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# GREENHOUSE GAS RELEASE FROM STORED DAIRY-CATTLE MANURE SLURRY

N. Patni, H. Jackson, D. Massé, M. Wolynetz, R. Kinsman<sup>1</sup>

## ABSTRACT

Emission of methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) from 8 to 9% dry matter content dairy cattle manure slurry, stored in a below-grade 296 m<sup>3</sup> covered concrete storage tank (7.2 x 14.7 x 2.8 m deep) was determined during winter ('93-'94) and summer ('94) seasons. Mean daily temperature of ambient air at the site ranged from -28° to 15°C and 6° to 30°C during the winter and summer determinations, respectively. Slurry temperature varied with depth, the warmest manure being near the bottom during the winter (4 - 10°C) and near the surface during the summer (14° - 23°C). Biogas was collected in floating-cover gas collectors under which the slurry was either confined in a pipe or unconfined. Daily biogas production was variable and was lower in winter than in summer. Production from confined manure was about twice that from unconfined manure. Cumulative biogas production amounted to 1.3 and 0.6 liter per liter of stored manure during 118 days of summer storage. Methane content of the biogas ranged from 27 to 34%. Results of this study suggest that greenhouse gas release from stored dairy cattle manure slurry would be low under cool climatic conditions similar to those of eastern Ontario.

**KEYWORDS.** Greenhouse gas, methane, manure slurry, manure gas.

## INTRODUCTION

Global warming, observed in the recent past, has been attributed to increases in the concentration of the so-called greenhouse gases in the atmosphere due to anthropogenic activities. The main greenhouse gases of concern with respect to livestock production and rearing are carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) which are released into the atmosphere by ruminants due to enteric fermentation, and from manure due to anaerobic and aerobic decomposition. Over a 100-year time horizon, the global warming potential of methane directly and indirectly (due to transformation into another greenhouse gas) is 11 and 22 times more, respectively, than CO<sub>2</sub> (USEPA, 1994). The oceans and the atmosphere are large reservoirs of CO<sub>2</sub>. Control of CO<sub>2</sub> release from farm animals would have a small impact on global CO<sub>2</sub> concentrations. In contrast, the global anthropogenic CH<sub>4</sub> emissions from livestock and their manure in 1990 were estimated to be about 25% of the global total of 69 to 104 Tg (Teragram = 10<sup>12</sup>grams = 10<sup>6</sup>tonnes) (Adler, 1994). About 4% of this global CH<sub>4</sub> emission was estimated to be from manure. There is considerable uncertainty in these estimates, particularly for manure. Although considerable information exists on CH<sub>4</sub> generation by anaerobic digestion, relatively little is known about CH<sub>4</sub> and CO<sub>2</sub> release from manure stored at farms, which is usually at a much lower temperature than the mesophilic and thermophilic temperatures at which CH<sub>4</sub> emissions have been studied. Information is required to reduce the uncertainty in the above estimates. The objective of the study reported here was to determine CH<sub>4</sub> and CO<sub>2</sub> emission from confined and unconfined dairy cattle manure slurry (DCMS) stored in farm-scale, below-grade covered concrete tanks, in order to establish their significance in greenhouse gas contribution into the atmosphere.

<sup>1</sup> N. Patni, Research Scientist; H. Jackson, Research Engineer; D. Massé, Research Engineer; M. Wolynetz, Research Scientist; and R. Kinsman, Research Assistant, Research Branch, Agriculture and Agri-Food Canada, Central Experimental Farm, Ottawa, Ontario, K1A 0C6, Canada.

Under the confined condition, biogas was collected in floating cover placed directly above long pipes within which the manure was confined. Slurry was unconfined when no such pipe was used under the floating cover gas collector.

