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COMMUNICATIONS

Measurement of Methane Emissions from Ruminant Livestock Using a SF_6 Tracer Technique

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Introduction

Methane is an important atmospheric constituent in terms of chemistry and radiation balance. Not only is methane a potent greenhouse gas due to its interaction with planetary infrared emissions, but tropospheric reactions between methane and the hydroxyl radical influence oxidant concentrations in background air masses. Ambient monitoring programs during the 1980s have shown that tropospheric methane concentrations are increasing at a rate of approximately 1% per year. Currently, tropospheric methane concentrations are about 1750 ppb in comparison to levels of approximately 800 ppb prior to the human population explosion that has accompanied the industrial revolution. At present, a reason(s) for the recent buildup in methane is not clearly understood. Several groups have presented methane inventories that differ in their estimations of the various source strengths (*1–7*). Consequently, considerable effort is focused on quantifying tropospheric sources and sinks of methane. Most of the emphasis has been on sources, since there are few known sinks. Atmospheric oxidation by the hydroxyl radical is the primary loss mechanism.

Past analyses of the global methane cycle have placed source strengths between ~300 and 700 Tg/yr (*8–11*). The range has been narrowed to 500 ± 100 Tg/yr in the most recent studies. For example, Crutzen (*11*) has employed a type of top-down inventorying method in which sources and sinks were balanced, while taking into account the annual increase measured in the troposphere. Methane sinks are estimated to remove 460 ± 100 Tg/yr from the troposphere. The dominant sink is by far the reaction with OH at 420 Tg/yr, with soil uptake (30 Tg/yr) and transport into the stratosphere (10 Tg/yr) acting as minor removal mechanisms. The annual increase in tropospheric methane amounts to 45 ± 5 Tg/yr. Thus, a methane source strength of 505 (± 105) Tg/yr is required to balance the sink and buildup terms. About 100 (± 20) Tg of this is fossil methane primarily from coal mining and natural gas leakage. This leaves a modern source of approximately 405 Tg, of which about half (215 Tg/yr) is emitted by wetlands (natural and agricultural) and 20% (80 Tg/yr) by ruminant animals. The remaining 25–30% is released from a combination of sources such as landfills, oceans, insects, and biomass burning.

Assigning release rates to the various modern carbon sources requires the more usual bottom-up inventorying approach whereby an emission factor for a specific unit is multiplied by the number of units. For example, the 80 Tg/yr associated with ruminant livestock is based on mean emission factors times the number of animals in a variety of ruminant groups.

The methane emission factors derived by Crutzen et al. (*6*) have been the foundation for most ruminant inventories. The global methane emissions from ruminant livestock are dominated by cattle (~70%) with the remainder coming from buffalo, sheep, goats, camels, horses, etc. Crutzen and co-workers assigned methane emission factors of 55 kg/yr for cattle residing in developed countries and 35 kg/yr in developing nations. Data from energy balance studies were used to derive these methane emission rates. Energy balance experiments require a cow, fed a diet of known quality and quantity, be placed in a respiration calorimetry chamber for a few days. The partitioning of the energy intake between the various metabolic pathways is carefully measured, as are methane emissions. From this information, the percentage of gross energy intake (GEI) that is expired as methane can be calculated. Methane production normally represents between 2 and 12% of the GEI (*12*). The GEI depends both on the quantity and the quality of the feed. Generally, when cattle are fed diets to promote rapid growth, high quality feed, the proportion of feed energy lost as methane is reduced. For example, the percent of GEI converted to methane in cattle fed high grain diets typical of feedlot operations would be expected to be toward the lower end of the range (i.e., ~2–4%).

Blaxter and Clapperton (*13*) developed a statistical relationship (eq 1) between feed intake, diet digestibility, and methane production that was used by Crutzen et al. (*6*) to derive the emission factors mentioned previously. The Blaxter–Clapperton relationship and an equation reported by Moe and Tyrrell (*14*) have been used almost

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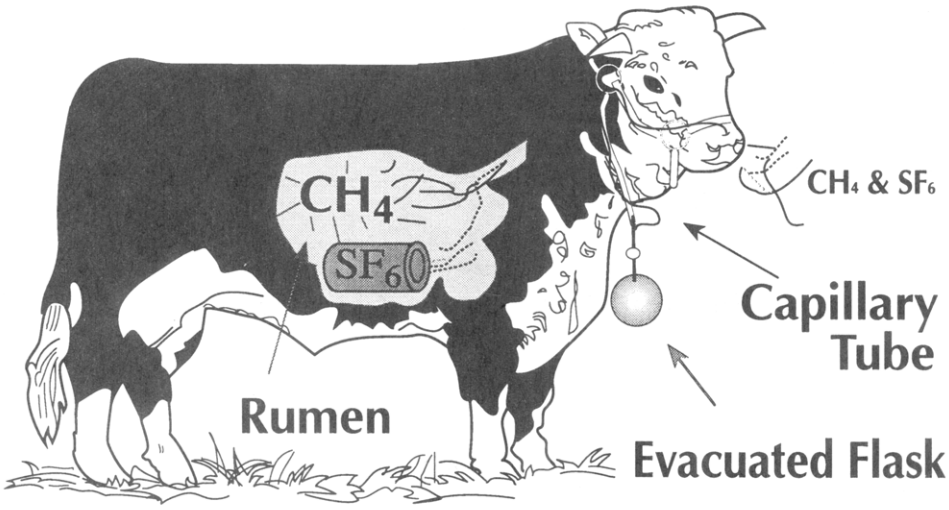

