Emissions of ammonia, nitrous oxide, methane, and carbon dioxide during storage of dairy cow manure as affected by dietary forage-to-concentrate ratio and crust formation

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ABSTRACT

Sixteen 200-L barrels were used to determine the effects of dietary forage-to-concentrate (F:C) ratio on the rate of $\text{NH}_3\text{-N}$, N_2O , CH_4 , and CO_2 emissions from dairy manure during a 77-d storage period. Manure was obtained from a companion study where cows were assigned to total mixed rations that included the following F:C ratio: 47:53, 54:46, 61:39, and 68:32 (diet dry matter basis) and housed in air-flow-controlled chambers constructed in a modified tiestall barn. On d 0 of this study, deposited manure and bedding from each emission chamber was thoroughly mixed, diluted with water (1.9 to 1 manure-to-water ratio) and loaded in barrels. In addition, on d 0, 7, 14, 28, 35, 49, 56, 63, 70, and 77 of storage, the rate of $\text{NH}_3\text{-N}$, N_2O , CH_4 , and CO_2 emissions from each barrel were measured with a dynamic chamber and gas concentration measured with a photoacoustic multi-gas monitor. Data were analyzed as a randomized complete block with 4 replications. Dietary F:C ratio had no effect on manure dry matter, total N and total ammoniacal-N ($\text{NH}_3\text{-N} + \text{NH}_4^+\text{-N}$), or pH at the time of storage (mean $\pm$ SD: $10.6 \pm 0.6\%$, $3.0 \pm 0.2\%$, 93.1 ± 18.1 mg/dL, and 7.8 ± 0.5 , respectively). No treatment differences were observed in the overall rate of manure $\text{NH}_3\text{-N}$, N_2O , CH_4 , and CO_2 emissions (mean $\pm$ SD over the 77-d storage period; 117 ± 25 , 30 ± 7 , 299 ± 62 , and $15,396 \pm 753$ mg/hr per m^2 , respectively). The presence of straw bedding in manure promoted the formation of a surface crust that became air dried after about 1 mo of storage, and was associated with an altered pattern in $\text{NH}_3\text{-N}$ and N_2O emissions in particular. Whereas $\text{NH}_3\text{-N}$ emission rate was highest on d 0 and gradually decreased until reaching negligible levels on d 35, N_2O emission rate was almost zero the first 2 wk of storage, increased sharply to peak on d 35, and decreased subsequently. The emission rate

of CH_4 and CO_2 peaked simultaneously on d 7, but decreased subsequently until the end of the storage period. In this study, C:N ratio of gaseous losses was 32:1, reflecting higher volatile C loss than volatile N loss during storage. On a CO_2 -equivalent basis, the most important source of non- CO_2 greenhouse gas emitted was CH_4 until formation of an air-dried crust, but N_2O thereafter. Taken together, these results suggested that the formation of an air-dried crust resulting from the straw bedding present in the manure reduced drastically $\text{NH}_3\text{-N}$, and CH_4 emissions, but was conducive of N_2O production and emission.

Key words: ammonia, nitrous oxide, methane, manure

INTRODUCTION

National (NRC, 2003; EPA 2009) and international (FAO, 2006) reports have concluded that animal feeding operations are important sources of undesirable gaseous emissions that affect natural ecosystems and human health (NH_3) and contribute to emissions of non- CO_2 greenhouse gases (CH_4 and N_2O). Although several strategies have been evaluated for reducing emission of NH_3 (Ndegwa et al., 2008; VanderZaag et al., 2008) and non- CO_2 greenhouse gases (Benchaar et al. 2001; Boadi et al., 2004; Martin et al., 2010), few of the proposed mitigation strategies so far have emerged from experiments in which multiple gases were measured simultaneously (Külling et al., 2001). In addition, most studies have tended to compartmentalize gaseous emissions at either the housing and collection subsystem, the storage subsystem, or the field application subsystem. Few studies have crossed subsystem boundaries (Amon et al., 2001).