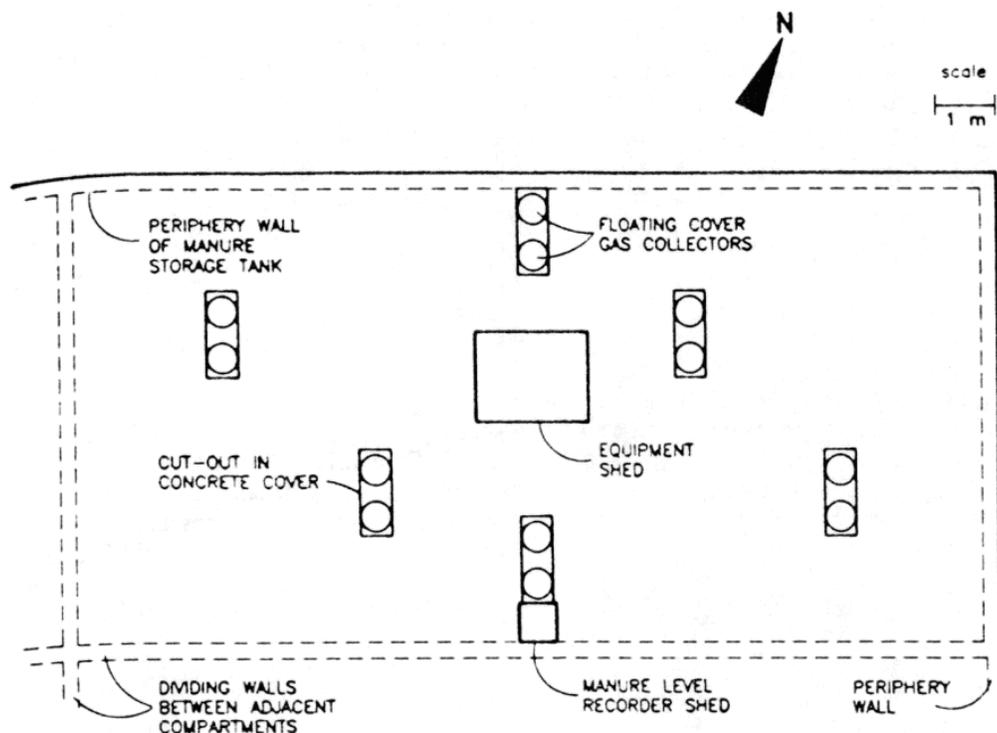
Patni and Jui (1985, 1987) studied composition changes in DCMS stored in concrete 'anaerobic' tanks, similar to the one used in this study, during winter and summer. It was reported that volatile fatty acid (VFA) concentrations increased in the slurry even when the slurry temperature dropped to about 5°C. A carbon balance revealed that about 25% of the carbon initially present in the slurry was lost during five to nine months of storage. Carbon loss was attributed to gaseous losses, largely as CO<sub>2</sub>, because of unfavourable temperature, pH, C/N ratio and VFA concentrations for CH<sub>4</sub> generation. Husted (1993) described an open chamber technique which was used to measure CH<sub>4</sub> emissions from farm scale storages for slurry and solid manure from pigs in Denmark. A wide variation in spatial and temporal emission rate was noted and it was concluded that reliable annual estimates cannot be made with a few seasonal measurements. In the slurry, gas emission was controlled by resistance in the liquid phase. This technique was used subsequently (Husted, 1994) to study CH<sub>4</sub> emissions over a one-year period from farm-stored solid and slurry manures from cattle and pigs. Emission rates were measured at two week intervals. Slurry was transferred and removed from the storage tanks during this period. High spatial and seasonal variability in CH<sub>4</sub> emission was again observed. Safley and Westerman (1988, 1989, 1990, 1992) studied biogas production at several anaerobic lagoons in North Carolina. Floating covers were used over unconfined manure in the lagoons. Considerable spatial and temporal variability in gas emission rate was again noted. Concentrations of CH<sub>4</sub> up to 80% in biogas were reported.

The study reported here differed from the above-noted studies in two respects. The storage tank was batch-filled with manure at the beginning to avoid possible confounding effect of manure additions and removals from the storage tanks while emissions were being monitored. Also emissions were determined for confined and unconfined conditions of manure storage. Under confined conditions, all gas released by the manure was captured.

