CHARACTERIZATION OF BIOGAS FROM ANAEROBICALLY DIGESTED DAIRY WASTE FOR ENERGY USE

A Thesis

Presented to the Faculty of the Graduate School

of Cornell University

in Partial Fulfillment of the Requirements for the Degree of

Master of Science

by

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May 2007

ABSTRACT

As the third largest dairy producer in the United States, New York is faced with the critical issue of agricultural waste management. The environmental impacts and high long-term costs of poor waste disposal have pushed the industry to realize the potential of turning this problem into an economic and sustainable initiative. The anaerobic digestion of dairy manure-derived agricultural waste produces biogas, a valuable energy resource. Anaerobic digestion offers an effective way to manage manure by addressing the principal problem of odor control while offering an opportunity to create energy from conversion of biogas with a system of combined heat and power (CHP).

Anaerobic digestion is a microbial process that produces biogas, a gas consisting of primarily methane (CH_4) and carbon dioxide (CO_2). The use of biogas as an energy source has numerous applications. However, all of the possible applications require knowledge about the composition and quantity of constituents in the biogas stream.

This thesis presents the findings of a study conducted over several months at five New York farms to evaluate the characteristics of dairy manure-derived biogas. Relatively long term measurements of a biogas stream at Dairy Development International (DDI) provided information about the composition and quantity of the constituents of biogas over time (day, week, months). At DDI, methane averaged 60.3% (±1%) of the total gas composition with an average BTU per standard cubic foot of 612 (±12 BTU/SCF). Carbon dioxide averaged 38.2% (±1%) during this period with nitrogen at 1.52% (±1.1%). Hydrogen sulfide, a particularly hazardous component of biogas affecting the ultimate end use of biogas in energy generation technologies measured an average of 1984 ppm (±570 ppm) at DDI where measurements were taken about every 3 hours over numerous 24 hour periods from July to November 2003. Biogas samples at the

other four dairies illustrated rather wide variations in hydrogen sulfide concentrations from about 600 ppm to over 7000 ppm. It is suggested that the lower H_2S concentrations may be due to additions of food waste to the anaerobic digester at the dairy with the low H_2S concentration. The high H_2S concentrations measured at another dairy are believed to be related to the significantly higher concentrations of sulfur in the farm water. For dairies not adding food wastes and not having high sulfur content in the farm water, the H_2S concentrations ranged between approximately 1000 and 3600 ppm.

Water, waste and feed samples were also collected from the five dairies to determine whether the digester inputs had an effect on the components of the biogas as well as to explore the range in biogas quality at various dairies in the region. Based on the preliminary results shown in this study, it is suspected that higher sulfur contents present in feed water may have an impact on the hydrogen sulfide content in biogas generated through the anaerobic digestion of dairy manure.

These results agree with often well-quoted generalized concentrations of approximately 60% CH_4, 40% CO_2 and 600 BTU/SCF for dairy-derived biogas. The data also show that the H_2S concentration can vary significantly depending on the type of additives in the diet and the quality of the farm water, anywhere from 600 ppm to 7000 ppm.

Key Words:
Anaerobic digestion, dairy manure-derived biogas, biogas characterization, methane, hydrogen sulfide

BIOGRAPHICAL SKETCH

Kim Bothi was raised in Southern Alberta, Canada on a dryland grain farm with her parents Lynda and Steve and twin brother Steven. After graduating from high school, Kim completed a diploma of Environmental Technology from Mount Royal College in Calgary, Alberta and continued her education with a degree in Agricultural and Biosystems Engineering from McGill University in Montreal. After traveling abroad and working as a Project Manager for an environmental consulting firm in Calgary, Kim began her studies in the Department of Biological and Environmental Engineering at Cornell University in 2002.

Kim is currently conducting research on collaborations in water supply projects throughout West Africa in the Department of Education at Cornell University.

ACKNOWLEDGEMENTS

The author would like to thank fellow graduate sudent, Steven Zicari as well as undergraduate student, Michelle Wright, for their assistance with data collection. A sincere thank you is also given to Dr. Norman Scott for his support of the following research.

Five participating dairies, used for data acquisition, are acknowledged for their important contributions: Dairy Development International (DDI), AA Dairy, Ridgeline, Noblehurst, and Twin Birch. Special thanks go to DDI, particularly Larry Jones, who provided the opportunity to acquire "real data" with on-site experimentation.

Funding for this research was provided through New York State Energy Research and Development Authority (NYSERDA) Agreement No.7250. Many of the findings presented in this thesis have been included in the NYSERDA final project report, *Biogas Processing*, submitted in February 2006.

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CHAPTER 1

INTRODUCTION

A driving force in the field of renewable energy is to develop systems which minimize impacts on the environment, yet deliver the opportunity to create energy options. Large dairy farms, more technically known in the industry as Confined Animal Feeding Operations (CAFO's), produce a large portion of the United States total agricultural wastes. NY state produces around 2% of the country's total animal waste, at 18,000,000 tons/year.[1] A vast majority of these wastes are generated by dairy farms. With over nine million milk cows, the dairy industry produces 4.29 billion cubic feet of animal waste each year.[2] With rising concerns about environmental quality and resource management, the agricultural sector is being driven towards greater responsibility for the wastes generated. An improved understanding of the constituents and typical quantities of biogas generated from the anerobic generation of dairy manure will aid in the evaluation of methods to appropriately utilise this valuable resource.

In 2004, Governor Pataki announced the need to "improve our environment and reduce our dependence on imported foreign energy by leading the nation in the development and deployment of renewable energy resources like…biomass." New York is the third largest dairy state in the US, with nearly 7,000 dairy farms and 650,000 dairy cows.[3] This suggests a significant potential energy market if the waste generated from these animals was used to generate electricity and heat. In 2001, Scott (2004) estimated the

[1] http://www.scorecard.org
[2] Dairy cows net excretion estimated at 260 L/week (1.3 ft^3/day) per animal weighing 1000 lb according to the USDA Agricultural Waste Management Field Handbook. Calculation based on 9.05 million milk cows in the US as of July 1, 2005, http://usda.mannlib.cornell.edu/reports/nassr/livestock/pct-bb/catl0705.pdf.
[3] Based on 2005 data from the United States Department of National Agricultural Statistics Services available at http://www.nass.usda.gov/QucickStats.

total amount of dairy manure biomass generated annually in New York to be potentially enough to produce 280 GWh, supporting the electricity needs of approximately 47,000 households with the use of diesel generators. This electrical potential is estimated to be more than double with the alternative use of fuel cells. Because it is unlikely that all of this waste can be used in anaerobic digestion systems, half of this value is more realistic to illustrate New York's agricultural biomass (dairy manure) potential. The more efficient technologies, including fuel cells, require more intensive gas treatment techniques, making them a more costly option for electricity generation. This detracts from the long-term sustainability of biogas generation, especially in rural settings where the economic costs of upgrading biogas for many electricity generation technologies far exceed the benefits. The heat energy produced from diesel generators and other "lower-technology" options is often the most desireable output for smaller dairy operators with anaerobic digesters. Until the corrosive constitutents of biogas can be cost-effectively removed, using diesel generators and other similar "proven" technologies, available to smaller operators such as in many NY state dairy farms, are the most tangible way to turn animal wastes into a marketable commodity.

CHAPTER 2

BACKGROUND

Anaerobic digesters have been in use around the world to break down organic matter into useable energy sources. On the farm, the process for anaerobic digestion is relatively simple. The raw material (i.e. raw dairy cow manure) enters an enclosed, impermeable and often insulated container called a digester in the absence of oxygen. Depending on the characteristics of the raw material, the size of the digester and a number of external factors such as ambient temperature, the manure must remain in the digester for a minimum holding period to allow for sufficient breakdown of the organic material. In many digesters, including the common plug-flow, an equal amount of "treated" manure or effluent exits the container as raw manure is introduced to the system. The digester will function most effectively with the use of organic matter free of sand and other inorganic particulates and while maintaining a constant temperature and pH. Temperatures around 95°F are generally considered optimal for gas production for mesophilic digestion. This means that in colder climates, anaerobic digesters must be heated to accommodate this desired temperature..

The following flow diagram (Figure 2.1) depicts the layout of a typical single-stage digester and the basic functional requirements.

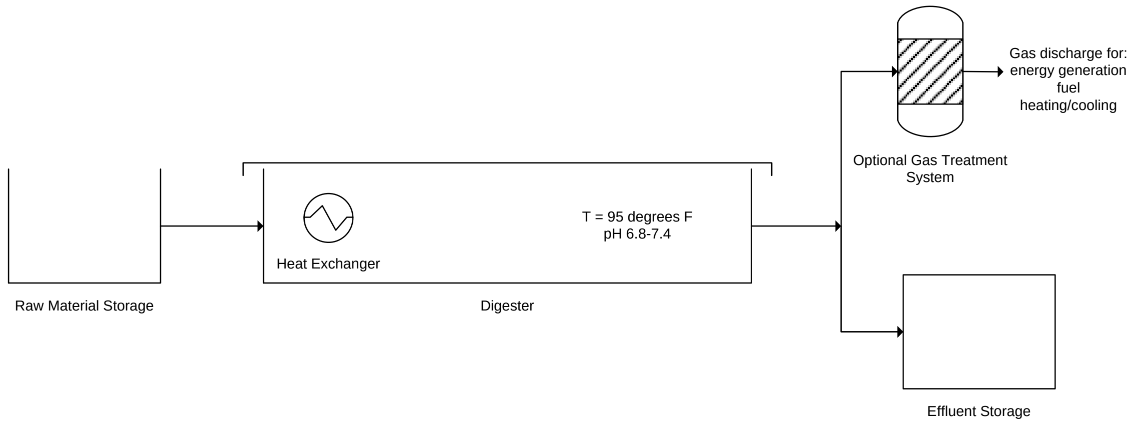

Figure 2.1 Single-stage anaerobic digester system.

Anaerobic digestion is a microbiological process that produces biogas, consisting primarily of methane (CH_4) and carbon dioxide (CO_2) in the absence of oxygen. The digestion process occurs in three stages (Mata-Alvarez, 2000; Monnet, 2003).

The first stage involves *hydrolysis*, where complex organic compounds are broken into simple soluble sugars, amino acids, fatty acids, and peptides by hydrolytic bacteria. The second stage, or *acidogenesis*, occurs where these compounds are further broken down into simple molecules by acid-forming bacteria. During this stage, by-products such as ammonia, carbon dioxide and hydrogen sulfide are produced. The simple moecules from acidogenesis are broken down further producing acids such as acetic acid, butyric acid, propionoic acid and ethanol. In the third stage of the anaerobic digestion process, *methanogenesis* occurs. Here, methanogenic bacteria convert the acids into CH_4 gas and CO_2 (Figure 2.2).

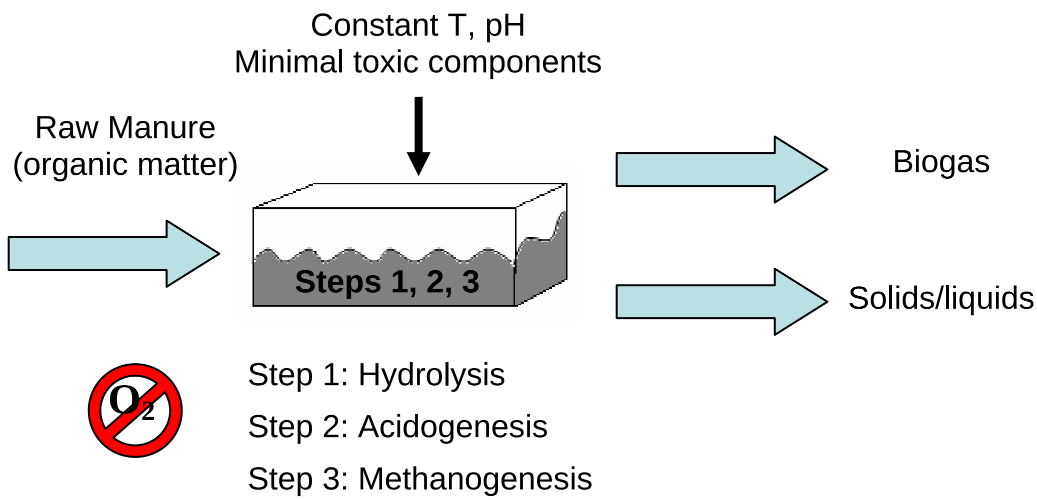

Figure 2.2 Microbial process of anaerobic digestion.