Results from a companion study (Aguerre et al., 2011) designed to determine the effects of forage-to-concentrate (F:C) ratios in the diet on cow performance and gaseous emission showed that increasing forage concentration from 47 to 68% of DM in isonitrogenous diets increased CH_4 emission per unit of ECM by 25%

Received January 12, 2012.

Accepted August 11, 2012.

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but did not alter $\text{NH}_3\text{-N}$ emission when cows were housed in a tiestall barn. The objective of this study was to determine the effects of F:C ratios in the diet on gaseous emission during manure storage. Thus, the pattern of change in volatile C loss (CO_2 and CH_4) and volatile N loss (NH_3 and N_2O) during a 77-d storage period was determined using the manure and bedding collected from cows in the companion study.

MATERIALS AND METHODS

Manure Storage, Sampling, and Analyses

The manure and bedding used in this trial was collected from a companion study (Aguerre et al., 2011). Briefly, 16 lactating Holstein cows were assigned to 1 of 4 air-flow controlled chambers (4 cows per chamber) constructed in a modified tiestall barn and, in turn, chambers were assigned to a sequence of 4 dietary treatments in a single 4×4 Latin square design, with 21-d periods. Dietary treatments, fed as TMR, included the following F:C ratio: 47:53, 54:46, 61:39, and 68:32 (DM basis). Dietary CP was similar among treatments and averaged 16.2% (DM basis). In contrast, as the F:C ratio increased from 47:53 to 68:32, NDF concentration increased from 31.3 to 38.3% of dietary DM, forage NDF (percentage of total NDF) increased from 68 to 79%, and starch concentration decreased from 29 to 20% of dietary DM. Cows were bedded on rubber mats with daily addition of wheat straw as bedding. Details of animal management, diet composition, animal performance, and gaseous emission data from the air-flow controlled chambers were described elsewhere (Aguerre et al., 2011).

During the last day of each period, deposited manure and bedding from each emission chamber was allowed to accumulate for 8 h. While cows were in the milking parlor, accumulated manure (including bedding deposited in the collection pans) was weighed using a bench scale (Ohaus ES Series Bench Scale; Ohaus Co, Pine Brook, NJ), loaded in 200-L barrels (90 and 61 cm in height and diameter, respectively), and diluted with water (1.9 to 1 manure-to-water ratio) to lower DM content to a range typically found in liquid manure (Rotz, 2004). Overall, the amount of manure-straw mixture and water added to a barrel averaged ($\pm$ SD) 114 ± 13 and 61 ± 7 kg, respectively. The average ($\pm$ SD) estimated amount of straw bedding ($0.81 \pm 0.17\%$ N and $71 \pm 0.7\%$ NDF) in the manure was 2.4 ± 0.7 kg, as calculated by difference between the amount of bedding added and recovered from the chamber.

The day the barrels were loaded (d 0), manure samples were collected from each barrel, preserved with 60% sulfuric acid, and stored at -20°C . Before

acidification, pH of a deionized water/manure mixture (2:1 ratio) was measured using a calibrated portable pH meter (Twin pH-meter model B-213; Spectrum Technologies Inc., Plainfield, IL). Manure samples were thawed at 5°C overnight and lyophilized in a Frezone 12 freeze dryer (Labonco Corp., Kansas City, MO). Before lyophilization, an acidified manure subsample was extracted with a 2 M KCl solution (Misselbrook et al., 2005) for total ammoniacal-N ($\text{TAN} = \text{NH}_3\text{-N} + \text{NH}_4^+\text{-N}$) determination by colorimetric assay (Chaney and Marbach, 1962). Lyophilized manure samples were ground through a 1-mm Wiley mill screen (Arthur H. Thomas Co., Philadelphia, PA) and analyzed for total N content (TN ; Leco FP-2000 nitrogen analyzer; Leco Instruments Inc., St. Joseph, MI) and analytical DM at 105°C for 24 h. Manure DM content was calculated as the amount of sample recovered after lyophilization. Neutral detergent fiber content was determined according to Van Soest et al. (1991) and adapted for an Ankom²⁰⁰ fiber analyzer (Ankom Technology Corp., Fairport, NY), using α -amylase (Sigma no. A3306; Sigma Chemical Co., St. Louis, MO) and sodium sulfite and corrected for ash concentration. Manure starch content was analyzed commercially (Dairyland Laboratories Inc., Arcadia, WI) using wet chemistry analysis (Bach-Knudsen, 1997). Furthermore, pH was measured on samples collected on d 77 following the procedure described above.

