METHANE AND CARBON DIOXIDE EMISSIONS FROM SIMULATED ANAEROBIC SWINE MANURE TREATMENT LAGOONS UNDER SUMMER CONDITIONS

D. W. Hamilton, I. N. Kourtchev, P . M. Ndegwa, H. J. Cumba, F. Gioelli

ABSTRACT. *Most estimates of carbonaceous gas emissions from manure treatment lagoons are based on biogas production from anaerobic digesters, gases collected over covered lagoons, or the CH_4 production potential of animal waste. More data from direct measurements are necessary for evaluating mitigation strategies. Researchers at Oklahoma State University have successfully operated a pilot-scale bioreactor consisting of four 270 L columns that recreate environmental conditions found in anaerobic lagoons as indicated by color, temperature, pH, and electrical conductivity (EC). The columns were loaded at a surface organic loading rate similar to lagoons treating manure from commercial swine farms in the state of Oklahoma (935 kg VS/ha-day). The simulated mid-to-late summer CH_4 emission rate was determined to range between 200 and 300 kg/ha-day, and the CO_2 emission rate ranged between 380 and 580 kg/ha-day. Approximately 65% of the total carbon applied to the surface of the lagoon simulator was recovered as CH_4 and CO_2 gases; however, lagoon methane production was greater than expected using chemical oxygen demand (COD) as a predictive standard. The daily patterns of gaseous emissions and volatile organic acid concentrations in the liquid suggest that CH_4 production takes place across the entire depth of the reactor. Easily digestible organic matter is converted in the upper layers; more slowly digested material settles and is converted at the sludge layer. Data on day versus night emissions show that biogas had a higher proportion of CO_2 during the day than during the night.*

Keywords. *Carbon dioxide, Emission, Lagoon, Manure, Methane, Simulation.*

Methane (CH_4) and carbon dioxide (CO_2) are the two major contributors to global warming among the anthropogenic gases (U.S. EPA, 1999, 2002). Emission of CH_4 is the greater concern, because CH_4 is estimated to be 21 times more effective at trapping heat in the atmosphere than CO_2 (IPCC, 2001). The major sources of methane emissions in the U.S. are energy production, decomposition of human-generated waste, and agriculture. Because of the potential for animal agriculture to contribute to the global greenhouse gases, accurate measurement of CH_4 and CO_2 emissions from anaerobic manure treatment lagoons is critical. Currently, only a few sets of CH_4 emission data measured directly from anaerobic swine waste treatment lagoons are available (Sharpe and Harper, 1999; Sharpe et al., 2002). Most CH_4 emissions estimates are either based on biogas production from anaerobic digesters, gases collected from covered lagoons, or from the CH_4 production potential based on the chemical oxygen demand (COD) of animal waste (Safley and Westerman, 1988, 1989). Clearly, the environment surrounding anaerobic lagoons is not the same as those of either conventional anaerobic digesters or covered lagoons. The environment in anaerobic digesters is completely anaerobic and well mixed. Covering a lagoon significantly alters environmental conditions compared to an uncovered lagoon.

The complexity of making measurements of full-scale lagoons is in no doubt a major factor in the limited CH_4 and CO_2 emission data from anaerobic lagoons. The difficulty arises from two hindrances: the ability to study cause and effect relationships under controlled conditions, and the ability to accurately measure emission of gases over the entire lagoon surface. Researchers at Oklahoma State University (OSU) have attempted to overcome these hindrances by constructing a pilot bioreactor consisting of four 270 L, 3.66 m deep columns that recreate environmental conditions found in anaerobic/facultative lagoons (Hamilton, 1998). By precisely controlling the environmental and operational conditions of the column section, cause and effect relationships can be explored. The problem of surface measurement is reduced by assuming that the layered biological communities found in lagoons can be recreated in the 3.66 m of column depth, and that the gases emitted from the top of this column represent emissions from the total lagoon surface.

Article was submitted for review in August 2004; approved for publication by the Structures & Environment Division of ASABE in November 2005.

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  ISSN 0001−2351

Table 1. Geometric data and organic loading rates of one pilot-scale bioreactor column and full-scale swine waste treatment lagoons.

Facility	Dimensions at Maximum Drawdown Level (m)				Sideslope	Volumetric Loading Rate (g VS/m^3-day)	Surface Loading Rate (kg VS/ha-day)
	Depth	Diameter	Width	Length			
Pilot bioreactor	3.66	0.305	––	––	––	25.2	935
OK1	2.22	––	36.3	65.1	2.7:1	67.6	1,160
OK2	2.29	––	37.4	61.0	3.5:1	61.0	922

Lagoons in temperate climates undergo an annual cycle of organic matter accumulation and destruction tied to the changing seasons (Hamilton et al., 2002). By late summer, accumulated organic matter has been digested, and lagoon temperatures have not cooled to the point that biological activity is diminished. Late summer is, therefore, the period of the year in which an equilibrium between the mass of carbon added to a lagoon and the mass of carbon emitted by the lagoon on a daily basis is most likely to occur.

Objectives

The overall objective of this research was to determine emissions of gaseous pollutants from anaerobic/facultative lagoons treating swine manure using a physical model operated to simulate the expected environmental and operational conditions experienced by lagoons. The specific objectives of this study were to determine emission rates of CH_4 and CO_2 during a typical mid-to-late summer day from a photosynthetically active, anaerobic lagoon located at 35° N latitude.