## STUDY PROCEDURE

The study was conducted at the Greenbelt Research Farm of Agriculture and Agri-Food Canada near Ottawa, Ontario. One compartment, 7.2 x 14.7 x 2.8 m deep, of a four-compartment, below-grade, covered concrete tank was washed with clean water and then batch-filled with DCMS once in the winter (November, 1993), and once again, in the summer (June, 1994) for biogas emission monitoring. Prior to filling, manure was collected for a 5 to 6-week period in a temporary storage tank at a 118-cow tie stall barn with a gutter scraper system. Lactating cows in the barn were fed a diet consisting of corn silage, wilted alfalfa silage, long hay and a concentrate supplement. Straw, used as bedding at the rate of 1 kg per cow per day, was included in the scraped manure. Manure level was monitored in the tank under study (Fig. 1) to determine seepage in or out of the tank. None was observed.

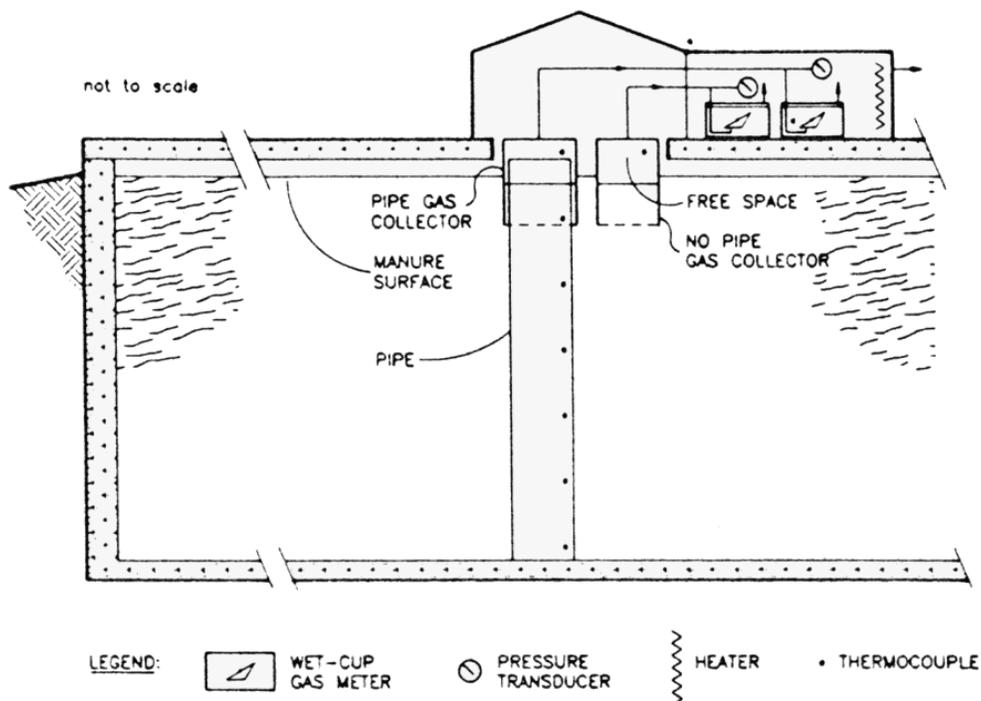
Six 0.5 x 1.5 m openings in the 50 mm thick concrete cover were used as six replicate sites for biogas monitoring (Fig. 1). After filling of the tank, in each opening, a 0.46 m diameter, 3.05 m long PVC pipe was lowered, and two floating-cover biogas collectors were installed as shown in Fig. 2.



**Figure 1.** Layout of the six replicate sites for floating-cover biogas collectors, data-logging equipment shed, and manure level recorder shed at the 7.2 x 14.7 x 2.8 m deep below-grade manure slurry storage tank. This tank formed one compartment of a four-compartment concrete tank.