Methane production can be affected by system pH, temperature, and the presence of a number of potentially toxic materials such as salts, heavy metals, ammonia, and antibiotics.[4] The optimal pH range for digestion is between 6.8 and 7.4. An increase in acidity can occur when acetogenic bacteria grow rapidly at times of high organic matter loading, causing elevated levels of volatile fatty acids. This situation can be controlled by simply buffering the system with an alkali such as lime during start-up or high-loading periods. Temperature can also have an impact on microbial productivity.[5] Various literature suggests that the optimal operating temperature within an anaerobic digester is in the higher end of the mesophillic range (75-100 degrees Fahrenheit) although digestion can also take place in the thermophillic range of 125-140 degrees Fahrenheit with a greater risk of bacteria death (Engler et al, 1999; Duran and Speece, 1997). Heavy metals can generally be precipitated out with sulfides in the sludge but

[4] http://muextension.missouri.edu/explore/agguides/agengin/g01881.htm
[5] At the time of the study, the author was unable to find published literature on the effects of ambient temperatures on biogas quality.

high concentrations of soluble metals such as copper can be toxic to the bacteria in the digester. Copper is a common metal present in digester wastes from farms using copper sulfate anti-fungal foot baths. Small concentrations of salts are necessary for optimal bacterial growth in the digester, however, if salts accumulate beyond the requirements of the bacteria, digestion can be inhibited. Ammonia toxicity is also an important concern for digester operation. High amounts of nitrogen are naturally present in animal manure and in the digester, this nitrogen is converted to ammonia which can accumulate and become toxic to the bacteria. For optimum biogas production and increased methane content, loading rates and each of these factors must be controlled.

Biogas generated from anaerobic digestion has numerous applications. The primary benefits of anaerobic digestion are odor control, nutrient recycling and waste treatment. A secondary benefit, more applicable to larger digester operations, is biogas production, particularly the potential for energy production.

This project provides information about the fundamental characteristics of biogas. By better understanding its components, biogas can be processed and utilized in a more efficient, cost-effective way. As shown in Table 2.1, biogas contains primarily CH_4 with the balance being mostly CO_2 and a small amount of trace components. Biogas has approximately two-thirds the energy potential of refined natural gas due to the significant amount of CO_2 and lower CH_4 content, lowering the energy value relative to that of natural gas. In addition, the relatively minute concentrations of trace components can have a particularly complicating effect on the way biogas can be processed and utilized. Despite these differences, however, biogas still contains a significant amount of CH_4 for use as a renewable energy source. Because biogas releases approximately half the carbon dioxide as most other conventional fuels and does not release carbon monoxide during combustion, it is considered a much more environmentally friendly fuel source.

Table 2.1 Biogas composition.[6]

Typical Bulk Biogas Components	**Trace Components**
Methane 50-60%	Hydrogen
Carbon Dioxide 38-48%	Hydrogen Sulfide
Trace Components 2%	Non-methane volatile organic carbons (NMVOC)
	Halocarbons

One of the project goals was to encourage total resource-recovery on the farm. This idea is generated from the concept of engineering agricultural systems for sustainable development where resources are recycled on the farm reducing the use of off-farm non-renewable resources. Thus, this project addresses this opportunity by investigating anaerobic digester (AD) biogas, and, thereby, increasing its utilization. Any system for conversion of biogas to energy either requires a method to remove toxic and corrosive contaminants from biogas, or special procedures to accommodate the deleterious effects of contaminants in the biogas stream. Presently, the internal combustion (IC) engine is the most effective and economically viable energy converter used with AD biogas. The two most common on-farm approaches are changing oil in IC engines on a regular basis (numerous operators change oil weekly), or use of Iron Sponge (iron impregnated wood chips) as a filter to remove contaminants, principally hydrogen

[6] Source: http://www.novaenergie.ch/iea-bioenergy-task37/Dokumente/Flaring_4-4.PDF

sulfide (H_2S), from biogas before introduction of biogas into the engine.[7] For more futuristic combined heat and power (CHP) systems such as microturbines and fuel cells, the removal of contaminants is as, or more, critical than for the IC engine. In general, biogas must be filtered and possibly even pre-treated before being used as an energy source or prior to entry into a pipeline system. The simplified process of transforming farm waste to an energy resource is shown in Figure 2.3.

As of 2002, the EPA's AgStar program had recognized 97 anaerobic digesters in the US, up from 34 in 1999 (Roos and Moser 2000, AgStar 2002).[8] The biogas end use for the majority of these digesters includes electricity and heat.

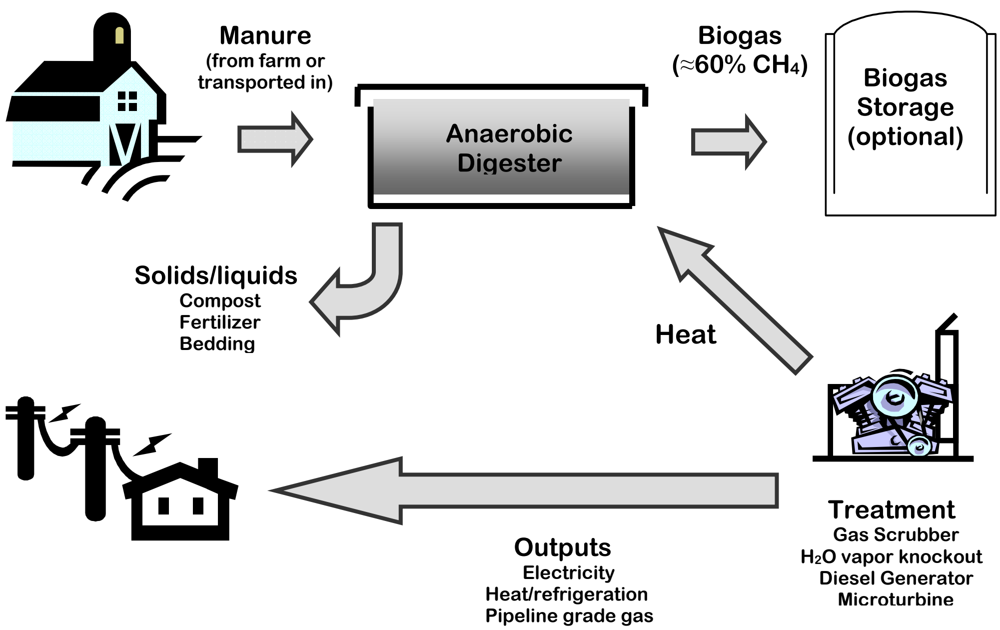

Figure 2.3 From waste to resource: Anaerobic digestion on the farm.

[7] Zicari (2003) provides a detailed analisis of the removal of H_2S from dairy manure-derived biogas.
[8] This includes operating digesters as well as those in the start-up and construction stages.

BIOGAS COMPOSITION

Although similar to natural gas, raw biogas has particular undesireable chemical and physical properties that can hinder processing and utilization as a renewable energy source. Below is a breakdown of the characterisctics of biogas produced from anaerobically digested dairy manure waste compared to natural gas.

Table 2.2 Comparison of constituents in natural gas and biogas.

Constituents	*Units*	*Natural Gas*	*Biogas*
Methane (CH_4)	Vol%	91	55-70
Ethane (C_2H_6)	Vol%	5.1	0
Propane (C_3H_8)	Vol%	1.8	0
Butane (C_4H_{10})	Vol%	0.9	0
Pentane (C_5H_{12})	Vol%	0.3	0
Carbon Dioxide (CO_2)	Vol%	0.61	30-45
Nitrogen (N_2)	Vol%	0.32	0-2
Volatile Organic Compunds (VOC)	Vol%	0	0
Hydrogen (H_2)	Vol%	0	0
Hydrogen Sulfide (H_2S)	ppm	~1	>500
Ammonia (NH_3)	ppm	0	~100
Carbon Monoxide (CO)	ppm	0	0
Water Dew Point	ºC	<-5	Saturated
Heating Value	BTU/SCF	1031	~600

Source: Jensen and Jensen (2000) referenced in Monnet (2003).

Chemical Characteristics

Methane

Methane (CH_4) gas consists of one carbon and four hydrogen atoms and is the main component of natural gas. Both odorless and colorless, CH_4 provides approximately 1000 BTUs of heat energy per cubic foot when burned. One BTU is the energy required to raise the temperature of one pound of water one degree Fahrenheit. Methane is produced as a non-renewable fossil fuel that is generated over a period of thousands or millions of years. Decayed plant and animal matter trapped deep beneath bedrock is changed into petroleum products (coal, oil and natural gas) by extreme pressure and heat. In the absence of oxygen, methanogenic bacteria are responsible for converting organic matter into CH_4 (the same process that occurs in anaerobic digestion discussed earlier). Once this resource is extracted from natural storage reservoirs in the subsurface, it is no longer available, at least not until the process repeats itself over another thousand years or more. The explosive limits of methane are 5-15% when mixed with air.[9] The process of anaerobic digestion yields between 50-60% CH_4 for dairy manure wastes (Pellerin et al., 1987). The higher the content of CH_4 in biogas, the higher the heat content and the greater BTU's available.

Carbon Dioxide

Carbon dioxide is an atmospheric gas consisting of one carbon and two oxygen atoms. Like methane, it is both odorless and colorless. CO_2 is produced either by the combustion of organic matter in the presence of oxygen or by microbial fermentation and plant respiration. In biogas, CO_2 is produced when methanogenic bacteria break down simple organic compounds, through the process of fermentation. The two main

[9] Safety hazards of methane and hydrogen sulfide available at http://www.cdc.gov/niosh/90-103.html.

components of biogas are CH_4 and CO_2, products of the conversion of simple organic compounds by methanogenic bacteria. Since CO_2 can be readily measured in the field, the balance is usually considered to be CH_4. Thus high levels of CO_2 are indicative of poor methane content and therefore a lower energy value. Although high CO_2 concentrations in biogas may hinder some energy applications, Scott and Minott (2003) noted the relatively high CO_2 in biogas can actual aid in replenishing the essential carbonate electrolyte in molten carbonate fuel cells. On the other hand, high levels of CO_2 can add to the acidic environment in diesel generators and may require removal for more high-volume biogas utilization activities such as integrating biogas into commercial natural gas pipeline streams. Removing CO_2 and other contaminants from the biogas stream can be costly, especially for small agricultural operations.

Trace Components

The trace components make up less than 2% of dairy manure-digested biogas. The common trace components of anaerobically digested dairy manure include ammonia, hydrogen sulfide (H_2S), and water vapour. Depending on the use of the biogas, most trace components must be removed from the biogas. Water vapour can be particularly hazardous because it is highly corrossive when combined with acidic components such as hydrogen sulfide (H_2S) and to a lesser extent, carbon dioxide (CO_2). The major contaminant in biogas is H_2S. This component is both poisonous and corrosive, and causes significant damage to piping, equipment and instrumentation. In combustion, H_2S present in the gas is also released as sulfur dioxide, contributing to atmospheric pollution.

During anaerobic digestion, head gas containing greater than 6% H_2S can limit methanogenesis (Chynoweth and Isaacson, 1987). Measurements at AA Dairy in Candor, NY indicated concentrations of H_2S averaged 1500 ppm (0.15%), far from this limiting level (Zicari, 2003). After anaerobic digestion, there are numerous chemical, physical and biological methods used for the removal of H_2S from the biogas stream. Many of these methods are labor intensive and generate a waste stream that poses environmental disposal concerns and risks. One of the common methods of removing H_2S on rural AD systems is with a technology called "Iron Sponge", which uses hydrated iron impregnated wood chips to bind with the sulfur.