Materials and Methods

Facility Description

The model pilot bioreactor used in this study is made of four insulated PVC pipes, 0.305 m (1 ft) in nominal diameter, and 3.66 m (12 ft) in depth (table 1). Hamilton (1998) gives a complete description of the bioreactor design. Two sets of two columns are coupled with the same lighting and heating systems to achieve two replicated sets of conditions from the four columns. The columns are labeled A, B, C, and D; therefore, the two column sets consist of AB and CD. The pilot facility was inoculated with effluent and sludge from a facultative lagoon located at the OSU Swine Research Center (OSU-SRC) in the fall of 1998, and has been programmed ever since to repeat the heating, mixing, and lighting patterns experienced by a typical anaerobic/facultative lagoon under late-summer conditions at 35° N latitude in Oklahoma.

Comparison to Oklahoma Lagoons

Three Oklahoma lagoons were monitored to determine the environmental conditions experienced by lagoons at 35° N latitude. An intensive chemical and physical survey was conducted on the OSU-SRC lagoon during the summer of 1997. This survey entailed monitoring conditions on the lagoon every 2 h for a period of 24 h for three days in June and July. After completion of this survey, remote temperature loggers (Stow Away Tidbit, HOBO, Onset Computer, Pocasset, Mass.) were installed in the OSU-SRC lagoon at depths of 0.15, 0.31, 0.61, 0.91, 1.22, 1.83, and 2.44 m. Hourly temperatures were continuously monitored from November 1997 until November 1999. These temperature data have been previously reported by Hamilton and Cumba (2000). Two additional lagoons, operated at organic loading rates more typical of lagoons found on commercial swine farms, have been monitored on an annual basis for a study of sludge accumulation (Hamilton, 2004). These lagoons, labeled OK1 (located in Pottawatomie County, Okla.; 35° 10′ N, 97° 00′ W) and OK2 (located in LeFlore County, Okla.; 35° 05′ N, 94° 30′ W), were used to set the surface organic matter loading rate on the pilot facility (table 1).

Swine Waste Acquisition and Loading

Swine waste was collected from pigs housed in metabolic chambers and fed a fortified corn-soybean meal diet (table 2). The metabolic chambers were operated to mimic pits in pit-recharge buildings. Both feces and urine were mixed in a pan below the animals. The mixture was allowed to stand for one week in the chambers, and then placed in buckets. The buckets were frozen and remained frozen until the raw manure was used to feed the bioreactor columns. In all, manure collection lasted about 2 weeks; this gave sufficient manure to use in the year-and-a-half long study. Reverse osmosis (RO) water was added to the raw manure at the time of column feeding to dilute the slurry to a consistency equal to that of manure produced in pit-recharge systems. Raw manure was, thus, diluted in a ratio of 65:750 with water to produce a feed concentration of 1.06% TS by weight. Concentration of analytes in the raw manure, concentration of analytes in the diluted manure as it was fed to the column, and daily mass loading of analytes to bioreactor columns are shown in table 3. Each column was manually fed the same amount of manure each day at 12:00 noon. The amount of the

Table 2. Composition of diet fed to grow-finisher pigs in metabolic chambers.

Ingredient	Quantity	Unit
Corn, grain	68.85	%
Soybean meal, hull-less	25.86	%
Soybean oil	3.00	%
Ground limestone	0.95	%
Dicalcium phosphate	0.68	%
Sodium chloride	0.25	%
OSU trace mineral mix	0.15	%
OSU vitamin mix	0.15	%
Aureo-50[a]	0.10	%
Ca	6,000.00	mg/kg
Mg	1,900.00	mg/kg
Mn	65.19	mg/kg
Na	900.00	mg/kg
K	7,800.00	mg/kg
P	5,000.00	mg/kg
S	2,100.00	mg/kg
Cl	2,000.00	mg/kg
Fe	281.60	mg/kg
Zn	191.82	mg/kg
Cu	23.76	mg/kg
Se	0.42	mg/kg

[a] Aureomycin 50g/lb.

Table 3. Characteristics of manure fed to the pilot-scale bioreactors.

	Raw Manure (mg/L or units)	Diluted Manure as Fed (mg/L)	Mass Loaded per Column (mg/day)
TS	120,000	11,000	8,250
VS	96,000	8,300	6,200
pH (units)	6.77	––	––
COD	100,000	8,800	6,600
TC	58,000	5,000	3,750
TKN	11,000	950	710
NH_4^+-N	4,800	420	315
Acetate	4,900	430	320
Propionate	5,000	440	330
Butyrate	8,400	640	480
Lactate	2,200	190	140

manure slurry fed to each of the columns corresponds to a volumetric loading rate of 25.2 g VS/m^3-day (1.57 lbs VS/1000 ft^3-day) and a surface loading rate of 935 kg VS/ha-day (830 lbs VS/acre-day), as indicated in table 1.

Bioreactor Operation

The procedures outlined in the following paragraphs were used to simulate late-summer environmental conditions, maintain a constant lagoon liquid level, create a hydraulic balance and mixing conditions consistent with full-sized lagoons, and maintain an undisturbed sludge layer.

Water baths were used to heat and cool water circulated in polypropylene coils to recreate the temperature profile with depth. A combination of fluorescent and incandescent lights, designed to have the same intensity and wavelength as sunlight, were turned on at 7:00 and turned off at 19:00 every day.

