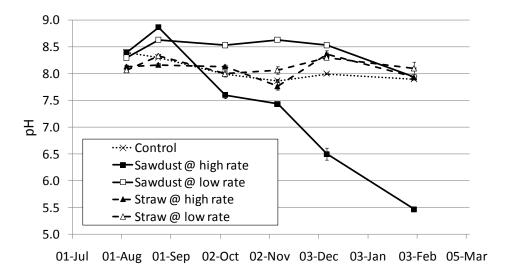


Figure 1. Mean changes in manure pH in five types of manures during 7 months storage. Error bars represent ± SEM.

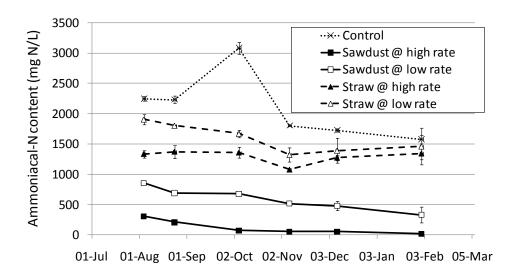


Figure 2. Mean changes in ammoniacal-N contents (mg N/L) in five types of manures during 7 months storage. Error bars represent \pm SEM.

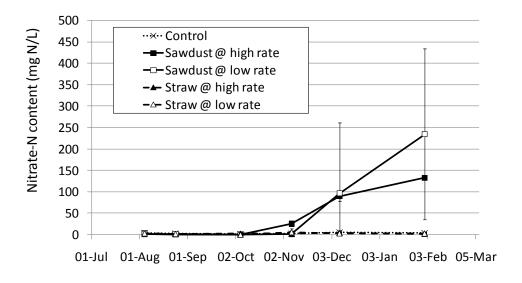


Figure 3. Mean changes in nitrate-N contents (mg N/L) in five types of manures during 7 months storage. Error bars represent \pm SEM.

Ammonia emissions

The addition of straw and sawdust significantly reduced the rate of NH₃ volatilisation throughout the entire storage trial, with the level of reduction increasing with increasing amounts of C added (Fig. 4). Consequently, sawdust at the high rate was the most effective at reducing the rate of NH₃ loss. The low pH of the manure with the highest rate of sawdust (Fig. 1) probably contributed to the low NH₃ emissions observed for this treatment. During mixing of manures, a large amount of NH₃ gas was released which was presumably trapped within the manure substrate. Most of the treatments returned to NH₃ volatilisation rates similar to those prior to the mixing. One exception, however, was the straw low rate

treatment, which maintained high NH_3 volatilisation rates over the two week period following manure mixing (Fig. 4). Cumulative NH_3 loss during excreta storage was 48% of the initial N content of the excreta. This was significantly reduced (P < 0.001) with straw and sawdust addition, particularly when high rates of sawdust were added, resulting in a total NH_3 loss of 3% of the initial excreta-N content. When the losses following the mixing of the manure were included, the difference between non-amended excreta and amended excreta was greater, whereby losses decreasing from 58% to 3% with the addition of high rates of sawdust (Table 3).

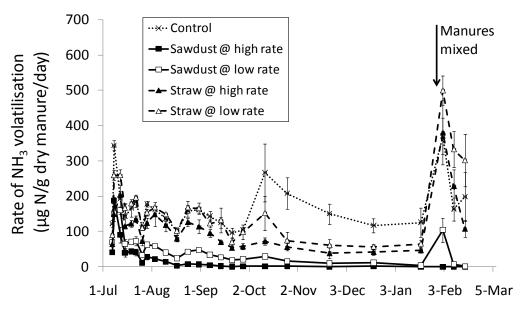


Figure nure treatments

4. Rates of NH₃ volatilisation (µg NH₃-N/g dry manure/day) from five manure treatments stored for 7 months, then mixed to simulate emptying of storage facilities.