The floating covers, also made of PVC, were 0.76 m long, with the top end capped. Floating covers had a diameter of 0.50 m and 0.46 m in the pipe and no-pipe system, respectively. They were anchored to the concrete cover and were sheltered in an insulated plywood box. Biogas collected under the floating covers flowed through 10 mm diameter Tygon tubing to inverted tipping-bucket gas flow meters. The tipping bucket, kept submerged in water at 20°C, tipped once for every 100 mL of gas flow. A counter attached to the gas flow meter registered the number of tips from which total gas flow was calculated. The pre-calibrated flow meters were kept inside an insulated plywood box, the temperature inside which was thermostatically controlled at 20°C using electric blankets for car battery warming. Static pressure of 100 to 125 mm water gage was required in the floating covers for the biogas to flow through the gas flow meters. Temperature was monitored at various locations using type T thermocouples (Figs. 1 and 2). An automatic data acquisition system, which could be remotely monitored, was installed at the site as described previously by Jackson et al. (1994).

At approximately weekly intervals, 10 mL biogas samples were collected, in glass syringes, from a septum-equipped tee-section in the biogas discharge tube between the floating covers and the gas meters. Gas samples were analyzed for CH<sub>4</sub>, CO<sub>2</sub>, hydrogen sulfide and nitrogen using a Carle model 400AC gas chromatograph equipped with a thermal conductivity detector.



**Figure 2.** Section through manure tank showing the pipe and no-pipe biogas collection systems.

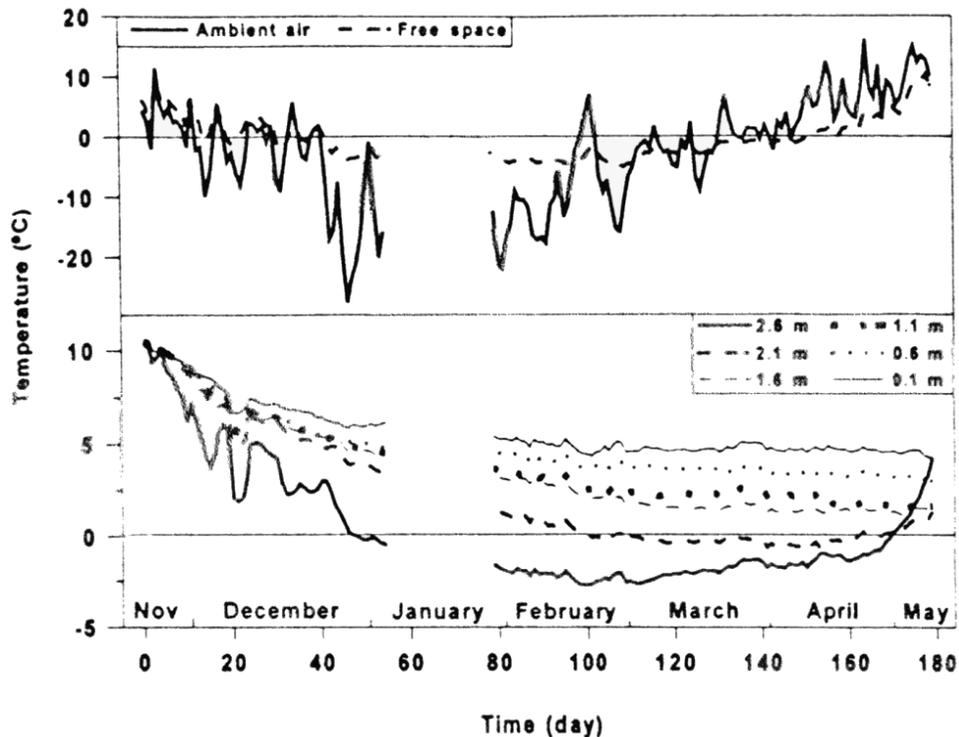
One-liter samples of well-mixed manure were collected at the beginning and the end of the winter and summer storage periods, for determination of composition and properties (API-1A, 1992). Slurry samples were also collected at monthly intervals from undisturbed slurry. During winter storage, samples were collected from both inside and outside the pipes (Fig. 2) to determine possible differences in composition changes. This necessitated removal of floating covers above the pipes, with the resultant periodic loss of static pressure in the floating covers, and introduction of air in the free space above the pipes. In the second part of the study, during summer storage, manure slurry samples were collected from outside the pipes only.

## RESULTS AND DISCUSSION

Results relating to temperature distribution in the slurry, and production and composition of biogas are discussed below. Results on slurry composition and properties are not included in this paper. The initial dry matter content of DCMS was 8.7 and 83% in the winter and summer biogas emission studies, respectively.