Safety Hazards

The main safety hazards with biogas include explosion, asphyxiation, or hydrogen sulfide poisoning. The explosive limits of hydrogen sulfide, or the volume of the component that must be present in the air for an ignition or explosion to occur, is between 4.3 and 46%.[10] As mentioned previously, the CH_4 content in biogas can create an explosive hazard if mixed in the air within this range. To ignite, there must be between 5 and 15% of methane by volume in the air. There have been few reported incidents of this occurring at anaerobic digesters worldwide. Both CO_2 and CH_4 can cause asphyxiation and in severe cases, unconsciousness, cardiac arrest or central nervous system damage.

Hydrogen sulfide poses probably the most significant safety concerns of anaerobic digesters. Exposure to H_2S can cause irreversible damage to human health depending on the concentration of H_2S and length of exposure.

[10] MSDS of Hydrogen sulfide available at http://www.cdc.gov/niosh/nmam/pdfs/6013.pdf.

Table 2.3 Effects of H_2S on People[11]

Parts per million (ppm)	Health Effects
0.01-0.3	• Odor is detectable
1-10	• Moderate to strong odor • People may experience nausea, tearing of the eyes, headaches and loss of sleep following prolonged exposure effects appear to be reversible and not serious for the general population, although more susceptible individuals may respond more severely
10-150	• increasing degree of irritation to eyes and lungs
150-750	• severe health effects, which may lead to death, become more likely as concentration and exposure time increase
>750	• death may occur in minutes or less

To mitigate asphyxiation, explosion and gas poisoning concerns, all equipment must be in well-ventilated areas and entering confined spaces should be avoided without first verifying the absence of these gases.

Biogas Utilization for Energy Generation

The concentrations of various components of biogas has an impact on its utlimate end use. While boilers can withstand concentrations of H_2S up to 1000 ppm, and relatively low pressures, internal combustion engines operate best when H_2S is maintained below 100 ppm (Wellinger and Linberg, 2000). In some cases, pretreatment for H_2S in IC engines is compensated by more frequent oil changes. This is the procedure at AA Dairy in Candor, NY where 70 quart oil changes are performed on a weekly basis (Zicari, 2003). Microturbines are more H_2S tolerant, withstanding concentrations up to 70,000 ppm when parts in the microturbine have been retrofitted to withstand the acid

[11] Sour Gas: Questions and Answers, Canadian Centre for Energy Information (2000), available at http://www.centreforenergy.com.

environment. The pressure of the biogas must also be increased to 520 kPa for these systems (Capstone Turbine Corporation, 2002). Dairy Development International in Homer, NY had installed retrofitted microturbines for use with biogas but the units were not yet operational at the time of this study. Fuel cells, an emerging technology in biogas utlization, generally require significant H_2S reduction to levels between 20 ppm and 1 ppm depending on the technology (XENERGY 2002). Microturbines, fuel cells, and IC engines may also require significant water vapor removal from the biogas stream prior to use. Stirling engines on the other hand, are capable of using biogas with low H_2S levels with a small amount of pressure upgrade (STM Power, 2005). Upgrading biogas to commercial pipeline quality, is arguably the most costly since it requires more stringent parameters than use in direct on-site electrical generation processes. Methane and CO_2 must be at greater than 95% and lower than 2% respectively. Hydrogen sulfide must be removed to less than 4 ppm and water vapor cannot exceed 2.2×10^{-4} lb/MMSCF (Wellinger and Linberg, 2000; Kohl and Neilsen, 1997). Pressure must also be brought up to that of the commercial pipeline stream, in the area of 3000 kPa.[12]

PURPOSE OF STUDY

The goal of this study was to evaluate the variability of the composition of dairy-derived biogas from anaerobic digestion systems through extensive monitoring of biogas composition. This report presents the results from the sampling of biogas from dairy AD systems for composition and variations in biogas composition over time. A limited analysis of feed, water, and manure digester inputs was also performed to observe their potential effects on biogas quality and production.

[12] This pressure may not be as high for local gas transportation systems.

FARM PARTICIPANT INFORMATION

New York dairy demographics for 1993 to 2005 show a very slight shift in dairy population from mostly small farms (<100 cows) to more medium (100-500 cows) and large (> 500 cows) farms. This trend is demonstrated in Figure and Table 2.4, which show that in 2005, 22% of the cow population resided on medium to large farms as opposed to 17% in 1993. While larger dairy operations may see a greater economic gain in implementing an anaerobic digester, dairy waste from small farms need not and cannot be ignored because effluent from livestock agriculture accounts for a significant portion of the drinking water pollution in New York waters (Minott et al., 2000). However, small farms, which do not own their own digester, might explore the benefits by a shared "community" digester (Bothi and Aldrich, 2005).

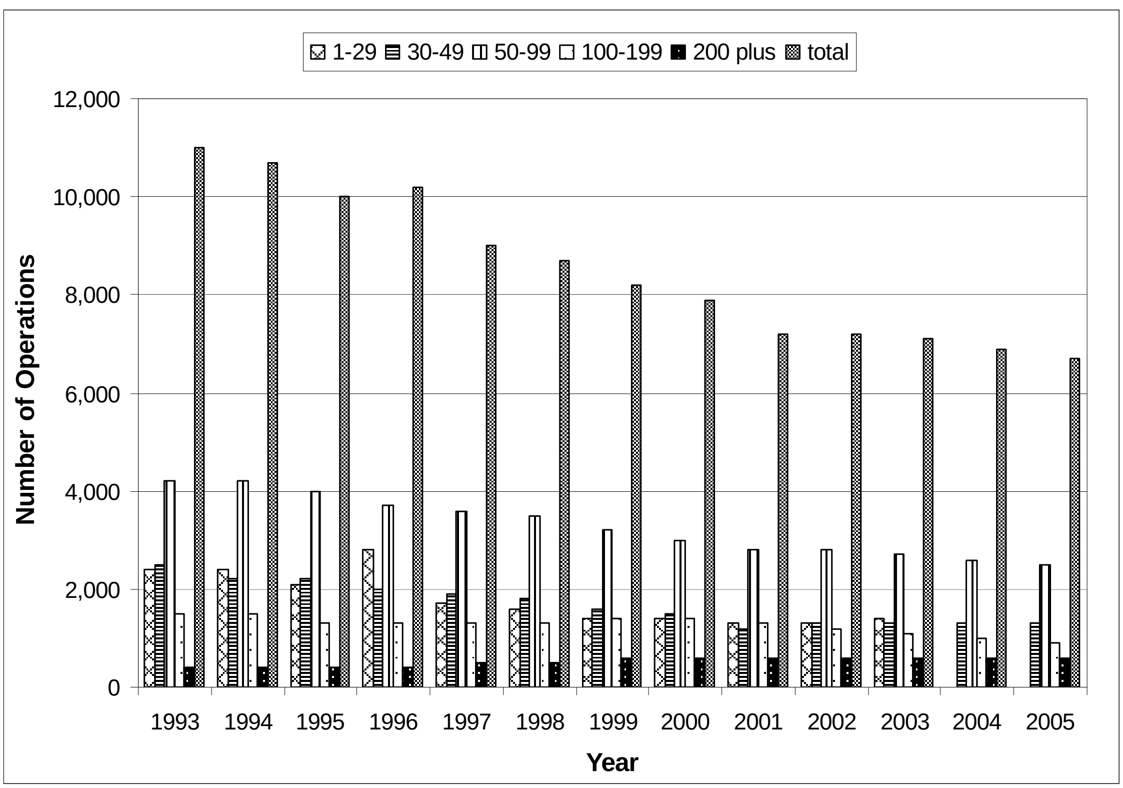

Figure 2.4 Number of dairy operations by herd size in NY between 1993 – 2005.

Table 2.4 NY milking operations by herd size and total (1993-2005).[13]

Year	*Number of Milk cows per herd*						**Small farms***
	1-29	**30-49**	**50-99**	**100-199**	**200 plus**	**Total**	
1993	2,400	2,500	4,200	1,500	400	11,000	83%
1994	2,400	2,200	4,200	1,500	400	10,700	82%
1995	2,100	2,200	4,000	1,300	400	10,000	83%
1996	2,800	2,000	3,700	1,300	400	10,200	83%
1997	1,700	1,900	3,600	1,300	500	9,000	80%
1998	1,600	1,800	3,500	1,300	500	8,700	79%
1999	1,400	1,600	3,200	1,400	600	8,200	76%
2000	1,400	1,500	3,000	1,400	600	7,900	75%
2001	1,300	1,200	2,800	1,300	600	7,200	74%
2002	1,300	1,300	2,800	1,200	600	7,200	75%
2003	1,400	1,300	2,700	1,100	600	7,100	76%
2004	1,400	1,300	2,600	1,000	600	6,900	77%
2005	1,400	1,300	2,500	890	600	6,700	78%

**small farm <100 milk cows*

[13] Data compiled from http://www.nass.usda.gov/Statistics_by_State/New_York/index.asp.

DDI

DDI is a 30-acre dairy complex and agri-research facility in Cortland County, approximately 26 miles north of Ithaca, NY. With the capacity to house and milk 850 cows, DDI's facilities include two free-stall barns, a special needs barn, a milking parlor, feed storage grain bins, and a plug-flow anaerobic digester. The soft-top horizontal plug-flow anaerobic digester at DDI has a retention time of 21 days. The gases are separated from solids for heat generation and then the slurry is separated and solids are collected for sale as fertilizer. Biogas production is estimated around 70,000 ft^3/day.[14] Although microturbines have been installed to generate electricity for the farms needs or for sale to the grid in the future, the majority of the biogas is being used to fuel a 1.5 billion BTU boiler for the heating needs of the farm. At the time of the study, the microturbines were not operational. Any excess biogas generated is flared. DDI is the primary location for the experiments described in this report.

AA Dairy

AA Dairy, a medium-sized farm in Tioga County outside of Candor, NY, has approximately 500 milking cows and an operating plug-flow digester with IC genset. Between 35,000-50,000 ft^3/day of biogas is produced from the digester. AA Dairy is located 20 miles from Ithaca. This combination of characteristics, along with the farmers' track record of maintaining data records make AA Dairy a desirable location to use as a sample collection site.

Ridgeline Dairy

Located in Chautauqua County near Clymer, NY, Ridgeline Dairy houses 750 cows in free stall barns. Approximately 76,440 ft^3/day of higher-methane, lower-H_2S biogas is

[14] Estimate based on biogas production of 90-100ft3/day per cow.

generated from the plug-flow digester making it an interesting sampling site. It has been suggested that the higher methane and reduced H_2S content is due to the addition of food wastes to the manure in the digester. The biogas is collected and used with an engine-generator to produce electricity for the farm. Ridgeline is located 220 miles from Ithaca. At the time of the study, Ridgeline was called Matlink Dairy. All data samples and descriptions in this report are noted as Ridgeline to reflect the name change.

Noblehurst

Noblehurst Farms, Inc., located close to the Town of York in Livingston County, is a 1,100 milking cow commercial dairy. Biogas production is estimated to be about 72,000 ft^3/day from the plug-flow digester. An IC engine-generator is also used to produce electricity on the farm.

Twin Birch

Twin Birch operates a 1,200 cow dairy near Owasco, NY in Cayuga County. Approximately 72,000 ft^3 of biogas is produced each day from a concrete covered complete-mix digester. Microturbines have been installed to generate electricity, however, the system continued to encounter obstacles during this study and was not operational. One important initial observation that led to further sampling at Twin Birch was the unusually high concentration of H_2S in the biogas.

Figure 2.5 identifies the geographical location of the dairies with respect to the Cornell University BEE laboratory.