In Oklahoma, lagoon effluent is not generally irrigated during the latter part of the summer, and in fact, fresh water is often added to maintain the treatment volume of the lagoon. Liquid levels on the columns were held constant at 3.66 m., and daily hydraulic balance was maintained on the columns in order to simulate the yearly hydraulic balance of the lagoon. Lagoons receive rainfall, as well as recycled liquids. The mixture of manure and RO water entering the column was balanced against liquid losses from evaporation, sampling, and effluent wasting to reach a column EC that approximated that of the full-sized lagoons. Daily hydraulic loading was determined to be 750 mL per column per day. Effluent was drawn from both columns in a two-column set at a depth of 1.37 m (4.5 ft), mixed, and returned to both columns at a depth of 0.15 m (0.50 ft) to recreate natural lagoon mixing. This recirculation was performed daily at 7:00 a.m. for 10 min.

Solids retention time in a lagoon approaches infinity if the sludge layer of the lagoon is undisturbed. Sludge was sporadically sampled from the columns before the intensive gas sampling period in order to establish system equilibrium, and was not disturbed from column set AB at all during the sampling period.

Bioreactor and Lagoon Liquid Analyses

The following parameters were determined for all samples drawn from the pilot-scale bioreactors and full-scale lagoons using standard laboratory methods (APHA, 1998): total solids (TS), volatile solids (VS), total suspended solids (TSS), volatile suspended solids (VSS), and total Kjeldahl nitrogen (TKN). Sample pH was measured using a pH meter and electrode (model 1001, Accumet, Cole-Parmer, Vernon Hills, Ill.), while electric-conductivity (EC) was measured with a salinity-conductivity-temperature meter (model YSI 30, YSI, Inc., Yellow Springs, Ohio).

Table 4. Ion chromotography eluent concentration gradient for VFA analysis.

Run Time (min)	Eluent Proportions
0-2	94% DI H_2O, 7% 5 mM NaOH
2-6	100% 5 mM NaOH
6-9	50% 5 mM NaOH, 50% 50 mM NaOH
9-19	50% 5 mM NaOH, 50% 50 mM NaOH
19-26	93% DI H_2O, 7% 5 mM NaOH

The volatile fatty acid (VFA) concentrations in lagoon liquids were analyzed by ion chromatography using a DX 600 Ion Chromatograph (IC) (Dionex, Sunnyvale, Cal.) equipped with a conductivity detector (ED50), an IonPack column (AC11-HC), a suppressor (ASRS) and trap column (ATC-1), and a 25 μL loop. Eluents used were deionized water, 5 mM NaOh, and 50 mM NaoH. Eluents were mixed in the proportions shown in table 4 (Kourtchev, 2002). The ammonium nitrogen (NH_4-N) concentration of the simulator liquids was also analyzed using the Dionex DX 600 IC, with a CS12-A Ion Pack 3X150 mm column, a CS12A 4 mm and CTC-1 trap columns, and a 25 mL loop. Eluent used was 33 mM Mehansulfonic acid. Total flow rate was 1.0 mL/min (Kourtchev, 2002).

Gaseous Emissions Measurements

Emission rates of CH_4 and CO_2 from the lagoon simulator were measured using a closed-chamber system. The atmosphere immediately above the liquid surface was covered by a modified version of the chamber used by Ball et al. (1999) for soil analysis. The chamber used in this study was a 0.2 m tall, 0.09 m diameter polypropylene (Nalgene) cylinder, which was held in a floating position by a 0.15 × 0.15 m block of Styrofoam. Working headspace of the gas collecting cylinder was 800 mL. The cylinder rested on top of the liquid, and at no time was the 800 mL headspace submerged below the liquid surface. A short piece of tubing was inserted into the top of the cylinder. Samples were taken using a 5 mL glass syringe (VICI Precision Sampling, Baton Rouge, La.) by inserting the syringe needle into this tubing. The sampled gas was immediately analyzed in a gas chromatograph (model 8610 C, SRI Instruments, Torrance, Cal.) fitted with a thermal conductivity detector (TCD) and a helium ionization detector (HID). Units of analysis were volumetric fraction of each gas.

After sampling, the closed chamber was removed from the system, and accumulated CH_4 and CO_2 gases were purged using compressed air. The chamber was then returned to the column surface for the next sampling period. Headspace CH_4 and CO_2 concentrations increased as these gases were emitted from the liquid surface. As long as the concentration of gas in the chamber remained dilute, the atmosphere above the liquid did not interfere with movement of gases out of the liquid. Experimentation showed that when gas production was relatively constant (early morning hours), concentrations in the chamber increased linearly for 60 min with CH_4 and for 90 min with CO_2. Volume of emitted gas in the chamber was determined by multiplying the volume of the chamber by the volume fraction measured by the GC.

Number of moles present in the chamber was determined using the ideal gas law. If the increase in gas concentration is linear, then the molar emission rate for the time between chamber flushing and sampling can be determined by dividing moles of gas trapped in the chamber by time (30 min) and emission area (6.4×10^{-3} m^2).

Daily mass of CH_4 and CO_2 emitted was calculated by multiplying the molar emission rate by the time interval over which it was measured, and summing masses for all the measurement intervals for the day. There were forty-eight 30 min intervals over a typical 24 h sampling period. If a measurement interval was skipped, then the rates measured in the time periods immediately before and after the period skipped were used to determine a linear interpolation of rates between the known measurements.