### Temperature Distribution

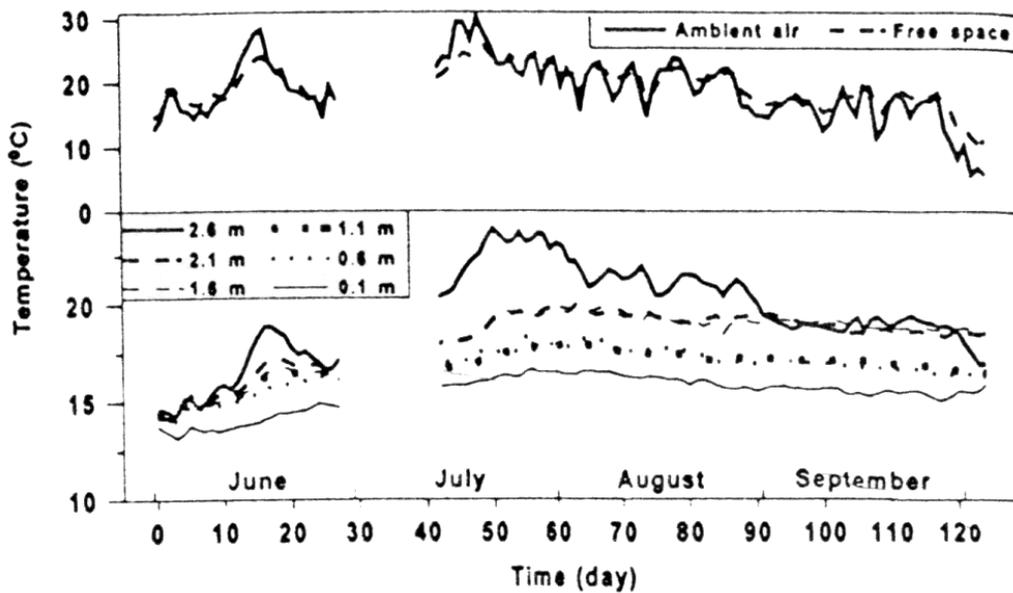
Figures 3 and 4 show the change in average temperature at various locations during winter and summer, respectively. A definite "layering" of temperature in the slurry was evident in both the



**Figure 3.** Ambient temperature, and average slurry and free-space temperature during the winter. Slurry temperature is shown at various distances from the bottom. Temperature recording was interrupted in January to install a new datalogging system.

summer and the winter. In the winter, the warmest manure was at the bottom of the tank, where the temperature fell from an initial 10° to about 4.5° by February end, and stayed close to that level until early May when the winter monitoring of biogas was terminated. The '93-'94 winter was characterised by unusually low temperatures as shown in the top half of Fig. 3. Even though the average temperature of the ambient air reached -20°C, the free space biogas temperature remained close to 0°C. This indicates the effect of heat stored in the manure which was gradually lost as the manure temperatures dropped. Slurry storage compartment south of the tank being studied (Fig. 1) was filled by about mid December, and the compartment on the west side by about the end of January. Thus the heat loss from the slurry in the tank under study probably occurred mostly through the surface which apparently kept the free-space relatively warm. In the summer, slurry heat transfer mechanisms had less influence on temperatures in the free space (Fig. 4). In contrast to winter, slurry during the summer was coolest at the bottom of the tank and warmest close to the surface. Average temperatures in the free space tended to vary in the same pattern as the ambient air. These winter and summer temperature distributions in slurry are consistent with those observed in previous studies (Patni and Jui, 1985, 1987).

Temperature plays an important role in the rate and type of biochemical reactions. Results in Figs. 3 and 4 suggest that microbes in the stored slurry would have to continuously adapt to changing temperature not only with time, but also with depth. Thus one would expect a longer lag phase in biogas production rate compared to that in systems where slurry temperature variation is small.