Gas Emissions Measurement

Each of the 4 barrels filled with manurial treatment at the end of each period of the 4×4 Latin Square design and a blank barrel with no manure were stored with no covering lid in an open-storage room located near the barn entrance, where temperature control was not possible. A 77-d storage period was chosen to avoid the effect of low seasonal temperature on emissions measurements. Four dynamic chambers were used to measure gas emission from each of the 4 groups of staggered barrels over a 1-h period on d 0, 7, 14, 28, 35, 49, 56, 63, 70, and 77 of storage following a procedure adapted from Misselbrook et al. (2005). A fifth dynamic chamber was used for the blank barrel. Thus, gas emission measurements were conducted over 140 d. Modified circular lids with a centrally located fan (model DB200; Suncourt Inc., Durant, IA; 0.10-m diameter) drew air across the manure surface through 4 inlet holes (0.025-m diameter) cut at regular intervals around the perimeter of the lid. Overall, the headspace (mean height between stored manure and the lid) was 22 ± 7 cm (mean $\pm$ SD). With increasing days of sampling, a general increase in the headspace occurred due to water and DM loss. Thus, headspace depth was

measured before starting each emission measurement. Based on the changes in headspace depth, central duct fans were regulated to obtain an air velocity across the manure surface of approximately 0.06 m/s and approximately 13 headspace changes per minute. Five cross-sectional samplers were constructed with Teflon tubing (Nalgene, Rochester, NY) to sample the air that passed through the headspace of the manure storage. Each sampler consisted of 4 round arms that cover the entire circumference of the fan. On each arm, 4 sampling holes were drilled at equal distance from the center of the sampler. Air samples were drawn through Teflon tubing (6.4-mm o.d., 4.8-mm i.d.; Nalgene) connected to a Whatman Hepa-Vent Filter (Fischer Scientific, Pittsburgh, PA). Air samples were sequentially drawn from each of the 5 samplers using a computer-controlled sequencer (Mark 3 Intelligent Sampler; California Analytical Instruments Inc., Orange, CA) and analyzed for NH_3 , N_2O , CH_4 , and CO_2 concentration with a manufactured-calibrated photo-acoustic multi-gas monitor (Innova model 1412; AirTech Instruments A/S, Ballerup, Denmark). The sequencer continuously collected an air sample from a barrel during 60 s to flush sampling tubing. Then, it sent an air sample to the gas analyzer and flushed the analyzer measurement chamber for 55 s. Finally, a single concentration (parts per million volume, **ppmv**) was measured sequentially for each gas in a 29-s period (a total sampling time for a single barrel of 2 min and 24s). As a result, air from each barrel was sampled once every 12 min. Measurements from the blank barrels were used to account for background gaseous concentrations. Concentration (g/m^3) of the measured gases was calculated with the following equation:

$$G = (C_o - C_i) \times 1,000 \times \text{MW}/V \times 1/1,000,000, \quad [1]$$

where G is the gas concentration in the outlet air (g/m^3); C_o is the concentration of the gas in the outlet air (ppmv); C_i is the concentration of the gas in the inlet air (outlet air of blank barrel; ppmv); MW is the molecular weight of the gas (16.04, 17.03, 44.01, and 44.01 g/mol for CH_4 , NH_3 , CO_2 , and N_2O , respectively); and V is the volume occupied by 1 mol of gas at the measured air temperature and pressure (L), obtained from a weather station in Prairie Du Sac, WI (accessed from <http://Wunderground.com>).

Air velocity and temperature through the central duct of the lid was measured using a hand-held rotating vane anemometer with a temperature sensor (model 8324 VelociCalc Plus; TSI Inc., Shoreview, MN). The volume of air through the central duct during each sampling interval ($\text{m}^3/12 \text{ min}$) was calculated as the

product of the air velocity through the central duct (m/min) and the surface area of the duct (m^2).