Experimental Timeline

Feeding the columns at the 25.2 g VS/m^3-day rate began in September 2001. Weekly samples of all four column liquids were analyzed for TS, VS, TSS, VSS, pH, EC, NH_4-N, and TKN to determine when equilibrium conditions had been reached. There were no major changes in monitored parameters after June 2002 (Kourtchev, 2002). Weekly monitoring of these parameters continued on a weekly basis until 29 September 2002.

Because of the complexity and time involved in collecting emissions from the closed chamber, emission rates were only measured on column A. Chemical analyses were performed on all four columns to ensure that the performance of column A did not deviate from the other three columns. Gaseous emissions were measured on column A at 30 min time intervals from 6:00 to 18:00 on 22 June 2002. Emissions were again measured from 16:00 on 24 June 2002 to 6:00 on 25 June 2002. Gaseous emissions, as well as liquid VFA concentrations, were continuously measured on column A at 30 min intervals beginning at 4:30 on 17 July 2002 and ending at 2:30 on 18 July 2002. Gaseous emissions and VFAs were again continuously measured on column A at 30 min intervals from 11:00 on 10 August 2002 until 9:00 on 11 August 2002. A spot check of gaseous emissions and VFA concentration of column A was performed by collecting samples at 30 min intervals from 6:00 to 9:00, from 11:30 to 13:30, and from 17:30 to 18:30 on 1 September 2002, and from 2:00 to 3:30 on 2 September 2002.

Results and Discussion

Heating and Cooling Cycle

The maximum temperature of 27°C at a depth of 2 m in the OSU-SRC lagoon occurs during late August. A typical daily heating pattern obtained using temperatures sensors on 28 August 1998 is shown in figure 1. Water baths were programmed to approximate these late-summer heating and cooling conditions in the pilot-scale bioreactors. The heating pattern in one typical bioreactor column (column A) recorded on 9 September 2002 is shown in figure 2.

Mixing the column set at 7:00 seems to have little effect on the temperature profile in the columns, most probably because mixing occurred at a time when the temperature at 1.37 m is equal to the temperature at 0.15 m. A temperature spike occurred at 12:00 as the water baths responded to column feeding. The water baths were controlled by a temperature sensor located at the center of the column at 0.15 m depth. The temperature dropped in the vicinity of the sensor as the column was fed, but because the thermocouple measuring the column temperature at 0.15 m was located near the heating coil at the column wall, an apparent rise in column temperature occurred as the heating coil responded to the water bath controller. This was registered as a temperature spike.

Comparison to Full-Sized Lagoons in Oklahoma

The EC profiles shown in figure 3 were used to compare the response of loading rate and hydraulic balance of the pilot-scale bioreactor to full-sized lagoons. The bioreactor EC is the average of all four columns measured during the test period (5 July and 5 August 2002). The EC data for the bioreactors are also given in table 5. The EC data for lagoons

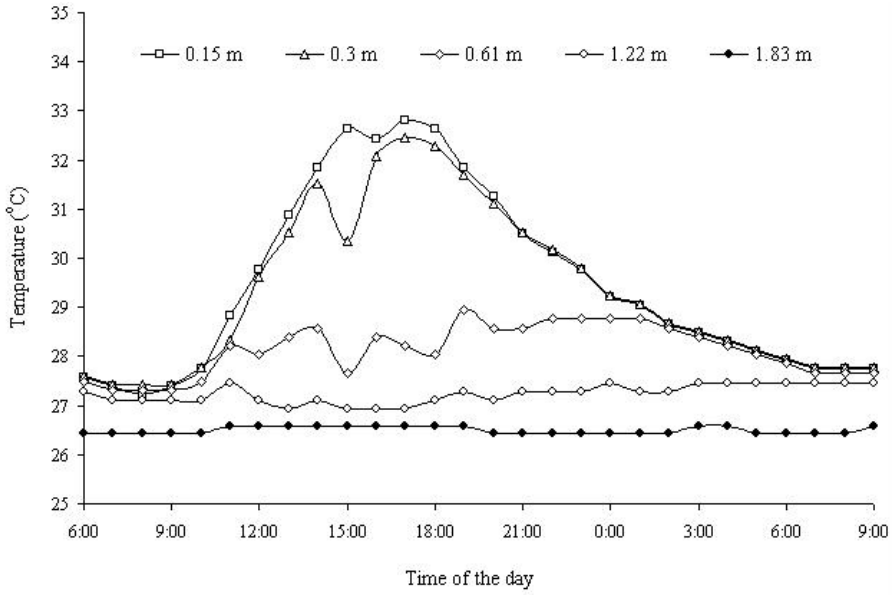

Figure 1. Heating pattern in the OSU swine waste treatment lagoon recorded on 28 August 1998.