Figure 1. Illustration of tracer methodology.

exclusively for predicting methane emissions:

$$\% \ CH_4 = 1.3 + 0.112D + L(2.37 - 0.05D) \qquad (1)$$

This prediction equation does not accurately predict methane production under all conditions, however. There have been several experiments which compared the actual methane yields to those predicted by the Blaxter–Clapperton equation and have found 10–30% overestimation of methane output (*15*). Recently a modeling approach has been described which attempts to simulate rumen fermentation (*16*). The model provides estimates of the amount of methane formed and emitted from the microbial fermentation in the rumen as a result of the chemical characteristics of the diet.

Both the statistical and modeling approaches depend on respiration chamber studies for the relationship of energy intake to methane production. A weakness in use of this chamber data is the question of the environment in which the animal is measured. A chamber is an artificial, constrained environment. The extent to which chamber results can be extrapolated to cattle in real-world environments (i.e., range, pasture, feedlots, etc.) is open to question. Respiration chamber measurements are also limited by the time it takes to train an animal for measurements, the number of animals available, and the large expense of building and maintaining chambers. The purpose of this manuscript is to describe an alternate method for determining methane emission factors for cattle. The technique involves the direct measurement of methane emissions from livestock in their natural environment. A small permeation tube containing SF_6 is placed in the cow's rumen, and SF_6 and CH_4 concentrations are measured near the mouth and nostrils of the cow. The SF_6 release provides a way to account for the dilution of gases near the animal's mouth. The CH_4 emission rate can be calculated from the known SF_6 emission rate and the measured SF_6 and CH_4 concentrations.

Procedures

Tracer Method. The tracer method utilizes SF_6 to account for dilution as gases exiting the cow's mouth mix with ambient air. It is assumed that the SF_6 emission exactly simulates the CH_4 emission; thus, the dilution rates for SF_6 and CH_4 are identical. Mixing due to turbulent diffusion is much more important than molecular diffusion in the atmosphere. Similarily, gas transport from the rumen out of the mouth is dominated by forceful contractions and eructation so that molecular diffusion is an unimportant component in the emission process. The methane emission rate can then be calculated from measured CH_4 and SF_6 concentrations and the known release rate of SF_6 (eq 2).

$$Q_{CH_4} = Q_{SF_6} \times [CH_4]/[SF_6] \qquad (2)$$

SF_6 permeation tubes were prepared in our laboratory by collecting liquid SF_6 in a threaded stainless steel tube and capping it with a 1/4-in. Swaglok nut containing a permeable Teflon disk. The newly prepared permeation tubes were placed in a temperature bath at 39 °C and routinely weighed until an accurate loss rate was determined. We have found permeation rates of 500–1000 ng of SF_6/min to be most useful. These permeation devices were placed in a cow's rumen with a balling gun. Figure 1 provides an illustration of the tracer methodology.

Sample Collection. The sampling apparatus consisted of a 1-L stainless steel collection vessel and a capillary tube extending from the collection canister to just above the animal's mouth and nostrils. The canister was attached to a collar around the neck of the cow. Stainless steel tubing with an inside diameter of 0.005 in. served as the transfer line. Immediately prior to sampling, the collection canister was evaculated (<200 μm). To initiate sample collection, the canister was attached to the collar and connected to the transfer line, and a valve on the collection vessel was opened. The evacuated canister was filled at a constant rate until it reached about 0.5 atm, at which time sample collection was stopped by closing the canister valve. Sample integration time is controlled by the length of the capillary transfer line. We have employed collection times of 2–6 h using this apparatus. A filter (50 μm) was placed on the upstream end of the capillary line to keep it from plugging. Prior to being analyzed for methane and SF_6, the canister was pressurized to approximately 1.5 atm with nitrogen gas.