Nitrous oxide

Addition of sawdust to excreta resulted in an increase in N_2O emissions, with greater losses detected from manure containing the low rate of sawdust (Fig. 5). These losses were increased following the mixing of the manure and remained high at the conclusion of the storage trial in mid-February. An increase in N_2O emissions was observed from the high rate of sawdust approximately 1 month earlier than from the low sawdust rate, however these emissions remained relatively low before returning to levels similar to the control by the end of the trial. In contrast, N_2O emissions were virtually zero from the straw and control treatments for the entire trial (Fig. 5).

Cumulative N_2O emissions, as a percentage of the initial excreta-N content, were greatest following the addition of sawdust, with 1.1 and 0.9% being measured from excreta amended with sawdust at a high rate and low rate, respectively (Table 3). In contrast, cumulative N_2O emissions were significantly lower (P < 0.001), at less than 0.01% from the excreta only and the straw amended excreta. Mixing stimulated N_2O emissions from the sawdust treatment, resulting in 1.4% and 4.3% of the initial excreta-N being emitted from the high and low rates of sawdust addition, respectively (Table 3). The other treatments showed very little change in cumulative N_2O emissions following mixing.

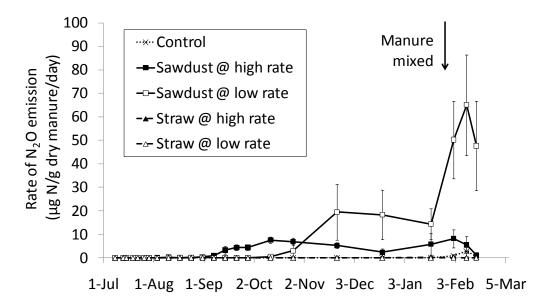


Figure 5. Rates of N_2O emission ($\mu g N_2O$ -N/g dry manure/day) from five manure treatments stored for 7 months, then mixed to simulate emptying of storage facilities.

Methane

Addition of straw to excreta increased the rate of CH₄ emitted relative to non-amended excreta ('control' treatment) over the 7½ month storage period (Fig. 6). Initially, CH₄ emissions peaked in the control treatment; however 4 months after the trial was initiated (November), CH₄ emissions began to increase from both straw treatments. The mixing of the manure initially reduced and then stimulated CH₄ emissions from the straw treatments. In contrast, adding sawdust to excreta suppressed CH₄ emissions entirely, during both the storage and post-mixing periods (Fig. 6).

The total amount of C lost as CH_4 during 7 months storage of excreta only was 0.6% of the initial excreta-C content. Sawdust suppressed CH_4 emissions to near zero, which was significantly lower than observed for the control treatment during the 7 month storage period, and also when including the 2 weeks period following mixing of the manure (Table 3, P < 0.001). Addition of straw did not significantly alter CH_4 emissions (P > 0.05), resulting in 0.8-0.9% of the initial excreta-C being emitted as CH_4 (Table 3). Following mixing, cumulative CH_4 emissions from the straw-amended excreta increased to between 1.2 and 1.4% of the initial excreta-C content; however this was not significantly different from the excreta-only treatment (P > 0.05).

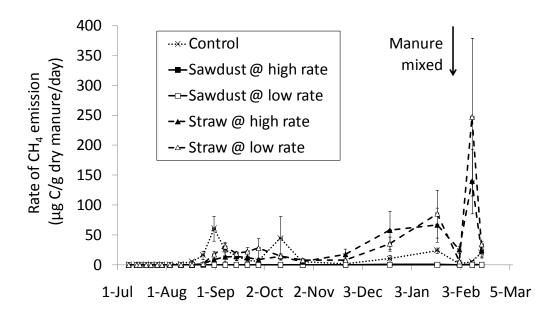


Figure 6. Rates of CH₄ emission (µg CH₄-C/g dry manure/day) from five manure treatments stored for 7 months, then mixed to simulate emptying of storage facilities.

Table 3: Cumulative NH₃, N₂O and CH₄ emissions (% of initial total N or C in excreta) over two periods: 'Storage' relates to 7 months of storage, 'Storage + Mixing' includes emissions measured in the 7 months of storage and 2 weeks following mixing of manure.