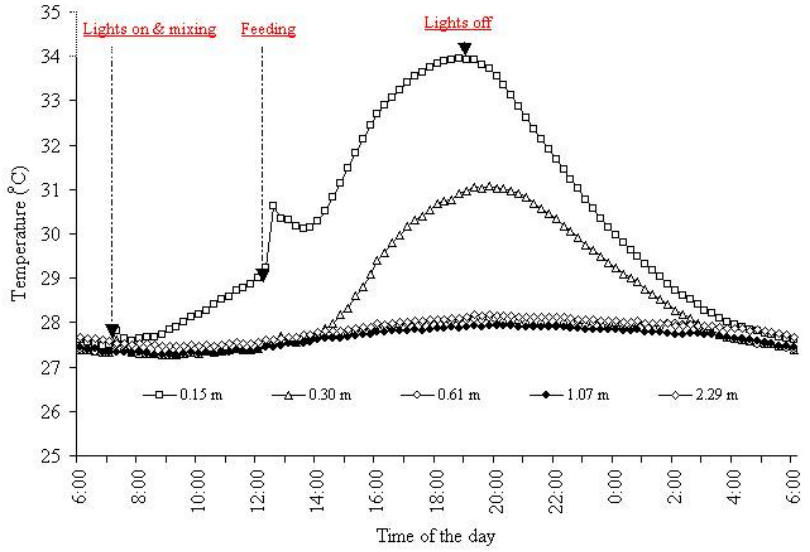

Figure 2. Heating pattern recorded in bioreactor column A programmed to simulate mid-to-late summer conditions.

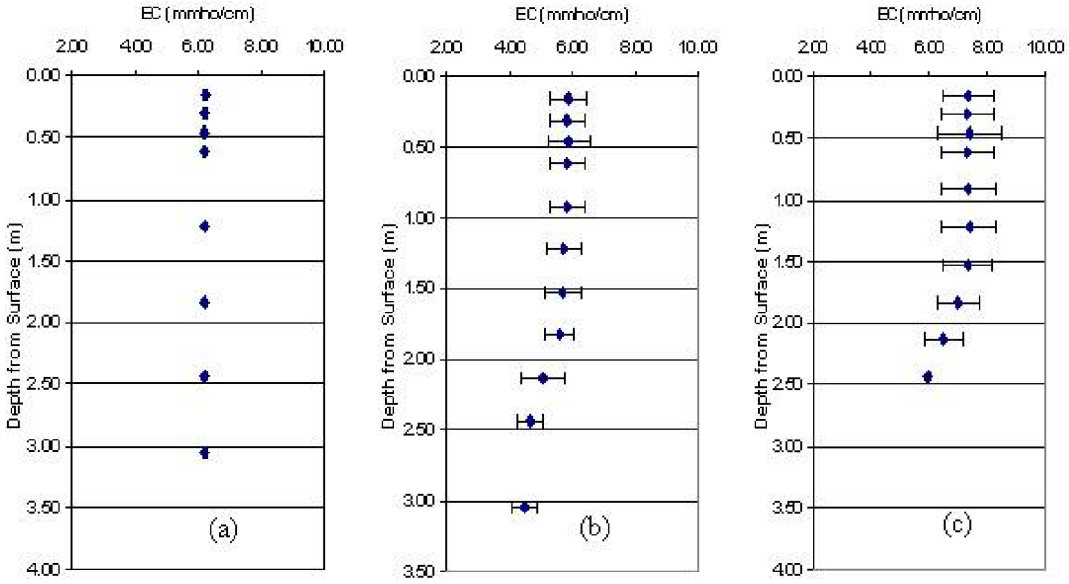

Figure 3. Electric conductivity profiles using pooled data for (a) all four bioreactor columns operated under mid-to-late summer condition and for full-sized lagoons (b) OK1 and (c) OK2 measured between the months of May and August in the years 1996 to 2002 (error bars indicate plus and minus one standard deviation).

Table 5. pH, EC, and nitrogen data collected from the pilot-scale bioreactors between 5 July and 5 August 2002 (X ±SD).[a]

Depth (m)	pH (n = 16 to 36)	EC (mmho/cm) (n = 32)	TKN (mg/L) (n = 4)	NH_4^+-N (mg/L) (n = 7)
0.15	7.47 ±0.09	6.23 ±0.05	391 ±31	321 ±49
0.30	7.47 ±0.10	6.22 ±0.05	393 ±17	330 ±41
0.46	––	6.22 ±0.05	––	––
0.61	––	6.22 ±0.05	––	––
1.22	7.45 ±0.09	6.22 ±0.03	386 ±18	322 ±48
1.83	––	6.23 ±0.03	––	––
2.44	7.40 ±0.07	6.23 ±0.04	414 ±35	331 ±50
2.90	7.37 ±0.09	––	––	––
3.05	6.96 ±0.06	6.23 ±0.04	––	923 ±212
3.66	––	––	3941 ±314	––

[a] X = mean, SD = standard deviation, and n = sample size.

OK1 and OK2 are the means of all observations made on the lagoons between 1996 and 2002 during the months of May and August. The EC patterns for the columns were accurately maintained within the ranges observed in full-sized lagoons during the period monitored.

Column pH measured during the sampling period is given in table 5. Column pH ranged between 6.96 and 7.47, and decreased with depth. The pH of both full-sized lagoons ranged between 7.37 and 8.08 at a depth of 0.51 m, and between 7.13 and 7.62 at depths greater than 1.22 m. Sharpe and Harper (1999) report a comparable pH range of 7.20 to 7.70 between the top and bottom of a lagoon monitored in Georgia over a period of one year.

All three of the full-sized lagoons used in this study remained red or violet-red in color year round, which indicates the presence of photosynthetically active, purple

Table 6. Summary data of solid fractions of samples drawn from the pilot bioreactor between April and September 2002.