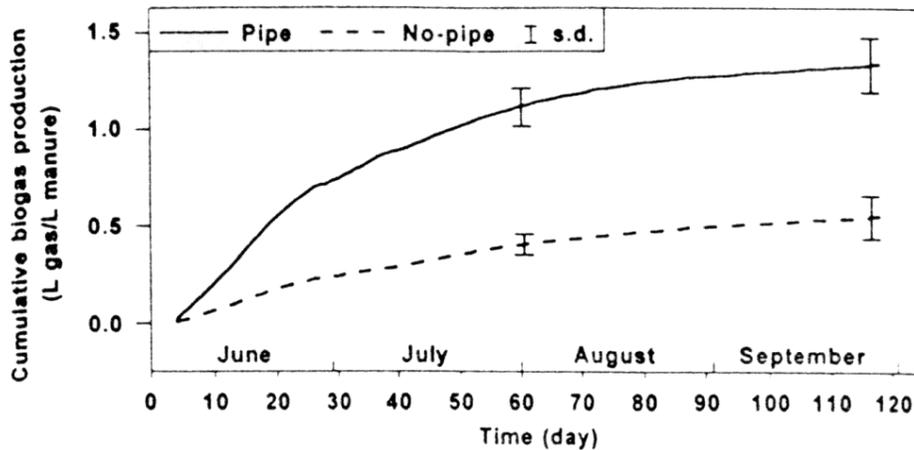


**Figure 4.** Ambient temperature, and average slurry and free-space temperature during the summer. Slurry temperature is shown at various distances from the bottom. Temperature recording was interrupted in July due to lightening damage to the datalogger.

### Biogas Production

During the winter, unusually low ambient temperatures caused operational problems in smooth functioning of the gas flow meters which had worked well under laboratory conditions and steady temperatures. Also, leaks developed at the joints in some floating covers, which had to be fixed. Consequently, reliable data on cumulative biogas production during winter could not be obtained. However, some data were obtained for daily biogas production. It was practically zero on many days particularly after the initial 8-9 weeks. Positive values for biogas production prior to that ranged from 0 to 0.01 and 0 to 0.005 L biogas L<sup>-1</sup> slurry under the 'pipe' and 'no-pipe' gas collection systems, respectively (Fig. 2). A greater production of biogas under the pipe system than under the no-pipe system appeared to exist. The existence of such a difference was confirmed in the subsequent summer study (Fig. 5). The cumulative biogas production in 118 days was 1.34 and 0.55 L L<sup>-1</sup> manure under the pipe and no-pipe systems, respectively. These emission rates are low compared to reported values for anaerobic digesters (Jackson et al., 1994). The biogas volumes reported above are not adjusted for temperature or pressure. Biogas release was affected by changes in atmospheric pressure. Gas production tended to increase slightly as the barometric pressure dropped, but this may simply have been due to release of dissolved gas rather than actual gas production. The observed gas production would also be affected by slurry temperature which would affect gas solubility.

There are at least two possible contributing factors for a lower biogas production from unconfined than confined slurry. Biogas is produced at microsites by microorganisms. Gas produced initially would be in the form of a micro-size bubble which would tend to rise due to the buoyancy force.