Amount of gas emitted (g) during each of the 12-min sampling intervals was calculated as the product of gas concentration in the outlet air (g/m^3) and the volume of air passing through ($\text{m}^3/12 \text{ min}$). The emission rate from the manure surface (g/h per m^2) was calculated by adding up the gas emitted at each of the five 12-min sampling intervals in the 1-h collection period (g/h) and expressed per square meter of surface area. In addition, emissions of CH_4 and N_2O were calculated as CO_2 equivalents, for a 100-yr time horizon, using a factor of 25 and 298 for CH_4 and N_2O , respectively (IPCC, 2007). The global warming potential was calculated as the sum of CO_2 equivalents emitted as CH_4 and N_2O . These emission measurements and calculations were used for treatment comparison and not as an attempt to determine emission factors. Gas emissions measured and reported here do not capture the numerous factors affecting gas emissions from manure storage on commercial farms.

Statistical Analyses

The experiment was conducted as a randomized complete block with 4 replicate and repeated measures. Manure composition on d 0 was analyzed with the mixed procedure in SAS (SAS Institute, 2004) with the following model:

$$Y_{ijk} = \mu + B_i + D_j + e_{ijk},$$

where Y_{ijk} is the dependent variable, μ is the overall mean, B_i is the effect of block ($i = 1$ to 4), D_j is the effect of diet ($j = 1$ to 4), and e_{ijk} is the residual error. All terms were considered fixed except for block and residual error.

For repeated measures including $\text{NH}_3\text{-N}$, CO_2 , CH_4 , and N_2O emission rates, the above model was expanded to include effect of day of storage and interaction between treatment and day of storage. All terms were considered fixed except for block and residual error. Due to heterogeneous variance across treatments, the first-order heterogeneous autoregressive covariance structure was used to fit the models (SAS Institute, 2004). To comply with the assumptions of normality and homoscedacity of residuals, gaseous emission rates were subjected to logarithmic transformation before statistical analysis. For these variables, reported arithmetic mean and standard error were from untransformed values, whereas P -values reflect statistical analysis of transformed data.

Preplanned orthogonal contrasts were used to test for linear and quadratic effects of treatments. Significance was declared for $P \leq 0.05$ and tendency for $0.05 < P \leq 0.10$. No interaction was observed between treatment and day of storage for any of the measured gases and results are presented as daily means.

RESULTS AND DISCUSSION

Manure Composition

Reported chemical components of manurial treatments (i.e., the mixture of feces, urine, diluting water, and straw) on d 0 were not influenced by the diet fed to the cows (Table 1). In contrast, Broderick (2003) reported higher manure TN excretion in isonitrogenous diets with increasing NDF content. Visual observation indicated that a crust started to form for all manurial treatments after 7 d of storage and the crust surface became dry between d 14 and 28; however, neither thickness nor moisture measurements were conducted to further characterize the crust. On d 77, a tendency ($P = 0.10$) was observed for a linear increase in manure pH as dietary forage increased (6.63, 6.75, 6.77, and 6.98 for F:C ratio of 47:53, 54:46, 61:39, and 68:32, respectively).

Ammonia-N Emission

Under the conditions of this trial, the 77-d average $\text{NH}_3\text{-N}$ emission rate (Table 2) did not differ among treatments (mean $\pm$ SD; 117 ± 25 mg/h per m^2). Similarly, varying the dietary F:C ratio had no effect on short-term manure $\text{NH}_3\text{-N}$ emissions from a barn floor (Lascano et al., 2008) or under controlled laboratory