Depth (m)	Total Solids, X (mg/L) ±SD (n)[a]	Total Volatile Solids, X (mg/L) ±SD (n)[a]	Calculated Average Solids Fractions (mg/L)[b]			
			VSS	VDS	FSS	FDS
0.30	3,300 ±140 (2)	1,150 ±71 (2)	380	820	90	2,000
1.22	3,300 ±110 (7)	1,200 ±140 (7)	380	890	83	2,000
2.44	3,550 ±71 (2)	1,300 ±0 (2)	460	840	120	2,100
3.05	62,000 ±7,500 (9)	33,500 ±11,500 (9)	––	––	––	––

[a] X = mean (mg/L), SD = standard deviation, and n = sample size.
[b] VSS = volatile suspended solids, VDS = volatile dissolved solids, FSS = fixed suspended solids, and FDS = fixed dissolved solids.

sulfur and/or purple non-sulfur anaerobic bacteria. Scum layers of windblown algae also frequently occurred in downwind corners of the lagoons. The bioreactor columns also maintain a red to red-violet color under a thin layer of algae. Algae were removed from the surface every day before feeding. Cooper (1962) determined that algae and photosynthetic bacteria always coexist in lagoons. When algae appear to dominate the system, purple sulfur bacteria are also present but in smaller numbers. Likewise, when purple bacteria dominate, algae are present. The purple or red color of lagoons depends on the presence of reduced sulfur in bacterial chromoplasts.

Chemical Analyses of Bioreactor Liquids

Data on EC, pH, and nitrogen content of samples drawn from the bioreactors between 5 July and 5 August 2002 are presented in table 5. Analyses of solids between April and September 2002 are given in table 6. The TS data show a transition from liquid to sludge (liquid-sludge interface) occurring between 2.44 and 3.05 m of column depth. Total solids concentration above 2.44 m was approximately 0.33% by weight, whereas TS concentration at 3.05 m was 6.2%. Above the sludge layer, the liquid was relatively homogeneous, with the majority of solids (60%) comprised of inorganic salts (FDS) and 80% of nitrogen in the form of ammonium. Below 3.05 m of depth, volatile solids became more prevalent, and nearly 80% of TKN was in the organic form.

Daily patterns of acetate and lactate concentrations at three depths (0.31, 1.22, and 3.05 m) in column A are given in figure 4. Acetic acid concentrations at 0.15 and 1.22 m responded to feeding. Concentrations were lowest between mixing and feeding, increased after feeding, and decreased 2 to 6 h after feeding. The acetic acid concentration at 3.05 m may show a delayed response to feeding. Lactic acid concentrations at all depths did not exhibit a response to feeding. These patterns suggest two pathways of organic matter removal in lagoons loaded from the surface: (1) easily digestible organic matter is converted to acetic acid and eventually to CH_4 and CO_2 in the upper portion of the lagoon, and (2) less digestible organic material settles to the liquid-sludge interface to be slowly and constantly converted to a mixture of organic acids, a portion of which are further converted to carbonaceous gases.

Methane and Carbon Dioxide Emissions

Individual measurements of CH_4 emissions are plotted against time of day in figure 5. Measurements of CO_2 emissions versus time of day are shown in figure 6. Average values of $CH_4 + CO_2$ gas emission rate and average values for molar CH_4:CO_2 ratio are plotted against time of day in figure 7. $CH_4 + CO_2$ gas emission was relatively constant at

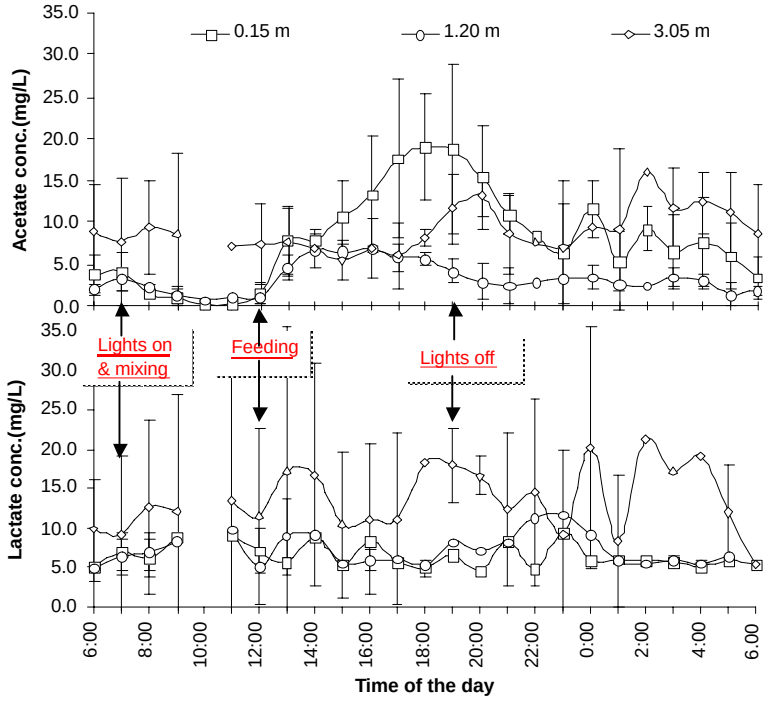

Figure 4. Average concentrations of acetic acid measured on 17 July, 10 August, and 1 September 2002 and lactic acid measured on 10 August and 1 September 2002 at three depths (0.31, 1.22, and 3.05 m) from the surface of bioreactor column A (error bars indicate plus and minus one standard deviation).