Excreta	NH ₃		N_2O		$\mathrm{CH_4}$		
	Storage	Storage + Mixing	Storage	Storage + Mixing	Storage	Storage + Mixing	
Control (excreta only)	47.7	58.2	<0.01	0.03	0.61	0.68	
Sawdust – high rate	2.8	2.8	1.14	1.38	0.01	0.01	
Sawdust – low rate	8.9	10.7	0.87	4.28	< 0.01	< 0.01	
Straw – high rate	22.4	32.1	< 0.01	<0.01	0.77	1.21	
Straw – low rate	32.9	47.6	< 0.01	< 0.01	0.86	1.39	
P-value	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	

Total greenhouse gas emissions

The eCO₂ analysis showed that during the storage phase of the trial, the excreta only treatment produced 223 kg eCO₂/t dry weight excreta (Table 4). The addition of C-material had no significant effect on the total eCO₂ emissions (P > 0.05) during the storage period. When GHG emissions following the mixing were included, there was a significant difference observed (P < 0.001), solely due to the low rate of sawdust treatment producing significantly higher eCO₂ emissions compared to the other treatments (Table 4).

Table 4: Amounts of NH₃, N₂O, CH₄ and total GHGs emitted from excreta, all presented as carbon dioxide equivalents (kg eCO₂/t dry weight excreta) over two periods: 'Storage' relates to 7 months of storage; 'Storage + Mixing' includes emissions measured in the 7 months of storage and 2 weeks following mixing of manure.

Excreta	NH ₃ -eCO ₂		N ₂ O-eCO ₂		CH ₄ -eCO ₂		Total eCO ₂ ^A	
	Storage	Storage + Mixing	Storage	Storage + Mixing	Storage	Storage + Mixing	Storage	Storage + Mixing
Control (excreta only)	142	174	<1	7	80	89	223	269
Sawdust - high rate	8	8	370	449	1	2	380	459
Sawdust - low rate	27	32	271	1391	<1	<1	298	1423
Straw – high rate	67	96	1	2	100	158	168	256
Straw – low rate	98	142	1	1	113	181	212	324
P-value	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	NS	< 0.001

A Rounding off to whole numbers may mean totals do not reflect sum of individual parts.

DISCUSSION

Ammonia

Amending excreta with C-rich material reduced NH_3 emissions, presumably primarily due to immobilisation of NH_4^+/NH_3 and/or an increased cation exchange capacity (CEC) from the material helping to retain NH_3 (Willers et al., 1996). The low pH of the sawdust may have contributed to the overall lower NH_3 losses from the sawdust-amended manures by influencing the NH_4^+/NH_3 equilibrium; however, this effect was likely to be secondary to the main effects of immobilisation and increased CEC. This is supported by the significant

decrease in NH₃ losses from the low rate of sawdust compared to the two straw treatments, where the pH changes were similar across all three treatments (Fig. 1) but the C inputs differed (Tables 1 & 2).

Nitrous Oxide emissions

The supply of mineral N (NH_4^+ and NO_3^-) and available C has a major effect on the production of N_2O by biological nitrification and denitrification processes. The N_2O emissions were very low for the control treatments, suggesting low nitrification and denitrification activities in the stored excreta. The lack of aeration in the stored excreta probably inhibited nitrification, as there was no, or little, NO_3^- formed. Furthermore, the high moisture conditions of the excreta may have affected the transport of N_2O to the surface.

Addition of sawdust to excreta resulted in a rapid increase in NO_3 -N content via nitrification, beginning in November (Fig. 3), when manure temperatures had increased to 17-18 °C (data not shown). Indeed, there was a more rapid increase in NO_3 -N levels in the low sawdust treatment, presumably due to nitrification activity being less limited by NH_4 -N supply than for the high sawdust treatment, which had declined to <50 mg N/L by early November (Fig. 2). This increase in nitrification, presumably coupled with denitrification, resulted in a rapid increase in N_2O emissions from the two sawdust treatments. Conditions within the manure, including low pH due to the acidic nature of the sawdust (pH 4.3), relatively low moisture content, and unlimited supply of NO_3 substrate via nitrification, may have all contributed to a high $N_2O:N_2$ ratio of the denitrification products.