conditions (Agle et al. 2010). The absence of differences in rate of $\text{NH}_3\text{-N}$ emissions among treatments was expected in part because of small differences in the initial amount of N placed in each barrel (Table 1) and no difference in TAN (mg/dL), TN (% of DM), and pH among treatments on d 0 of storage (Table 1). The tendency for a difference in pH among dietary treatments on d 77 could have affected the proportion of $\text{NH}_3/\text{NH}_4^+$ in the solution but any repercussion on $\text{NH}_3\text{-N}$ emission rate may have been curtailed after crust formation (Figure 1a). Ammonia-N emission rate was highest on d 0 (852 ± 404 mg/h per m^2), but was 76% lower on d 7, and gradually decreased to reach negligible levels on d 35 and thereafter (Figure 1a). These results were consistent with those of Aguerre et al. (2012) who observed a sharp decrease in NH_3 emission within the first 12 d of storage associated with a reduction in manure pH as a result of VFA formation from OM fermentation. In addition, de Bode (1991) reported that undisturbed manure with a high DM content formed a crust after 10 to 20 d of storage. Furthermore, the peak in CH_4 and CO_2 emission observed in this trial (Figure 1c and 1d) supported the results of Misselbrook et al. (2005), suggesting that an air-dried crust of undigested fiber forms after gas bubble formation (CO_2 and CH_4) and carries suspended particles to the surface. Interestingly, this process may be similar to the one responsible for stratification of ruminal content, whereby the specific gravity of fiber particles is lowered during fermentation (Wattiaux et al., 1991) thus contributing to the formation of a fibrous mat in the dorsal rumen. In short, the $\text{NH}_3\text{-N}$ emission reduction observed in this study is likely due to a reduction in manure pH during the first days of storage and the increase in transport resistance at the air-liquid interface once the crust was formed

Table 1. Composition of manure¹ obtained from cows fed different dietary forage-to-concentrate (F:C) ratios and amounts added to storage barrels on d 0 (n = 4)

Item ²	Dietary F:C ratio (DM basis)				SEM	P-value ³	
	47:53	54:46	61:39	68:32		L	Q
DM, % as is	10.6	10.9	10.7	10.3	0.35	0.44	0.33
TN, % of DM	3.10	3.05	2.95	2.96	0.10	0.20	0.77
TAN, mg/dL	85.9	100.1	97.5	88.7	9.52	0.87	0.20
Starch, % of DM	1.76	1.57	1.41	1.36	0.19	0.14	0.72
NDF, % of DM	40.2	41.0	41.3	41.1	0.89	0.45	0.56
pH	7.7	7.6	8.0	8.0	0.25	0.20	0.95
DM, kg	18.5	19.3	18.7	18.1	1.4	0.53	0.34
TN, g	574	585	554	538	52.2	0.29	0.64
TAN, g	152	175	170	154	17.9	0.98	0.22
Starch, g	329	303	260	246	49.8	0.17	0.90
NDF, g	7,451	7,899	7,723	7,429	589.5	0.87	0.29

¹Mixture of feces, urine, straw bedding, and diluting water.

²TN = total N; TAN = total ammoniacal-N.

³Probability of a linear (L) or quadratic (Q) effect of F:C ratio level in the diet.

Table 2. Arithmetic means (with SE in parentheses) of the 1-h $\text{NH}_3\text{-N}$, CH_4 , N_2O , and CO_2 manure¹ emission rates measured at different days of storage (d 0, 7, 14, 28, 35, 49, 56, 63, 70, and 77) when obtained from cows fed diets with different forage-to-concentrate (F:C) ratios

Item	Dietary F:C ratio (DM basis)				<i>P</i> -value ²	
	47:53	54:46	61:39	68:32	L	Q
$\text{NH}_3\text{-N}$, mg/h per m ²	120 (47)	92 (35)	150 (58)	104 (37)	0.82	0.61
CH_4 , mg/h per m ²	365 (97)	277 (65)	330 (78)	224 (66)	0.54	0.48
N_2O , mg/h per m ²	40 (10)	22 (5)	28 (7)	31 (8)	0.48	0.53
CO_2 , mg/h per m ²	15,490 (2,110)	15,572 (2,561)	16,162 (2,792)	14,360 (2,491)	0.77	0.85
CH_4 (CO_2 Eq), g/h per m ²	9 (2)	7 (2)	8 (2)	9 (3)	0.74	0.81
N_2O (CO_2 Eq), g/h per m ²	12 (3)	7 (1)	9 (2)	9 (3)	0.34	0.93

¹Mixture of feces, urine, bedding straw, and diluting water.²Probability of a linear (L) or quadratic (Q) effect of F:C ratio level in the diet.