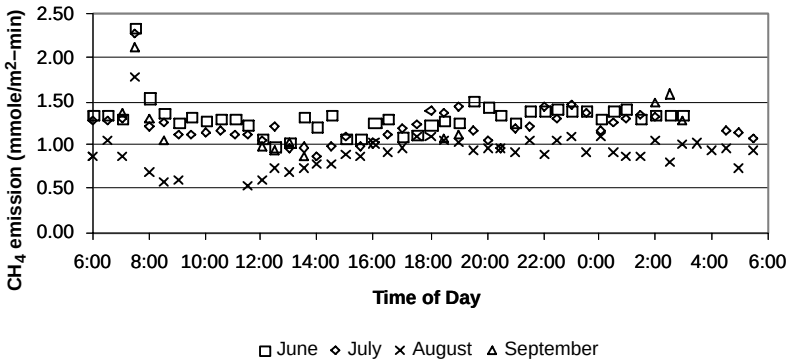

Figure 5. CH_4 emissions from column A measured on 22 June, 24 June, 17-18 July, 10-11 August, and 1-2 September 2002.

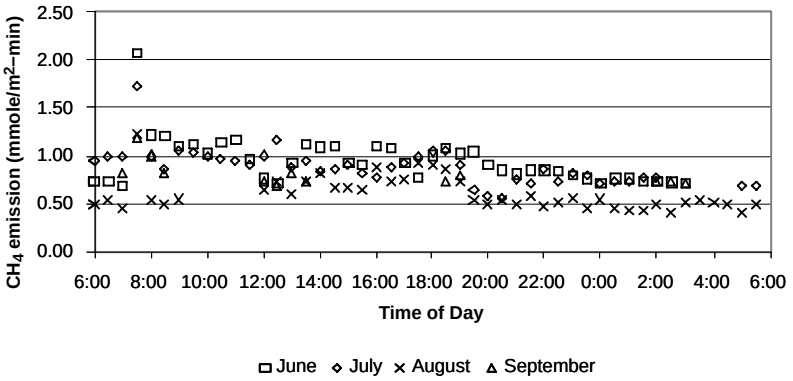

Figure 6. CO_2 emissions from column A measured on 22 June, 24 June, 17-18 July, 10-11 August, and 1-2 September 2002.

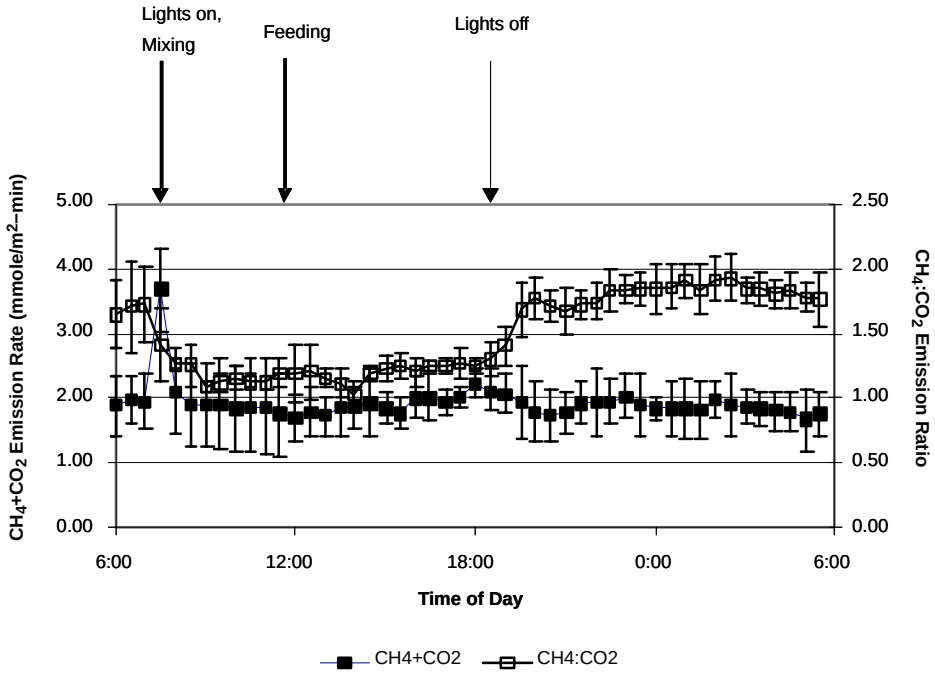

Figure 7. Average $CH_4 + CO_2$ emission rate and the corresponding molar ratio of gases emitted by bioreactor column A on 22 June, 24 June, 17-18 July, 10-11 August, and 1-2 September 2002 (error bars indicate plus and minus one standard deviation).

2 mmoles/m^2-min, with a slight increase after feeding, and a slight decrease after the lights were turned off. Mixing produced a spike in gas emission at 7:00. There was a remarkable difference in the CH_4:CO_2 ratio between day and night. The ratio of CH_4 to CO_2 dropped from 1.8 to 1.2 almost immediately after the lights were turned on, and returned to 1.8 after the lights went off. This changing pattern of CH_4:CO_2 ratio between day and night may be attributed to a combination of four processes: (1) aerobic and anaerobic photosynthetic organisms, and aerobic bacteria living symbiotically with

Table 7. Masses of methane, carbon dioxide, and total carbon emitted during 24 h test periods.