Methane Analysis. Air from the collection canister was passed through a 1.0-mL sample loop attached to a HP 5880 gas chromatograph. The GC system consisted of the sample loop, a 1/8-in. × 4-ft. column packed with Porapak N, and a flame ionization detector. Each analysis can be completed in less than 1 min. Analyses are always

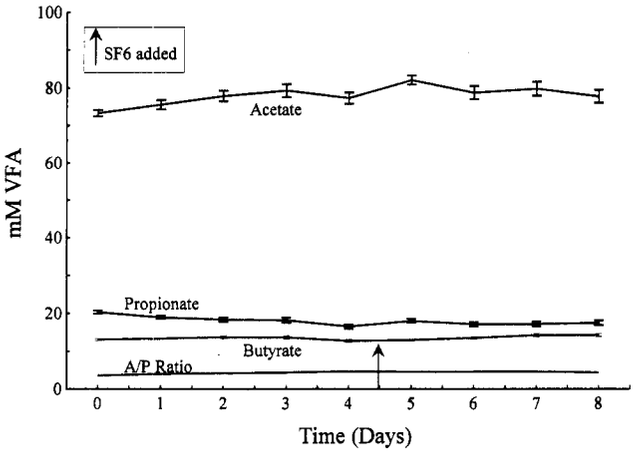

Figure 2. Volatile fatty acid (VFA) concentrations monitored in an artificial rumen with and without SF_6 present.

run in duplicate or triplicate with a reproducibililty generally less than 2%. Calibration of the GC was based on NIST methane SRM 1660a. A secondary standard (1.83 ppm methane) obtained from Scott was employed for routine span checks.

SF_6 Analysis. A custom-built electron capture gas chromatograph was employed for SF_6 analysis. The system employs a 1.0-mL gas sample loop, a Molecular Sieve 5A column (1/8-in. × 6-ft.), and a tritium foil detector. SF_6 elutes from the column prior to oxygen, and the GC has a lower detection limit of about 5 pptv for SF_6. Calibration of the system is accomplished with a series of ppt level SF_6 standards purchased from Scott-Marin. Standard concentrations ranged from about 29 to 3000 pptv SF_6.

Chamber Measurements. Open-circuit, indirect respiration calorimetry chambers were employed for determining methane emission rates from several ruminants that had been monitored via the SF_6 tracer technique. These chambers have been recently constructed in the Department of Animal Sciences laboratory complex on the Washington State University campus. They conform to animal protection standards in terms of size, food and water facilities, temperature control, and dehumidification. The chambers operate in a dynamic mode with the airflow monitored by dry gas meters. Concentration differences between the incoming and outgoing gas streams are determined with continuously recording instruments. Methane and carbon dioxide are monitored with infrared analyzers, and oxygen is monitored with a paramagnetic detector. All of the important parameters (trace gas concentrations, airflow, temperature, etc.) are measured simultaneously and recorded with the aid of a computerized data acquisition system. Prior to making animal measurements in the chambers, an extensive acclimation procedure is followed. Cattle are gentled, taught to lead with a halter, and slowly introduced to the chambers. This acclimation process takes several weeks.

Results

Before SF_6 permeation tubes were placed in the rumen of living animals, laboratory studies were conducted to ensure that the presence of SF_6 did not adversely affect rumen function. Earlier it had been reported that the replacement of N_2 by SF_6 in breathing air had no adverse effect on animals during lung function studies (*17*). Rumen biochemistry was simulated in the laboratory by placing 500 mL of rumen contents from a cow into 1-L glass vessels. These chemostats were equipped with stirring devices to simulate ruminal mixing contractions and with inlet ports for feeding, adding artificial saliva for pH regulation, and maintaining anaerobic conditions. Outlet ports were used to monitor volatile fatty acid production and methane and SF_6 levels downstream of the vessel. A water bath maintained the chemostat at 39 °C. SF_6 permeation tubes with varying emission rates were placed in these artificial rumen. In no case did we observe any adverse effects from the SF_6. As shown in Figure 2, volatile fatty acid (acetate, propionate, etc) concentrations remained stable with time. In addition, the acetate/propionate ratio was in the range normally found in the rumen of cattle fed the same types of diets. A detailed description of the artificial rumen work will be provided elsewhere (*18*).

Table 1. Methane Emissions from Heifer-X066 As Determined by Tracer Method

date	time	measured CH_4 emission rate (L/h)	daytime av CH_4 emission rate (L/h)
10/30/92	8:35 am–2:10 pm	14.6	
10/30/92	2:10 pm–7:15 pm	9.4	12.0
11/2/92	8:00 am–12:35 pm	17.4	
11/2/92	12:35 pm–5:15 pm	8.6	13.0
11/3/92	9:05 am–3:15 pm	13.7	
11/3/92	3:15 pm–6:45 pm	8.1	10.9
11/4/92	9:40 am–2:20 pm	15.1	
11/4/92	2:20 pm–6:50 pm	7.9	11.5
11/5/92	8:25 am–1:45 pm	13.7	
11/5/92	1:45 pm–6:45 pm	7.1	10.4
	av		11.6