The rapid increase in N_2O emission from the 'low rate' of sawdust following mixing was presumably due to enhanced mineralisation and coupled nitrification-denitrification of the manure, as a result of increased oxygen concentrations through the manure.

Addition of straw did not have the same effect as sawdust on N_2O production and emission (Fig. 5). The high moisture content of the excreta probably limited nitrification rates by limiting the availability of oxygen. Low oxygen and high C contents may also favour complete denitrification of NO_3^- through to N_2 gas rather than intermediary N_2O (Bolan et al., 2004). The lack of any NO_3^- being measured may be due to coupled nitrification-denitrification, with NO_3^- being rapidly denitrified once it has formed. Low NO_3^- content also favours N_2 over N_2O production, as a high NO_3^- content can inhibit N_2O reductase activity, which is required for the reduction of N_2O through to N_2 .

Methane emissions

Methane emissions from stored animal excreta are influenced by the amount of degradable organic matter, the excreta dry matter content and temperature. Greater CH₄ emissions from the "control excreta" compared to the straw-amended excreta during the earlier storage period (Fig. 5) may have been due to more degradable organic matter being available from the excreta in the "control excreta" treatment. The addition of straw material may have temporarily enhanced immobilisation of available C from the excreta, leading to less C available for methane production. Furthermore, the addition of straw may have increased aerobic conditions that effectively prevented methanogenesis during the earlier storage period. However, the degradable organic matter likely made available to microorganisms in the "straw added" excreta may have increased 4 months after the trial was initiated, leading to an increase in CH₄ production during the late storage period (Fig. 5). It is possible that the amounts of degradable organic matter in the "straw added" excreta were larger than in the

"control excreta" treatment, thereby more CH₄ was formed from the former excreta. This hypothesis is supported by the fact that more, albeit not significantly, CH₄ was produced and emitted from the "high straw rate" compared with that from the "low straw rate" excreta" (Table 3). The cumulative CH₄ loss from the excreta only and the straw-amended excreta was similar both during the storage and the storage + post-mixing phases.

It is not known why adding sawdust to excreta suppressed CH₄ emissions so greatly. We suspect that addition of sawdust may have inhibited methanogenic fermentation of organic materials due to the acidic nature of the sawdust (pH 4.3; Table 1). Addition of sawdust may have also enhanced O₂ diffusion to the stored excreta, thereby inhibiting methanogenesis. Additionally, methanogenic bacteria can metabolise only a restricted suite of compounds that provide energy for their growth, e.g. acetate, formate, methanol and methylated amines (Saggar et al., 2004). The sawdust we used in this trial may not contain or have produced these types of compounds.

Combined emissions based on global warming potentials

Both sawdust and straw were shown to effectively reduce NH₃ losses, with reductions increasing with increasing C inputs (Table 3). High rates of sawdust were also effective at reducing CH₄ emissions. However, this also led to high N₂O emissions. When converting these emissions to eCO₂ units, the high GWP of N₂O and CH₄, indicates sawdust addition, at the rates applied, had no effect on total emissions (Table 4). The increase in N₂O emissions from the low sawdust treatment following mixing (Fig. 5) was sufficient to significantly increase the total eCO₂ compared to the excreta only treatment. The straw treatment had no effect on the total eCO₂, which may be a consequence of the lower rates of C-amendment compared to the sawdust and/or differences in sawdust and straw carbon quality influencing microbial activity. Consequently, our study suggests we reject the hypothesis that GHG emissions will be lower when amending excreta with C-rich materials such as straw and sawdust.

IMPLICATIONS

The results from this study suggest addition of sawdust or straw as bedding material does not provide a mitigation option for lowering GHG emissions from excreta stored over a 7 month period.

The emission profiles of N_2O and CH_4 suggest the most practical option for mitigating total GHG emissions is to empty manure storage facilities as soon as soil conditions allow in spring. While this may have a minor impact on reducing NH_3 losses, the major contributors to the total GHG profile are N_2O and CH_4 , which showed an increase in emissions in late spring with increasing temperatures. Based on regional air temperatures, a broad guideline would be for Waikato farmers to empty their manure storage facilities by early October, while in the cooler south (e.g. Southland), empty by late October.

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