(VanderZaag et al., 2008). In addition, the air-dried crust may reduce surface pH, decreasing the proportion of TAN in the form of NH_3 (Xue et al., 1999). Finally, the presence of NH_3 -oxidizing bacteria in organic crusts (Hansen et al., 2009; Nielsen et al. 2010) may reduce the emission of NH_3 but be conducive to greater N_2O losses. Long-term reduction in NH_3 emission could be associated also with changes in the pool of labile N as a result of ongoing fermentation as time progress during storage (Sommer et al., 2006).

Nitrous Oxide Emission

Feeding varying F:C ratios to dairy cows had no effect on rate of N_2O emission during manure storage (Table 2). For all treatments, N_2O emission rates were barely detectable during the first 2 wk of storage, but increased sharply on d 28, reached a peak on d 35, and decreased subsequently until the end of the study (Figure 1b). This pattern was in agreement with a previous study in which an organic crust was established compared with no N_2O of emission in the absence of a crust (Sommer et al. 2000). As reviewed by Kebreab et al. (2006), N_2O is an intermediate product of both nitrification and denitrification processes that take place during manure storage. Hansen et al. (2009) and Nielsen et al. (2010) showed that drying of organic crust resulted in the formation of both oxic and anoxic zones and although dissolved TAN could be oxidized through nitrification into nitrite (NO_2^-) and then nitrate (NO_3^-) in the presence of oxygen, these products can be subsequently reduced under anoxic conditions to N_2 by denitrification. However, incomplete reduction gives rise to higher concentrations of N_2O and other volatile oxides of nitrogen. The gradual decrease in N_2O emission rate from d 35 to 77 of storage reported here suggested that subtle changes in crust environment may have important consequences. As storage progressed, increased moisture associated with crust deterioration may have reduced

oxygen supply and, thus, NO_2^- , NO_3^- , and N_2O formation through nitrification. In turn, the depletion of denitrification reactants (NO_2^- and NO_3^-) may have contributed to reducing N_2O emission. Although crust DM was not recorded in our study, others have shown that N_2O emission was favored by low crust moisture content (Sommer et al., 2000; Hansen et al., 2009).

Methane Emission

No differences in CH_4 emission among dietary treatments were observed during storage (Table 2). These results are consistent with the lack of difference in starch and fiber in the manure (Table 1). The same dietary treatments, however, had a major effect on enteric CH_4 emission from dairy cows (Aguerre et al. 2011). In contrast to our results, Lodman et al. (1993) reported a higher CH_4 emission rate from stored manure excreted by steers fed a high-grain diet (85% of diet DM) compared with a 100% forage diet. In the present study, straw bedding could have affected emission results through addition of fermentable NDF and indirectly through crust formation. Straw bedding contributed 23.0% of the NDF loaded in the barrels and, therefore, may have contributed to CO_2 and CH_4 emission. Compared with fecal NDF, straw-bedding NDF likely had higher emission potential because it had not been subjected to enteric fermentation before storage. However, this effect may have been mitigated because straw NDF was in the form of long particles (i.e., minimal processing), resulting in low surface area for microbial fermentation. Furthermore, NDF stratification that occurred with crust formation, a partially aerobic environment, would also reduce the contribution of straw NDF to CO_2 or CH_4 emission. Formation of a crust may have partially masked potential dietary treatment effects. As found in Aguerre et al. (2012), crust formation had a substantial effect on NH_3 emissions after 3 to 4 wk of storage. In the trial reported

Figure 1. Variation in manure emission rate of (a) $\text{NH}_3\text{-N}$, (b) N_2O , (c) CH_4 , and (d) CO_2 throughout the storage period. Error bars indicate standard errors.

here, no dietary effects were observed on NH_3 (see above) or CH_4 emission before crust formation (which occurred also after 3 to 4 wk of storage), suggesting limited effects of the constant amount of straw-bedding NDF that was part of mixture added to the barrels.