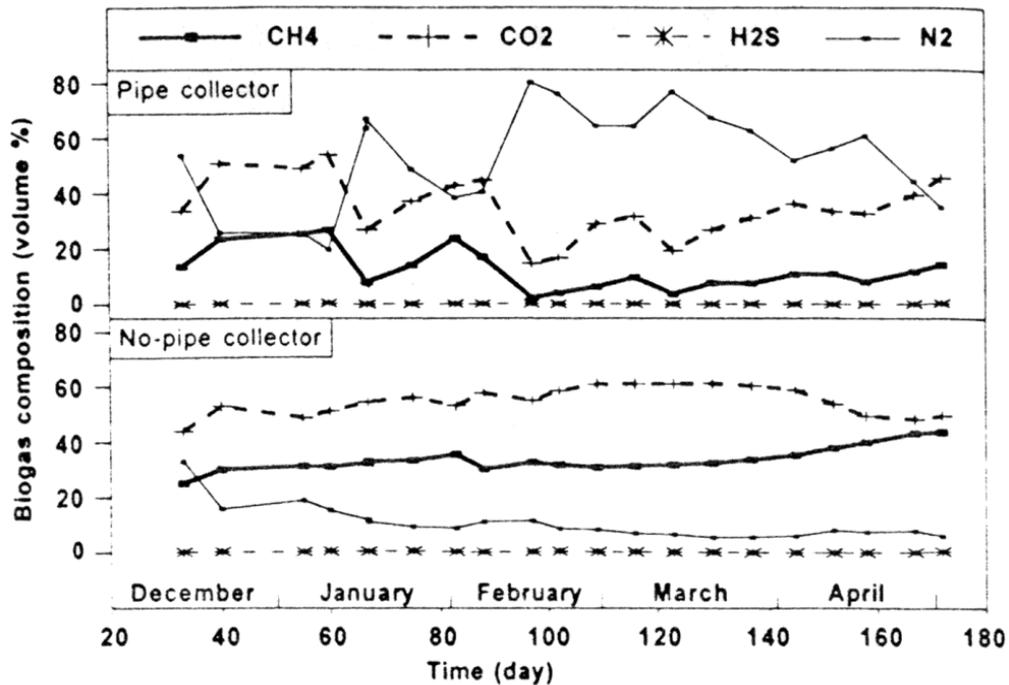
**Figure 5.** Average cumulative biogas production under pipe and no-pipe gas collectors in the manure tank during summer.

However, the bubble, at least when initially formed, is so small that its buoyancy force would be insignificant compared to the gravitational force on any suspended particle which would tend to block the upward movement of the micro-bubble. The tendency would be for the micro-bubble to move sideways and upwards until it could coalesce with other bubbles to form a large bubble with a high buoyancy force which would make it move upwards into the no-pipe gas collector. It appears that more gas moved away from than towards the no-pipe collector. In the confined manure system, the only path available to gas bubbles to escape from the slurry was through the gas collector above the confined manure. The second contributing factor could be the difference in the partial pressures of  $\text{CO}_2$  and  $\text{CH}_4$  in the free space within the floating cover gas collectors and the free space above the slurry outside the floating cover. This may have caused some movement of the gases away from the no-pipe gas collectors to the surrounding manure surface. In this process, gas movement would be driven by concentration gradients and diffusion through the liquid phase. As far as can be determined, such differences in biogas production from confined and unconfined manure at farm slurry storages have not been reported before. Further research is required to explain this observation.

In 118 days of DCMS storage during summer, biogas production was  $134 \text{ L L}^{-1}$  slurry, with an average  $\text{CH}_4$  content of 27%. Thus the average daily production of  $\text{CH}_4$  was about  $0.36 \text{ L L}^{-1}$  slurry over this time period. Using a manure production of  $45 \text{ L cow}^{-1} \text{ d}^{-1}$ , the daily  $\text{CH}_4$  production from manure per cow would be about  $16 \text{ L d}^{-1}$ , which is about 3% of the average release of  $542 \text{ L CH}_4 \text{ d}^{-1}$  per cow in a tie-stall dairy barn as determined by Jackson et al. (1993) at the same farm where this study was conducted. Since most of the gas production occurred in the initial 8 to 9-week period (Fig. 5), the average daily  $\text{CH}_4$  production in stored slurry would be higher for shorter storage periods and lower for longer ones than the  $0.36 \text{ L}$  as calculated above. Periodic addition of fresh manure to stored slurry may tend to increase the daily  $\text{CH}_4$  production.