Table 2. Methane Emissions from Heifer-X066 As Determined by Chamber Method

date	time	daytime av CH_4 emission rate (L/h)
10/27/92	9:35 am–7:00 pm	13.0
10/28/92	2:00 pm–7:00 pm	12.0
10/29/92	7:00 am–2:00 pm	13.6
	av	12.9

We have used the tracer method to determine methane emission rates from mature cows and several feedlot-type steers and heifers. These cattle were in individual pens with dimensions approximately 12 × 30 ft. At no time were they restrained in any way except by the boundary fences. Depending on the individual animal's previous contact with humans, it took from a day or two to a week for them to acclimate to the collection system. Diets ranged from 100% roughage to 85% grain. For validation purposes, methane emissions results from this newly developed tracer technique were compared to chamber data. Methane emissions from several heifers and steers have been determined using both methods. Following chamber measurements, the cattle were measured by the tracer method in the outdoor pens. Tables 1 and 2 and Figure 3 show the results for one of the heifers (X066).

Table 1 lists methane emissions recorded for this heifer on five separate days using the tracer method. The sampling period varied from 9 to 12 h and was broken into two intervals of approximately equal length. Heifer X066

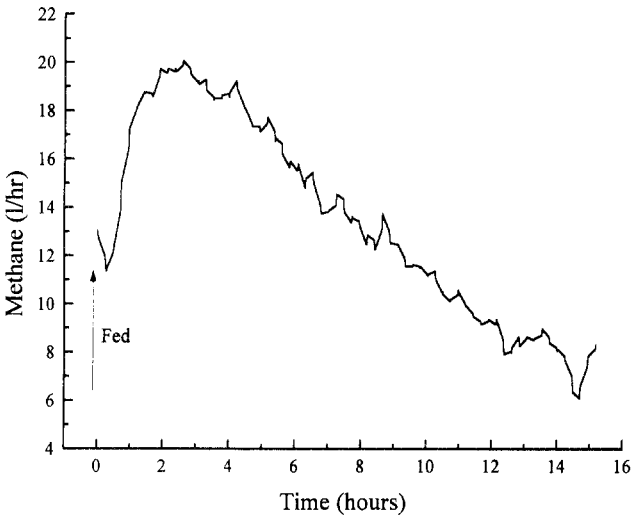

Figure 3. Typical methane emission pattern observed in chamber experiments with heifer-X066.

Table 3. Comparison of Tracer and Chamber Measurements

method	*N*	mean (L/h)	SE
tracer	55	11.03[a]	0.41
chamber	25	11:00[a]	0.33

[a] Means with different superscripts are different (P <0.10).

was fed half of her daily ration immediately prior to the morning sample collection period and the remainder in the evening following completion of sampling. Day to day methane emission patterns were very consistent, with the highest values recorded during the morning hours. This is to be expected based on the feeding schedule described previously. Combined morning and afternoon emission rates for the five days varied from 10.4 to 13.0 L/h. Average methane emission rates for the five days combined was 11.6 ± 3.7 L/h.

Figure 3 shows the typical methane emission pattern observed while X066 was fed in the chambers. The methane emission pattern observed in the chamber mimics that recorded using the tracer method. In both cases, peak emission levels occurred during the hours immediately after feeding. Quantitatively, the emission rates determined by the two methods agree very well. Table 2 lists chamber-derived hourly emission rates that can be directly compared to tracer-derived data. The emission rate data shown in Table 2 correspond as closely as possible to the same time frame as represented in the tracer work (Table 1). Thus, the methane emission rates listed in Table 2 are hourly averages for the 10 h following feeding. The average value of 12.9 ± 0.7 L/h calculated from the chamber measurements agrees very well with the tracer average of 11.6 ± 3.7 L/h.

During the period of these measurements, X066 was fed a diet which consisted of 95% chopped alfalfa and 5% supplement. Each day during the measurement period, the amount of food consumed by the heifer was carefully monitored. This provided the information needed to calculate the fraction of GEI that was lost as methane. This experimentally determined fraction of GEI converted to methane was 7.3% and 7.2%, on the basis of the chamber average (12.9 L/h) and the tracer average (11.6 L/h), respectively. The Blaxter–Clapperton equation (eq 1) predicts a slightly lower conversion to methane of 6.7%.

The good correlation between chamber- and tracer-derived methane emission rates demonstrated for X066 has been confirmed with other heifers and steers. Table 3 provides a summary of all of the heifers and steers used in validation measurements. With 55 measurements using the tracer method and 25 chamber measurements, no significant difference could be detected between the two methods.

Conclusions

We believe that the tracer method described herein will provide an easy means for acquiring a large methane emissions data base from domestic livestock. The low cost and simplicity should make it possible to monitor a large number of animals in countries throughout the world. An expanded data base of this type will help to reduce uncertainty in the ruminant contribution to the global methane budget.

Acknowledgments

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