As illustrated by Figure 1c, peak emissions were observed on d 7, and several possible explanations exist for the sharp subsequent decrease in CH_4 emission. Once formed, the solid air-dried crust may have acted as a physical barrier affecting gas transport that normally occurs across the aqueous boundary layer exposed to the atmosphere (VanderZaag et al., 2008). Furthermore, the organic crust may have acted as a site for CH_4 conversion to CO_2 via bacterial oxidation (Petersen et al., 2005). However, as time progressed during storage (after peak emissions), a reduction in CH_4 emissions could be associated with changes in manure characteristics (e.g., reduced pH) or other fermentation-related parameters associated with methanogenesis.

Carbon Dioxide Emission

The emission rate of CO_2 was not affected by manure treatment. Peak emissions were observed on d 7, and then progressively decreased until the end of the study (Figure 1d). Although CO_2 emission by cattle manure is not a net contributor to the increase in atmospheric CO_2 , because the carbon was previously removed from the atmosphere by photosynthesis, it still may have affected the mechanism of emission of other gases. For example, surface crusts started to form on d 7, coincidental with higher emission rates of both CO_2 and CH_4 (Figure 1c and 1d) that likely carried fiber particles to the surface (Misselbrook et al. 2005).

Rate of C and N Emission

Results from this study indicated proportionally higher volatile C loss than volatile N loss during storage

with a C:N ratio of 32:1. These results were in agreement with those of Aguerre et al. (2012), suggesting that the C:N ratio in gaseous loss (15:1) was greater than the C:N ratio of the manure (11:1). The higher rate of gaseous C:N observed in this study compared with Aguerre et al. (2012) was likely associated with the measurement technique (emission chamber vs. mass balance).

Emission of CH₄ and N₂O as CO₂ Equivalents

Dietary F:C ratio had no effect on the non-CO₂ greenhouse gases emission rate (CH₄ + N₂O expressed as CO₂ equivalents) from manure (data not shown). However, the relative contributions of CH₄ and N₂O to non-CO₂ greenhouse gas emission changed drastically during storage. Between d 0 and 14 of storage, CH₄ was by far the main contributor of emitted (mean $\pm$ SD) CO₂ equivalents (91 $\pm$ 10% in the first 14 d of storage; Figure 2). In spite of a decrease in CH₄ emissions between d 28 and 35, total emissions of CO₂ equivalents continued to increase due to a surge in N₂O emissions. Finally, from d 49 until the end of the storage period, emissions of CO₂ equivalents decreased and N₂O was the primary source of emissions (69 $\pm$ 14%, mean $\pm$ SD). These changes in contributions of each gas illustrated the importance of measuring greenhouse gases simultaneously and with long fermentation periods when evaluating treatment responses in manure storage studies.

Figure 2. Relative contribution of emitted N₂O and CH₄ to the total non-CO₂ greenhouse gas emission during the manure storage period.

CONCLUSIONS

Together, results of this study and the companion study (Aguerre et al., 2011) suggest that within the 47:53 to 68:32 dietary F:C ratio, dietary treatment effects on enteric CH₄ production had no carryover effects during storage. In this trial, dietary F:C ratio had no effect on NH₃-N, N₂O, CH₄, or CO₂ emission rate from stored manure. Although changes in fermentation pattern could contribute to reduction in emissions in the long term, an established air-dried crust at the surface of stored manure had a substantial effect on fermentation dynamics and associated emission. Our data suggested that crust formation may have multiple effects on gaseous emission. The crust may act as an emission retardant due to its physical properties. In addition, it may provide a growth environment for bacteria, first promoting those that use NH₃ and CH₄ as substrate and, thus, acting as a microbial sink for these compounds, but then, in a somewhat sequential manner, promoting microbial growth conducive of N₂O production and emission. The effects observed in this trial, especially those related to crust formation should not be extrapolated directly to commercial farm conditions, as wind velocity, solar radiation, temperature, precipitation, and other factors may have major effects.

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