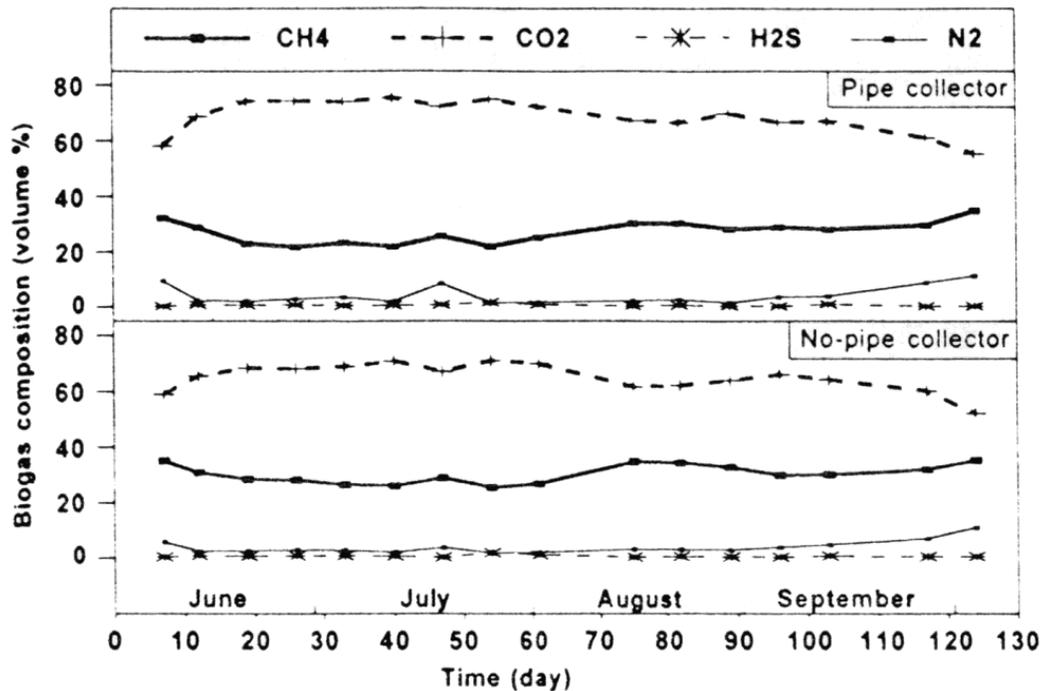
### Biogas Composition

Biogas composition during the winter and summer studies is shown in Figs. 6 and 7. Methane content of the biogas was low compared to reported values for anaerobic lagoons.



**Figure 6.** Average biogas composition in pipe and no-pipe gas collectors during winter. Gas concentration peaks in the pipe-system biogas resulted from introduction of air into the floating covers when they were removed from the pipes for monthly collection of slurry samples from inside the pipes.

It ranged from 22 to 35%, the average value being 34%, 27% and 30% (with a co-efficient of variation under 20%) for the winter-no-pipe, summer-pipe, and summer-no-pipe systems. Relatively low  $\text{CH}_4$  content of biogas suggests that insufficient time and low slurry temperatures, and possibly other inhibitory factors such as high volatile acid and ammonia concentrations, did not permit methanogenic bacteria to become dominant in the stored slurry. Introduction of an inoculum acclimatized to low temperature could conceivably increase the methane content in the biogas. Small quantities of nitrogen gas ( $\text{N}_2$ ) were detected in the biogas. Positive pressure in the free space of the floating covers precluded leaking in of the outside  $\text{N}_2$ . There were two potential sources of  $\text{N}_2$  entry into the free space under the floating covers, namely, the dissolved  $\text{N}_2$  in the manure slurry, and in the water used in the gas flow meters. Solubility of  $\text{N}_2$  is 2.33 g per 100  $\text{cm}^3$  water at  $0^\circ\text{C}$  (Weast, 1968), which is equivalent to about 37 L of dissolved  $\text{N}_2$  per liter of water. There was about 6 L of water in (each of) the gas flow meters, which were open to the atmosphere. Pressure fluctuations in the floating cover free space may have induced some  $\text{N}_2$  to be released into the system. Average concentration of hazardous hydrogen sulfide in the biogas was 0.4% (4000 parts per million) in the winter and 0.6% in the summer. These concentrations are sufficiently high to cause serious injury or death, in addition to corrosion of susceptible materials.



**Figure 7.** Average biogas composition in pipe and no-pipe gas collectors during summer.

## CONCLUSIONS

1. Farm-stored DCMS in cold climatic regions is unlikely to be a significant contributor of greenhouse gases into the atmosphere.
2. Confined manure seems to provide a higher yield of biogas than unconfined manure under floating-cover type of gas collectors.

## ACKNOWLEDGEMENTS

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