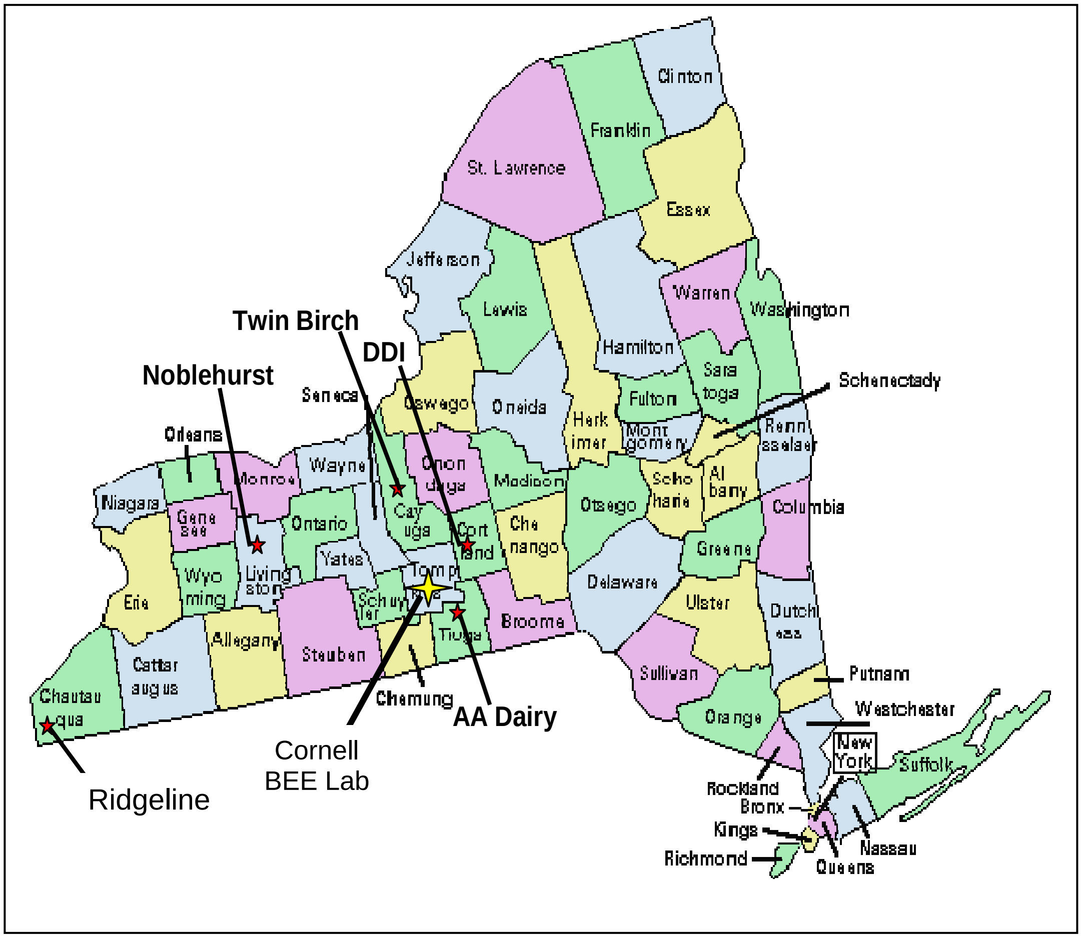

Figure 2.5 Map of NY State showing counties and locations of study participants.

Source: Base map of NY State Counties from http://www.rootsweb.com/~nygenweb/county.htm.

CHAPTER 3

MATERIALS AND METHODS

BIOGAS CHARACTERIZATION

In natural gas applications, a gas chromatograph provides an accurate and consistent method of monitoring the composition of the gas. Gas chromatography involves a sample being injected and vaporized onto the head of a chromatographic column to separate the components of a complex sample. When the sample enters through the injection port, it flows through the column with an inert, mobile gas called the carrier gas. Depending on the chemical and physical properties of the constituents of the sample and their interaction with the particular column filling, the constituents will pass in the carrier gas stream at different rates. The column contains a liquid stationary phase which is adsorbed onto the surface of an inert solid, causing the constituents to exit the column at different times (also know as retention times). A detector then identifies and measures each constituent as they exit the column. This is illustrated in Figure 3.1.

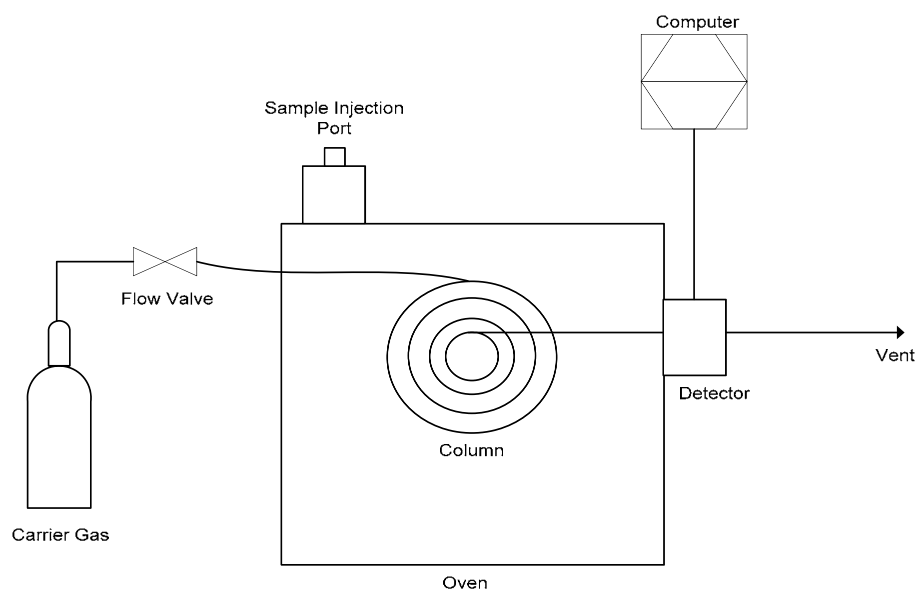

Figure 3.1 Basic gas chromatograph design.

Two gas chromatographs (GC's) were used to analyze biogas. One of the GC's, a Daniel Danalyzer 520 with micro-packed columns, was stationed at DDI for the duration of the project to monitor a steady raw biogas stream. The GC was inside an enclosed building without temperature control. At initial experimental set-up, a Daniel technician was present to perform the necessary maintenance and calibration to prepare the instrument for use with biogas. The technician also provided an orientation to the operation of this particular GC. The GC was calibrated at the start of the study and once every 1-2 weeks as specified by the Daniel technician using a Daniel specified 11-part calibration biogas mixture ordered and certified through Airgas East (Elmira, NY). The components of the calibration gas are shown below.

Table 3.1 Calibration mixture of biogas analysis with Daniel Danalyzer 520.

Component	*Vol%*
N-Hexane	0.05
Isopentane	0.1
Neopentane	0.1
N-Pentane	0.1
Isobutane	0.3
N-Butane	0.3
Carbon dioxide	1
Propane	1
Nitrogen	2.5
Ethane	5
Methane	Balance

The system was programmed to take measurements of the raw biogas stream approximately every 2 hours 45 minutes with a 235 second analysis time. The Danalyzer measured BTU, C_1-C_6^+, N_2, CO_2, and the balance, being CH_4. The Danalyzer was specifically designed to measure BTU with an accuracy of ±2.0% BTU/1000 (BTU/SCF) over a temperature range of 0-130ºF. The dry gross BTU (upper heating value) was measured in this study and data was corrected for 60ºF and 14.73 psia. At the point of exit from a digester the biogas is saturated with water vapor, but travels through a pipeline with temperature drops reduces this value. Based on data provided by Ludington (Draft 2006), the water vapor in saturated biogas at DDI would be 6.46% immediately exiting the digester at 100ºF, then would range from 4.75% to 1.21% when the ambient temperature of the biogas fell between 90ºF-50ºF during travel to the GC (see Table 3.2) At times ambient temperatures reach 30ºF – 40ºF, and the percent water vapor in the biogas would have been closer to 0.5%. To extend the life of the column, Daniel recommends reducing the water content to 0.5% in the biogas stream. Moisutre traps were installed in the input biogas line to knock out some of the water vapor in the biogas stream before passing through the GC. This dropped the water content closer to the maximum water content suggested to pass through the GC, but at times may not have been precisely ≤ 0.5%. This may reduce the lifespan of the GC column, however, it did not appear to affect the quality of data collected during the period of operation from July to November 2003. Throughout the analysis, the total constituent data came to 99.997%, suggesting the biogas stream contained a negligible amount of moisture (summary of DDI data is shown in the Appendix). The Daniel GC was equipped with a thermal conductivity detector (TCD), which measured the difference in thermal conductivity of each compound in the carrier gas. The carrier gas used in this application was certified helium from Airgas East (Elmira, NY). The input stream of carrier gas was regulated at 90 psig pressure into the GC. The biogas stream for GC analysis was tapped into the main biogas line from the anaerobic digester using stainless steel and laboratory-grade chemical resistant, higly durable Tygon® PVC tubing. A parastaltic pump was used to draw the biogas from the main line to the Daniel GC to maintain the input biogas pressure at a minimum of 5 psig. Although not the only components analyzed, there were four readings of significance gathered from each data set: % CH_4, % CO_2, % N_2, and BTU. The results were printed directly to a dot matrix printer attached to the Daniel GC and results were manually recorded and analyzed.

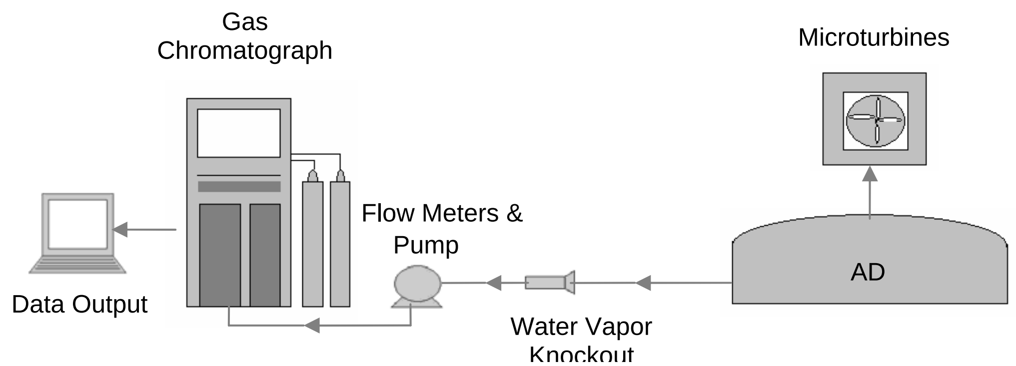

Figure 3.2 Experimental set-up for continuous biogas analysis at DDI.

Table 3.2 Properties of water vapor in biogas

Gas Temp (ºF)	*Partial Pressure* (mm Hg)*	*Volume Occupied***	
		Dry Gases (%)	*Water Vapor (%)*
50	9.21	98.8	1.21
60	14.67	98.1	1.93
70	18.78	97.5	2.47
80	26.23	96.5	3.45
90	36.12	95.2	4.75
100	49.11	93.5	6.46

Source: Ludington (Draft, 2006)
*International Critical Tables; **Assumes constant pressure

The second GC, a SRI 8610C, was set up at Cornell University. Equipped with multiple detectors, a TCD and PID/FPD, this GC has the capability of analyzing a greater number of compounds than the stationary Daniel GC. A flame ionization detector (FID) can be used to detect hydrocarbon peaks in a gas sample whereas a flame photometric detector (FPD) detects sulfur and phosphorus compounds. For the purposes of this study, however, the concentration of sulfur compounds present in the biogas was of greatest interest therefore the FPD was the key detector. The biogas sample was passed through a 0.3 m Haysep-D packed Teflon® column and was flashed through a hydrogen-air mixture flame. The spectrums of light emitted from the combustion of the sample in the hydrogen-rich flame were analyzed to determine the concentration of sulfur compounds in the biogas. Data was stored elctronically by SRI *PeakSimple* software (provided with the SRI 8610C). Further information about the SRI GC and detector operation can be found at http://www.srigc.com.