	22 and 24 June	17-18 July	10-11 August
Moles emitted (mmole/day)			
$CH_4 - C$	140	125	91
$CO_2 - C$	94	89	61
$CH_4 + CO_2 - C$	234	214	152
Masses emitted (mg/day)			
CH_4	2,200	2,000	1,450
CO_2	4,100	3,900	2,700
$CH_4 + CO_2 - C$	2,750	2,550	1,800
Masses emitted from an equivalent lagoon surface (kg/ha-day)			
CH_4	300	280	200
CO_2	580	550	380
$CH_4 + CO_2 - C$	390	360	260

aerobic photosynthetic organisms, produce higher volumes of CO_2 during daylight, (2) the small, but appreciable amount of oxygen produced by algae during daylight suppresses CH_4 production, (3) higher volumes of CO_2 are produced as complex organic matter is converted to acetate by both aerobic and anaerobic bacteria, and (4) excess CO_2 and H_2 are converted to CH_4 by methanogenic bacteria once acetate reserves become depleted.

Daily masses of gases emitted by the bioreactor were determined by integrating the area under the curve of the flux profile of each gas. Results for the three full days of emission testing are shown in table 7. Average mass of $CH_4 + CO_2 - C$ emitted was 2,400 mg/day. The mass of total carbon applied to the column each day was 3,750 mg/day (table 3); therefore, approximately 65% of the applied carbon is accounted for in $CH_4 + CO_2$ emission.

McCarty (1964), among others, stated that the mass of CH_4 theoretically created per mass of oxygen demand consumed is derived from the combustion of methane:

$$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$$

It is assumed that methane is the only component of biogas that reacts in the presence of oxygen to produce CO_2. This assumption is fairly accurate, because the proportion of other gases capable of oxidation (chiefly H_2, NH_3, and volatile organic compounds) in biogas is rather small −− about 5%. If methane is the only combustible gas, and if the measure of oxygen demand used takes into account all of the potentially digestible carbon, then one mass unit of CH_4 is released per four mass units of oxygen demand consumed (CH_4: molecular weight 16, $2O_2$: molecular weight 64). As shown in table 7, the mass of CH_4 emitted was as high as 2,200 mg/day. This mass exceeded the expected mass of methane produced by a 6,600 mg/day COD loading (table 3) by a factor of 130%.

The problem with using COD to estimate CH_4 emissions is the assumption that all of the potentially digestible organic matter can be measured in the COD test. The COD test is a relatively short digestion in a strong oxidizing environment, a mixture of sulfuric acid and potassium dichromate. Other studies (S. L. Mann, personal communication, 2 June 2005) have shown that the COD test underestimates the methane-yielding potential of manure solids compared with biological tests, such as the biological methane potential (BMP) test. In the BMP test, a sample is incubated with methane-producing bacteria for a period lasting as long as the solids retention time of the digester to be built. Lagoons have much longer solid detention times than digesters −− approaching infinity if settleable solids are completely retained; therefore, it is plausible that more CH_4 was emitted from our pilot-scale bioreactor than would be expected from the COD test.

Scaling the column emission data to full-sized lagoons suggests that late-summer CH_4 emissions from a lagoon loaded with swine manure at 935 kg VS/ha-day should be in range of 200 to 300 kg/ha-day. CO_2 emissions from similarly loaded lagoons in late summer should be in the range of 380 to 580 kg/ha-day.

Sharpe and Harper (1999) used tunable diode laser spectroscopy to measure CH_4 emission rate from a four-stage lagoon treating manure from a 12,000 hog farrow-to-finish farm located in the Coastal Plains of Georgia. The CH_4 emission rate ranged between 1 and 500 kg CH_4/ha-day and depended heavily on time of year. Earlier, the same authors measured springtime emissions from the first stage of the four-cell lagoon using a submerged carboy designed to capture gases released from the sludge layer. The authors did not give an organic matter loading rate for the lagoon cell, but using the stated surface area of the lagoon (3.5 ha) and the estimated mass of volatile solids produced by a farm of this size would give a surface loading rate slightly greater than 1,000 kg VS/ha-day. Sludge layer emission rate during spring was thus determined by Sharpe and Harper (1999) to be 126 kg CH_4/ha-day. Our results show that a larger mass of CH_4 was emitted per unit area (200 to 300 kg CH_4/ha-day). The springtime emissions reported by Sharpe and Harper (1999) using the submerged chamber gathered gases released from the sludge layer of the lagoon. The floating chamber used in our experiment gathered gases produced by both the sludge layer and the liquid portion of the lagoon. Our results show that CH_4 is produced in the liquid portion of the lagoon as well as in the sludge layer; therefore, the higher emissions recorded in this study are plausible.

CONCLUSIONS

The results of this study suggest that lagoons located at 35° N latitude and loaded at a rate of 935 kg VS/ha-day will emit between 200 and 300 kg CH_4 per hectare per day and 380 to 580 kg CO_2 per hectare per day during the late summer. Carbonaceous gas production takes place across the entire depth of the lagoon. Easily digestible organic matter is consumed in the upper layer of the lagoon, and more slowly digested material is converted in the sludge layer. Studies that collect only gases emitted by the sludge layer may underestimate lagoon carbon emissions. Photosynthetically active anaerobic lagoons produce biogas with a greater proportion of CO_2 during the daylight hours than during the night.

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