SAMPLING TECHNIQUES

Biogas Bag Samples

The first step in preparation of sample analysis at the lab was to calibrate the GC. The GC was calibrated by analyzing samples of premixed H_2S standards at 1000 ppm, 2000 ppm, 3000 ppm, and 5000 ppm three times each. The results were then entered into the program *PeakSimple* that sets the calibrations parameters according to the results of the standards analysis. This step must be performed prior to collecting samples to avoid delay in the actual sample analysis, if the same person collecting the samples performs calibration. Collecting the biogas samples should be the last task completed at the farm to ensure minimal sample holding time. Note: A small study was conducted in the lab to determine the integrity of the type of Tedlar® bags used to collect all biogas samples in this report. The results indicated that the samples should be analyzed within 8 hours of collection for greatest sample accuracy. The results from the Tedlar® study are provided in the Appendix.

Biogas samples were collected as follows:

1. Connect a short piece of clean PVC tubing to the barbed screw-lock valve of a 6” x 6” (0.5 L) Tedlar® sample bag.
2. Turn on gas line then unscrew valve to fill bag with biogas. Tighten valve before bag becomes over-pressurized and turn off the gas line.
3. Empty bag completely and repeat 2 additional times.
4. After bag has been purged with biogas to be sampled 3 times, reconnect bag/PVC extension line and turn on gas line. Fill sample bag and close valve. Turn off gas line and disconnect bag from line.
5. Transport to Cornell BEE lab for analysis.

On-site Monitoring

No special sampling requirements were necessary for the continuous DDI biogas analysis because the stream was directly routed to the GC from the main biogas line. The main biogas line ran underground from the digester to an enclosed work shop where the GC and other experimental equipment were set up. Smaller diameter stainless steel and Tygon® tubing diverted streams of biogas above ground from the main line to the GC. Since the equipment was continuously exposed to varying ambient temperatures and corrisive gas, a few important maintenance procedures were followed to ensure quality control of the analyses. These include:

1. Ensure proper seals between valves and line connectors.
2. Calibrate the GC regularly using a certified Daniel calibration gas.
3. Maintain continuous supply of carrier gas (helium) and ensure pressure maintained at 90 psig.
4. Replace Tygon® tubing if signs of wear appear.

Manure

Two different manure samples were required for each sampling event: the raw manure entering the digester from the mixing tank and the effluent exiting the digester. The same technique was used for both samples. The object is to obtain a representative (composite) sample of the material.

Raw Manure

1. Agitate (power on automated mixer) the manure within the storage pit until completely mixed.
2. Using sampling tool with extendable reach, fill one cup with manure and deposit in a clean plastic bucket. Repeat 10 times, trying to grab samples from various locations/depths in the pit.
3. Immediately mix the manure in the bucket.
4. Fill one 500 mL plastic or glass-sampling jar with manure from the bucket. This will be a representative composite sample of the raw manure.
5. Label jar with sample ID, description, date, and name of sampler.
6. Place jar in a cooler containing ice packs (maintain temperature around 39ºF or 4ºC).
7. Deliver to the third-party laboratory (Dairy One in Ithaca, NY).

Digested Effluent

1. Using sampling tool with extendable reach, fill one cup with manure and deposit in a clean plastic bucket. Repeat 10 times, trying to grab samples from various locations/depths in the effluent discharge pit.
2. Immediately mix the manure in the bucket.

3. Fill one sterile 500 mL plastic or glass-sampling jar with manure from the bucket. Secure lid firmly. This will be a representative composite sample of the digested manure.
4. Label jar with sample ID, description, date, and name of sampler.
5. Place jar in a cooler containing ice packs (maintain temperature around 39ºF or 4ºC).
6. Deliver to the third-party laboratory (Dairy One in Ithaca, NY).

Water

Faucet Sample

1. Remove any aerators or nozzles from the cold-water faucet.
2. Turn on tap and let run for 3-5 minutes.
3. Rinse a sterile 250 – 500 mL bottle once with water to be sampled.
4. Fill bottle completely, trying not to leave any headspace.
5. Tighten cap securely and label jar with sample ID, description, date, and name of sampler.
6. Place jar in a cooler containing ice packs (maintain temperature around 39ºF or 4ºC, but do not freeze).
7. Deliver sample to third-party laboratory (Dairy One in Ithaca, NY). **Note: water samples must be submitted to the lab within 24 hours to maintain sample integrity.**

Forage

Total Mixed Rations Sample

1. Collect only freshly blended rations.

2. Grab 10 handfuls of the mix at evenly spaced locations along the feed row. Samples should be collected at different depths (trying to avoid samples of forage exposed to the surface).
3. Repeat for each row of feed if required.
4. All sub samples should be mixed in a clean plastic bucket to form a composite and placed in a large plastic forage sampling bag.
5. Label sample bag with sample ID, description, date, and name of sampler.
6. Place bag in a cooler containing ice packs (maintain temperature around 39ºF or 4ºC).
7. Deliver to the third-party laboratory (Dairy One in Ithaca, NY).

ANALYTICAL TECHNIQUES

Determination of H_2S in biogas

Raw biogas samples collected in Tedlar® bags were transported to the Cornell Biological and Environmental Engineering (BEE) laboratory for immediate analysis using the SRI Model 8610C gas chromatograph. All samples were analyzed within 6 hours of sampling. Samples collected from DDI were analayzed within 3 hours of sample collection. Each bag was analyzed three times and the average taken as the recorded measurement. In cases where two duplicate bags were collected, the average of all GC analysis (i.e. 3 runs from each bag for a total of 6) was the recorded value. Table 3.3 shows the variation in sampling analysis from each analysis from DDI.

Table 3.3 Average and standard deviation of H_2S analysis from DDI samples.

Date of Anlysis	*Average H_2S (ppm)*	*Standard Deviation (+/- ppm H_2S)*
7/8/2003	2663	66
7/25/2003	2158	78
7/29/2003	2555	64
7/31/2003	2353	156
8/15/2003	1737	176
8/19/2003	2232	94
9/1/2003	2277	277
9/10/2003	1279	53
9/18/2003	991	145
9/25/2003	2195	141
11/5/2003	2923	34

The procedures for equipment calibration and analysis are as follows.

Calibration

1. As mentioned previously, GC calibration should be completed prior to sample analysis. It takes approximately 1.5 hours to calibrate the SRI for H_2S analysis. The time required to collect the sample and return to the laboratory should be taken into consideration. In most cases, it is best to calibrate the GC prior to actually collecting the sample (or have someone else perform the calibration while the sample is collected) to save time.
2. Open valve on hydrogen cylinder prior to starting GC. Turn on GC and press ignition switch until flame ignited. Allow the GC to warm for a minimum of 20 minutes or until proper temperatures are reached. Check manufacturer's guidelines to ensure settings are correct for type of analysis to be performed (column temperature, oven temperature, voltage, etc.).
3. While the GC is warming, prepare the calibration sample. Using 1000 ppm (99.99%+ purity) standardized H_2S, purge the sample bag three times, completely

evacuating all gas from the bag each time. Fill bag and close valve immediately to avoid gas loss or the entry of air. The H_2S calibration gas was supplied and certified by Airgas East (Elmira, NY).

4. Using a gastight glass syringe, withdraw a 0.1 mL sample from the bag and inject it in the external sample port. As soon as the entire sample has been injected, manually initiate the PeakSimple run by pressing either the “enter” button on the computer keyboard or the run button on the GC. Repeat 3 times. Record the value measured under “Area” in the results table in PeakSimple. This will provide the results for the 1000 ppm H_2S calibration. The GC must be calibrated within a suitable range relative to the expected concentration of H_2S in the biogas; therefore a calibration range of 1000-5000 ppm is used for the majority of the analyses in this study.
5. Repeat the above procedure for 2000, 3000, and 5000 ppm using syringe volumes of 0.2, 0.3, and 0.5 mL respectively.
6. Record these results in a new calibration file in PeakSimple.

Sample Analysis

1. Using the same technique as in the calibration procedures, inject 0.1 mL of the biogas sample into the external sample port and repeat 3 times for each sample bag. The volume 0.1 mL is used for each analysis.
2. The actual concentration of the biogas sample will be listed under “external” in the PeakSimple results file. Record this value.

Manure Water Forage Samples

Manure, water, and forage samples were submitted to Dairy One located in Ithaca, NY for analysis. The analytical procedures used for each of these mediums can be found in the Appendix as well as at http://www.dairyone.com/.

CHAPTER 4

RESULTS AND DISCUSSION

BIOGAS COLLECTION AND ANALYSIS

Biogas samples were collected at five farms in the central New York region: DDI, AA Dairy, Ridgeline, Noblehurst, and Twin Birch. As mentioned above, biogas from DDI was analyzed for H_2S, CH_4, CO_2, N_2, and BTU. Throughout the analysis, the composition of CH_4, CO_2 and N_2 contributed to 99.997% of the total biogas composition indicating consistent measurements from the Daniel GC between July and November 2003 (see Table A-2 in Appendix). H_2S concentrations were determined by collecting a sample of biogas in a 0.5L Tedlar® bag and transporting the sample to the Cornell University BEE Laboratory. The sample was then analyzed using the pre-calibrated GC. Duplicate, and sometimes triplicate, samples were collected for analysis. All samples collected from the other four farms were analyzed solely for H_2S in the same manner since the GC was instrumented for this particular analysis during the study. As mentioned earlier, to verify the quality of samples collected in the field using Tedlar® bags, an experiment was conducted in the laboratory. Samples of varying concentrations were analyzed repeatedly over a 25 hour period. The results indicated that sample integrity began to significantly diminish 8 hours after collection (Appendix). This meant that the GC always had to be calibrated prior to sample collection and that samples had to be returned to the lab for analysis as soon as possible. This was especially important for the Ridgeline samples due to the distance between Ridgeline and the Cornell laboratory.

Pellerin et al. (1987) reported that water-saturated biogas from dairy manure digesters consists primarily of 50-60% methane, 40-50% carbon dioxide, and less than 1% sulfur impurities, of which the majority exists as hydrogen sulfide. The results from the biogas analysis in this project were consistent with these ranges.

The following figures summarize the results of all biogas characterizations from DDI and H_2S monitoring from all five farms. Figures 4.1 to 4.6 represent data collected at DDI. The average concentration of H_2S from samples gathered on 13 different occasions between July 2003 and May 2004 was 1984 ppm (less than 0.2%) with a deviation of ± 570 ppm. The error bars indicate standard deviation in the actual analytical results for each sample. Two duplicate bags were collected for each sampling event and each sample was analyzed three times. The average of these results provided each point on a given date as shown on Figure 4.1. The average CH_4 measured 60.3% (±1%) between July and November 2003 (Figure 4.2) and correspondingly, the BTU/SCF averaged 612 for the same period (Figure 4.5). Figures 4.3 and 4.4 show N_2 and CO_2 at 1.5% and 38.2% respectively. CH_4 is generally measured as the balance of the biogas when CO_2 is known, or vise-versa when CH_4 is known. To check for any variation of CH_4 content in daily, weekly, monthly and total anaylses, the average % CH_4 was evaluated for each of these time periods (see Figure 4.2 and Table 4.1). There was only slight variation noted in the analysis, with maximum and minimum standard deviations of ±2.0 and 0.7 respectively. Further analysis of the daily variation of CH_4 content in the biogas showed the CH_4 at a maximum shortly after noon each day (see Appendix Figures A-5 to A-8). Although this increase is slight (a range of approximately 3% in most cases), it does suggest that the digester is reaching peak methance production at this time. Overall, however, there was very little variation in the CH_4 content during these different time periods confirming that CH_4 remains relatively constant in a stable digestion process where the composition of the raw manure and digester temperatures remain relatively constant over the duration of analysis.

The presence of N_2 in the biogas is likely due to air entering the biogas line before passing through the GC for analysis. In pure biogas, N_2 content should be negligible. Figures 4.6 and 4.7 show the daily properties of the biogas (CH_4, CO_2, N_2, BTU) from July to November 2003 at DDI. The percentages of these components tended to remain relatively constant over a four month period.

The error bars in these graphs generally became much shorter with time. It is possible that the range of results found over the entire sampling program may have been a result of improved sampling and analysis techniques as practice and experience was gained throughout the project. In addition, the operation of the digester and the characteristics of the inputs will influence the microbial performance, which ultimately affects biogas production. Further analysis of the digester inputs may explain some of the minor fluctuations in H_2S and CH_4 content in the biogas.

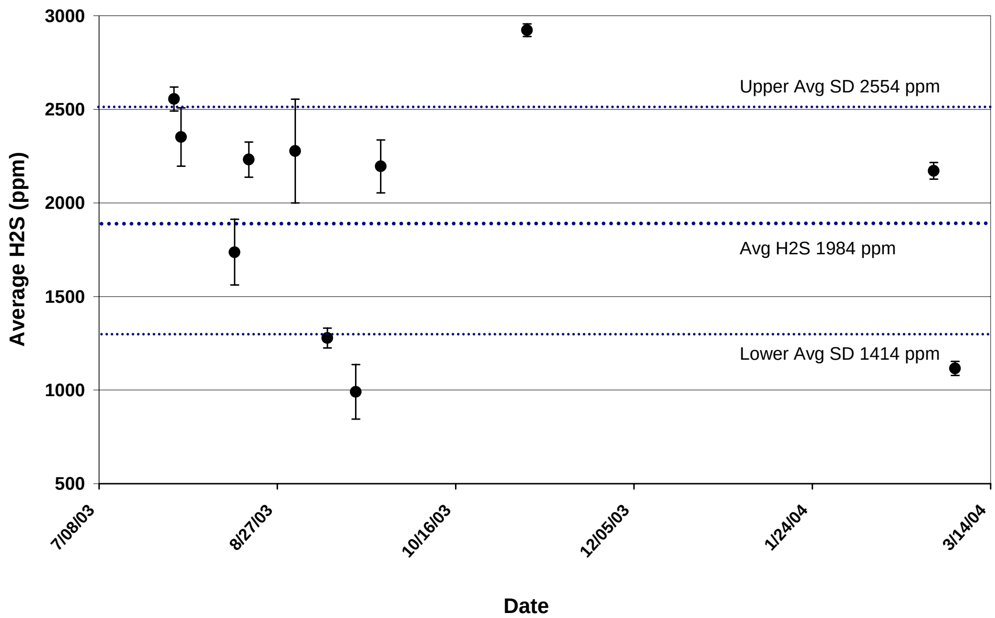

Figure 4.1 Average H_2S measured in biogas at DDI.
(July 2003 – March 2004)
Error bars showing standard deviation from the mean in daily sample analysis.

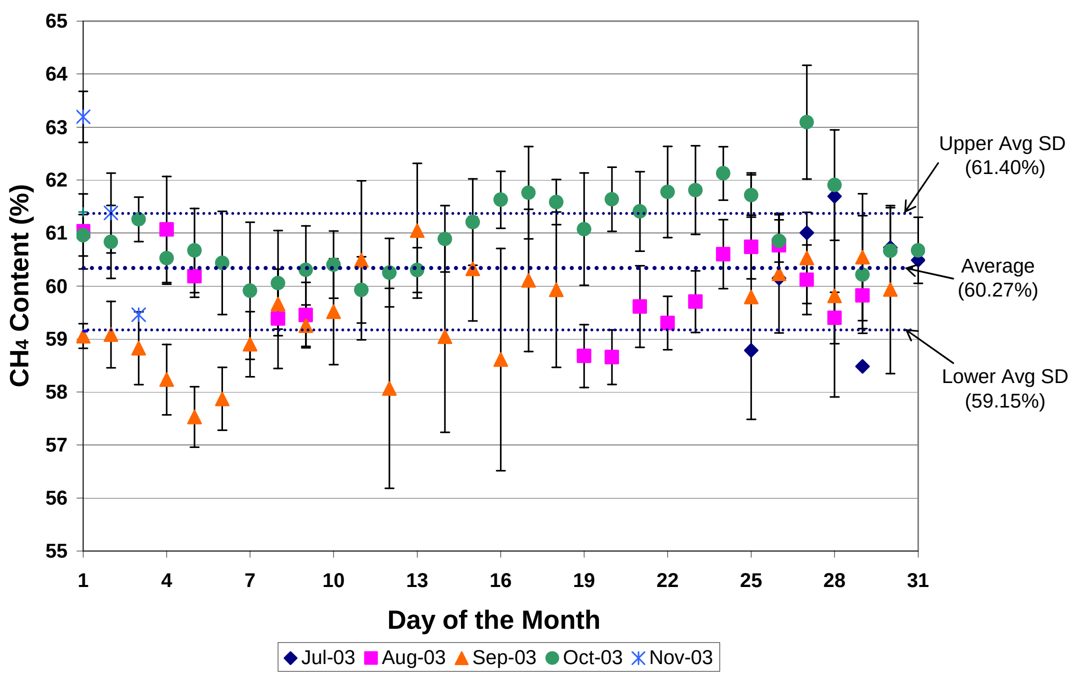

Figure 4.2 Average daily CH_4 measured in biogas at DDI.
(July – November 2003)
Error bars showing standard deviation from the mean in daily sample analysis.

Table 4.1 Average CH_4 over weekly, monthly and total periods.

Time Period	Date (2003)	Average % CH4	Upper Avg SD	Lower Avg SD
Weekly	July 25-31	60.31	61.56	59.06
	August 1-7	60.85	61.64	60.05
	August 8-14	59.42	60.14	58.70
	August 15-21	59.01	59.77	58.25
	August 22-28	59.02	59.75	58.29
	August 29-September 4	58.90	59.68	58.11
	September 5-11	59.04	60.28	57.80
	September 12-18	59.54	61.36	57.73
	September 19-25	60.00	62.06	57.95
	September 26-October 2	60.40	61.62	59.19
	October 3-9	60.46	61.38	59.53
	October 10-16	60.66	61.48	59.85
	October 17-23	61.58	62.37	60.80
	October 24-30	61.50	62.70	60.29
	October 30-November 3	61.72	62.94	60.49
Monthly	July	60.31	61.56	59.06
	August	59.89	60.83	58.94
	September	59.42	60.92	57.93
	October	61.03	62.05	60.00
	November	62.46	63.41	61.51
Total	July - November	60.27	61.40	59.15

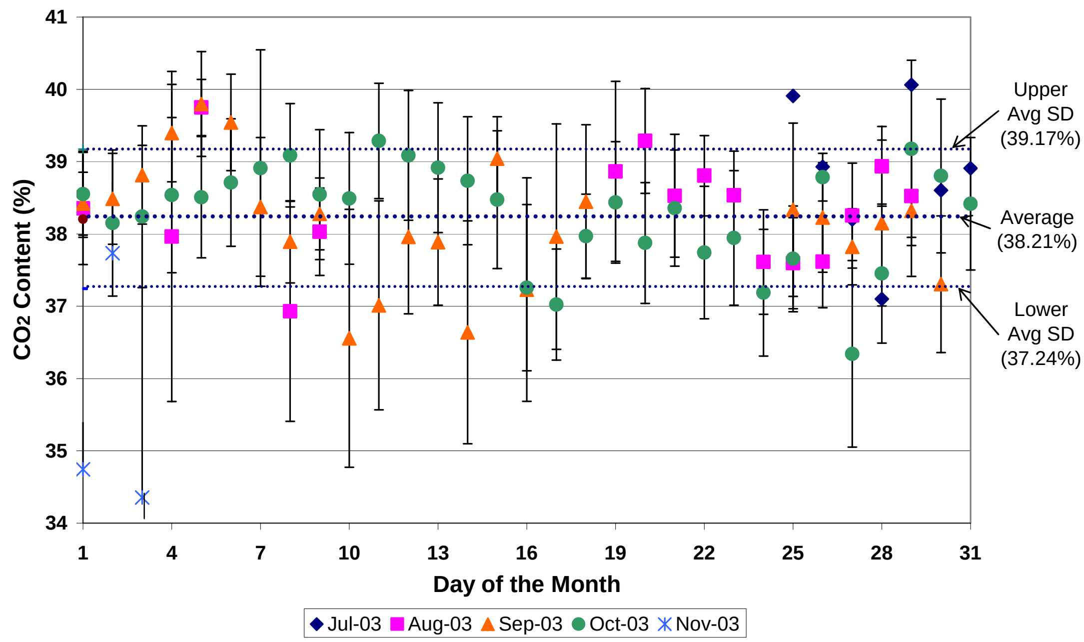

Figure 4.3 Average daily CO_2 measured in biogas at DDI.
(July – November 2003)
Error bars showing standard deviation from the mean in daily sample analysis.

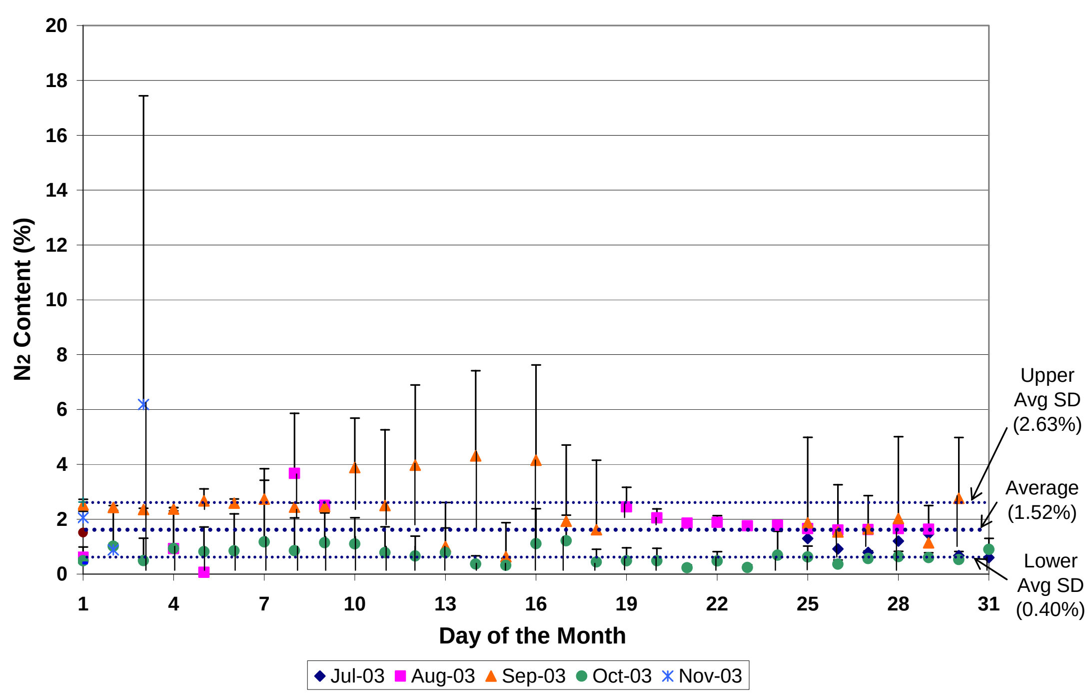

Figure 4.4 Average daily N_2 measured in biogas at DDI.
(July – November 2003)
Error bars showing standard deviation from the mean in daily sample analysis.

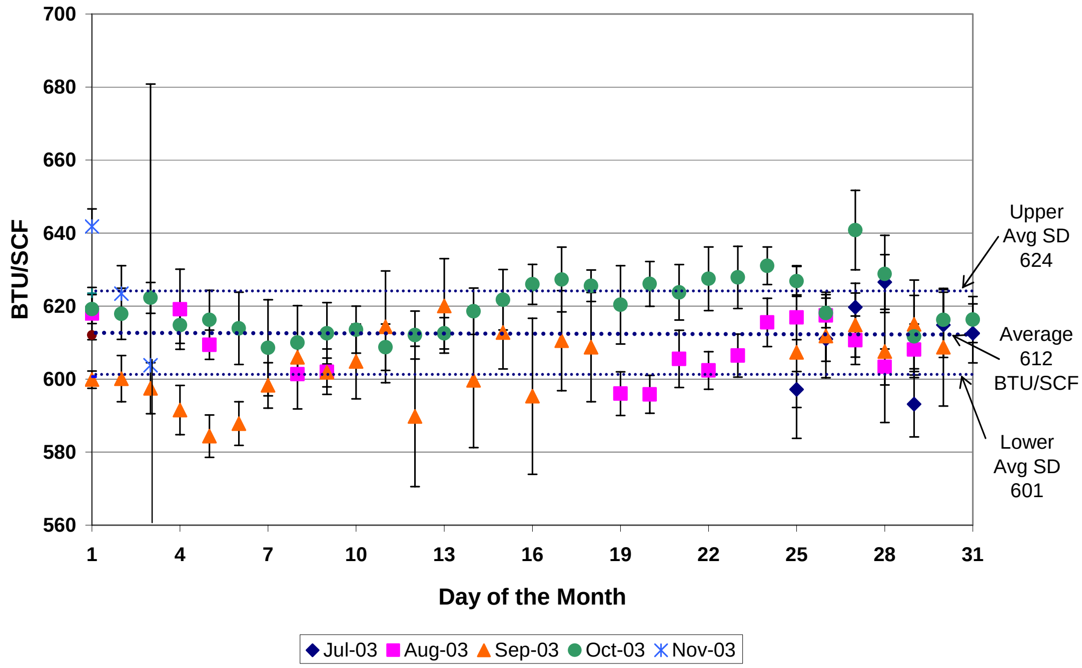

Figure 4.5 Average daily BTU/SCF measured in biogas at DDI.
(July – November 2003)
Error bars showing standard deviation from the mean in daily sample analysis.

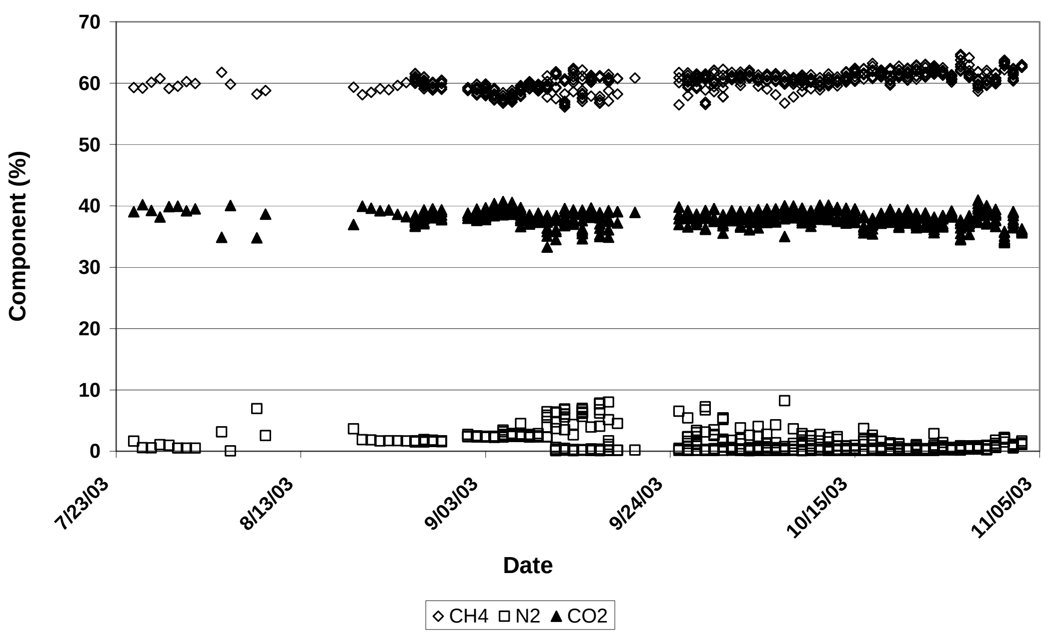

Figure 4.6 Raw biogas analysis at DDI.
(Total continuous analyses from July– November 2003)

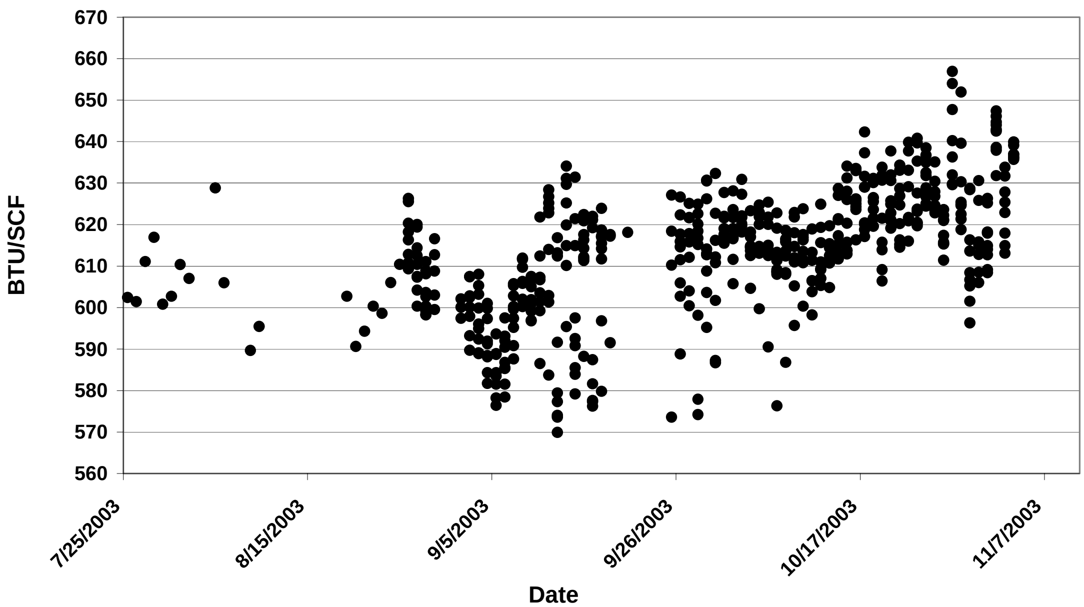

Figure 4.7 Raw biogas BTU at DDI.
(Total continuous analyses from July– November 2003)

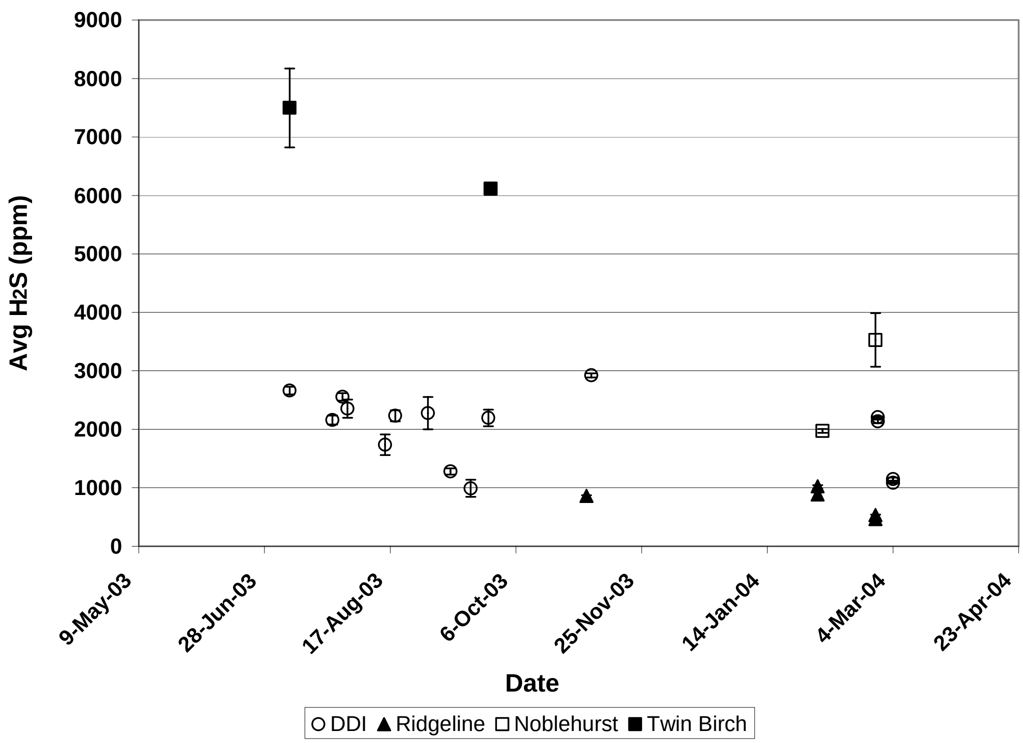

Figure 4.8 Average H_2S concentrations at 5 dairy farms in upstate New York.
(Total analyses from July– November 2003)
Error bars showing standard deviation from the mean in each sample analysis.

Figure 4.8 illustrates the variation over time of H_2S concentration in the biogas between the five farms. This suggests that the specific characteristics of the digester inputs and the environmental conditions influence the concentration of H_2S in the biogas generated. Of particular note is that the H_2S measurements at Ridgeline are substantially less than the other farms and this finding is potentially attributable to co-digestion with food wastes and manure. Little formal work in this area has been completed, however, "a few dairy farms with anaerobic digesters in the U.S. have tried mixing food wastes with dairy manure for biogas production. Successful results have been reported with increased biogas production and better gas quality" (Scott and Ma, 2004).

Temperature was also accounted for in the analysis of biogas at DDI. When the temperature of the digester fluctuates, a change in methane production is expected. The digester at DDI, however, stayed constant during the majority of the sampling period at 95ºF and as expected the methane content remained relatively consistent during this period, as shown in the analysis. In addition to the digester temperature, the ambient temperatures did not affect the analysis. Since the Daniel GC measures BTU ±2.0% BTU/1000 between abient temperatures ranging from 0 to 130ºF and corrects for temerpature and pressure to 60ºF and 14.73 psia, it is not surpising that the methane stayed around 60.3% with a standard deviation of ±1.2%.[15] We can therefore conclude that any minor variation in the analytical results at DDI are a result of chromatograph sensitivity.

[15] Daniel Instruments specifies ±2.0% BTU/1000 for landfill gas.

MANURE, WATER, AND FORAGE ANALYSES

Analyses of manure and water for four farms are given in Tables 4.2 and 4.3. Of special interest is the fact that Twin Birch has a much higher concentration of sulfur in the water compared to the other three farms. This may suggest that the significantly higher H_2S concentration (>6000 ppm) in the biogas at Twin Birch is at least partially attributed to the sulfur in the water. Further analysis should be conducted to confirm this relationship. In addition to elevated sulfates, the Twin Birch water had much higher elemental results, particularly with chlorides and total dissolved solids (not surprising with elevated chlorides and sulfates). The presense of elevated sulfur is believed to have the greatest influence on the biogas composition in this limited analysis. Although analysis of the digester inputs at Ridgeline Dairy were unavaiable, it is suspected that the input of food wastes in the raw manure mixture may reduce the H_2S content of the biogas. This, however, can only be speculated and this type of finding would depend greatly on the composition of the food waste involved.

A significant quantity of foreign materials can enter the manure wastes prior to digestion. Included in this may be bedding (i.e. wood chips, straw, and sand), wash water, milk parlor wash water, rainfall, feed, and soil. Large volumes of these materials may affect the chemical and physical properties of the waste stream, however, most of these components can generally be digested along with the manure waste (with the exceptions of non-biodegradeables such as sand bedding, which should be separated prior to entry into the digester) in reasonable quantities. Smaller amounts of foreign debris such as plastic, metal, wood, and glass may also enter the waste stream possibly interfering with the operation of the digestion equipment. An increase in the quantity of inorganic material entering the digester may have an impact on the quality and quantity of the biogas generated. Bedding materials easily enter the raw manure supply during scrapping and other manure collection techniques. Materials such as woodchips have high carbon content and can be digested by anaerobic processes but may require a longer retention time to break down the cellulose. The use of sand and other mineral components for bedding are not believed to have a direct influence on the raw inputs entering the digester; however, the inorganic nature of these materials can build up in the digester and prevent effective anaerobic digestion by reducing the effective volume of organic matter in the digester. This is believed to have a detrimental effect on the quality and quantity of biogas generated. Spilled feed wastes including grain products may have a greater impact on biogas properties based on the generally higher organic content of these materials.[16]

The raw manure and digester effluent samples showed similar sulfur contents in most of the samples (0.02-0.05% for AA and DDI), except Twin Birch showed a slightly higher sulfur content (0.08%) in the raw manure. This may have also correlated to the elevated H_2S measured at this location. There was a slight decrease in the sulfur content at DDI and Twin Birch from the raw manure to the effluent, suggesting that some of the sulfur was converted to H_2S during the anaerobic digestion process.

As shown in Table 4.4, the forage analyses did not suggest that the feed influenced the composition of the biogas. None of the samples had elevated concentrations of any particular component relative to one another. Given that the percent sulfur contents of each feed analysis were nearly identical for each dairy (0.17-0.25%), it is unlikely that it was high enough to influence the H_2S content in the biogas produced from the dairy manure.

[16] A discussion of this can be found in the document available at ftp://ftp.wcc.nrcs.usda.gov/downloads/wastemgmt/AWMFH/awmfh-chap4.pdf.

The feed and manure samples did not identify any particular component analyzed that may have an impact on the biogas composition. Relative to one another, each sample showed similar ranges of analytical parameters. In this study, the most likely identifiable component of the three mediums sampled to affect biogas quality was sulfur content, as found in the water sample at Twin Birch. At this location, the sulfur content in the water was 8.5 times greater than of the other farms sampled.

Table 4.2 Manure analysis at various NY State dairies.

Sample ID	6702500	6702510	6702520	6702530	6891820	6891830	6702540	6702550	***Expected****	
Date Sampled	09/26/03	09/26/03	09/19/03	09/19/03	11/24/03	11/24/03	09/18/03	09/18/03		
Location	TB E	TB R	AA E	AA R	AA E	AA R	DDI E	DDI R	Avg (%)*	+/- 1 sd*
Nitrogen (N)	0.46%	0.54%	0.48%	0.57%	0.46%	0.49%	0.38%	0.43%	0.39	0.18 - 0.61
Ammonia Nitrogen	0.25%	0.16%	0.23%	0.21%	0.26%	0.19%	0.21%	0.22%	0.15	0.06 - 0.24
Organic Nitrogen	0.22%	0.38%	0.25%	0.36%	0.20%	0.29%	0.17%	0.21%	0.24	0.08 - 0.41
Phosphorus (P)	0.08%	0.09%	0.14%	0.10%	0.06%	0.06%	0.06%	0.07%	0.08	0.01 - 16
Phosphate Equivalent (P205)	0.17%	0.20%	0.33%	0.23%	0.15%	0.14%	0.13%	0.17%	0.17	0.01 - 0.36
Potassium (K)	0.34%	0.31%	0.27%	0.29%	0.27%	0.29%	0.23%	0.29%	0.27	0.12 - 0.42
Potash Equivalent (K20)	0.42%	0.37%	0.32%	0.34%	0.32%	0.35%	0.28%	0.34%	0.33	0.15 - 0.51
Total Solids	8.16%	12.66%	11.92%	11.87%	8.31%	11.69%	6.28%	9.05%	12.2	3.9 - 20.5
Sulfur	0.04%	0.08%	0.05%	0.05%	0.02%	0.04%	0.02%	0.03%	n/a	n/a
Density	1.01 kg/l	0.95 kg/l	0.97 kg/l	0.88 kg/l	0.91 kg/l	0.94 kg/l	1.00 kg/l	0.98 kg/l	0.98	0.91 - 1.06

Notes: TB = Twin Birch, AA = AA Dairy, DDI = Dairy Development Int., E = Digester Effluent, R = Raw Manure
*Expected values are compiled by Dairy One using Manure Stats, Dairy One, Ithaca, NY (04/30/03).

Table 4.3 Water analysis at various NY State dairies.

Sample ID	6702440	6891810	6702450	6702460		
Date Sampled	09/19/03	11/24/03	09/26/03	09/18/03		
Location	AA	AA	TB	DDI	Possible problems for mature cattle	Expected*
Total Coliform/100 mL	-	< 1	-	-	15	< 1
e.Coli	-	-	-	-	-	-
Nitrates, ppm	-	42	-	-	100	0 - 44
Nitrates-Nitrogen, ppm	-	10	-	-	23	0 - 10
Sulfates, ppm	15	12	102	12	1000	0 - 250
Sulfates - Sulfur, ppm	5	4	34	4	333	0 - 83
Chlorides, ppm	26	18	59	33	300	0 - 250
Hardness, ppm CaCO3	385	349	579	247	-	0 - 370
Total Dissolved Solids (TDS), ppm	473	-	827	370	3000	0 - 500
Calcium (Ca), ppm	119.6	107.6	168	76.3	500	0 - 100
Magnesium (Mg), ppm	21	19.6	38.8	13.7	125	0 - 29
Potassium (K), ppm	-	< 0.1	-	-	20	0 - 20
Sodium (Na), ppm	16.9	13.5	26	23.5	300	0 - 100
Iron (Fe), ppm	<0.01	-	<0.01	<0.01	0.3 (taste)	0 - 0.3
pH	7.6	7.8	7.6	7.9	<5.5 or >8.5	6.8 - 7.5

Note: AA = AA Dairy, DDI = Dairy Development Int., TB = Twin Birch
*Expected values are compiled by Dairy One using laboratory Stats, Dairy One, Ithaca, NY (Source: Dairy Reference Manual, 3rd Edition, NRAES-63, June 1995).

Table 4.4 Feed analysis at various NY State dairies.

Sample ID		6702470	6702480	6891800	6702490			6702470	6702480	6891800	6702490
Date Sampled		9/26/03	9/19/03	11/24/03	9/18/03			9/26/03	9/19/03	11/24/03	9/18/03
Location		TB	AA	AA	DDI			TB	AA	AA	DDI
% Moisture	**As Fed**	54.4	56.6	61.8	56.4	**NEG, (Mcal/Lb)**	**As Fed**	0.21	0.2	0.17	0.19
	DM						**DM**	0.45	0.46	0.44	0.44
% Dry Matter	**As Fed**	45.6	43.4	38.2	43.6	**% Calcium**	**As Fed**	0.37	0.39	0.34	0.42
	DM						**DM**	0.81	0.9	0.9	0.96
% Crude Protein	**As Fed**	6.9	8.1	6.8	7.8	**% Phosphorus**	**As Fed**	0.16	0.2	0.16	0.17
	DM	15.2	18.7	17.7	18		**DM**	0.36	0.47	0.43	0.4
Soluble Protein % CP	**As Fed**					**% Magnesium**	**As Fed**	0.14	0.14	0.13	0.11
	DM	39	36	46	38		**DM**	0.32	0.32	0.33	0.25
% Acid Detergent Fiber	**As Fed**	10.9	9.5	9.6	10	**% Potassium**	**As Fed**	0.61	0.59	0.72	0.67
	DM	24	21.9	25.1	22.9		**DM**	1.35	1.36	1.89	1.53
% Neutral Detergent Fiber	**As Fed**	16.5	15.3	14.6	15.9	**% Sodium**	**As Fed**	0.194	0.154	0.105	0.152
	DM	36.1	35.4	38.2	36.5		**DM**	0.426	0.355	0.274	0.348
% NFC	**As Fed**	17	14.3	12.4	14.3	**PPM Iron**	**As Fed**	120	75	59	184
	DM	37.2	33	32.6	32.9		**DM**	264	172	155	422
% Crude Fat	**As Fed**	1.9	2.1	1.6	1.9	**PPM Zinc**	**As Fed**	26	34	15	31
	DM	4.2	4.7	4.1	4.4		**DM**	56	78	40	70
% Ash	**As Fed**	3.33	3.53	2.84	3.63	**PPM Copper**	**As Fed**	8	6	4	9
	DM	7.3	8.13	7.44	8.33		**DM**	17	15	10	22
% TDN	**As Fed**	31	30	26	30	**PPM Manganese**	**As Fed**	39	26	14	32
	DM	69	69	68	68		**DM**	86	60	37	73
NEL, (Mcal/Lb)	**As Fed**	0.33	0.32	0.28	0.31	**PPM Molybdenum**	**As Fed**	0.2	0.3	0.3	0.4
	DM	0.73	0.73	0.72	0.72		**DM**	0.4	0.7	0.9	1
NEM, (Mcal/Lb)	**As Fed**	0.33	0.32	0.27	0.31	**% Sulfur**	**As Fed**	0.11	0.11	0.09	0.08
	DM	0.73	0.73	0.71	0.71		**DM**	0.25	0.25	0.25	0.17

Results appear representative of soybean silage
Note: AA = AA Dairy, DDI = Dairy Development Int., TB = Twin Birch
As Fed = Sampling in natural state
DM = Dry matter (results of sample with water removed; shown since water can have diluting effect on reults)

CHAPTER 5

SUMMARY AND CONCLUSIONS

Biogas contains roughly 60% of the energy of natural gas and provides an important energy alternative for farms capable of implementing anaerobic digestion systems. Although the results from this study do not present significant new findings, a number of valuable insights were gained about the characteristics of biogas produced by anaerobically digested dairy manure.

Much of the published data available on biogas composition provides a snapshot of the constituents at a single given point in time. This study provided an evaluation of longer analysis periods to observe fluctuations of the main components over daily, weekly and monthly durations. With the use of continuous biogas stream analysis at one of the dairies, the composition of the biogas was found to be consistent within common ranges of CH_4, CO_2, N_2, and BTU provided in the literature. These components stayed quite consistent over time (day, week and month) with minimal fluctuation throughout the four month analayasis period and averages of 60%, 38%, 1.5% and 612 BTU/SCF respectively. As long as the composition of the diegster inputs and digester temperature remain consitent, the components of biogas appear to remain constant throughout the day and even months at a time.

Digester inputs may affect the presence of undesireable constituents in biogas. As discussed, hydrogen sulfide remains one of the greatest impedements to the quality of biogas. Since hydrogen sulfide can reduce the lifespan of treatment and energy generation equipment as a result of its corrosive properties, pre-treatment is an additional cost that farm operators must assess for on-site anaerobic digestion.

Although this study showed that most of the components of biogas (such as CH_4) appear to remain consistent, inputs including farm water mixed in raw manure appear to have a significant impact on the quality of the gas. This was found to be the case for H_2S in this study where the corrosive, toxic component was found to be especially variable in dairy biogas at the five test locations. This variability is believed to be attributable to to the nature of the digester input materials. High sulfate concentrations measured in the farm water at one dairy may be the cause of particularly high H_2S concentrations found in the biogas. The concentrations of H_2S were mesured around 6000 to 7500 ppm at the one location where the sulfates found in the farm water were 8.5 times that of the other farms. When food wastes were added to another dairy waste stream, the hydrogen sulfide concentrations were low in comparison to the other dairies with samples measuring around 500 and 1000 ppm. Where neither elevated sulfates or digester inputs appeared to have an effect on the biogas composition, the H_2S ranged between 1000 and 3600 ppm. The author suspects that further analysis of the digester inputs at these locations would verify both these findings. Any small variations in analysis are assumed to be attributed to instrumentation sensitivity.

The use of biogas as an energy source has significant potential in both urban and rural regions globally, particularly as an important energy product of agricultural wastes. Rudimentary biogas plants in developing nations such as China and India have been using such systems for cooking gas. In the developed world, the applications for biogas generation and use can been seen at notable scales. From biogas plants in the Netherlands to animal and food waste digesters in rural United States, corporations and farmers are finding value in reusing organic wastes to reduce energy costs and reduce the economic and environmental effects of waste disposal. As the components of biogas continue to be better understood, treatment options and energy use can be optimized to transform farm wastes to environmentally sustainable, valuable economic resources.

CHAPTER 6

FUTURE WORK AND RECOMMENDATIONS

Based on the research conducted in this study, it is suggested that further analysis be conducted to evaluate the effects of input materials on the characteristics of biogas. Further analysis of the input materials may uncover new trends related to biogas production efficiency and constituent quality.

As suspected with the biogas analysis from Ridgeline, food waste mixed with dairy manure may also affect the composition of biogas. Mixing waste streams may have an impact on the quality of the biogas such as reducing the hydrogen sulfide concentration. In addition to reducing the H_2S content in the biogas stream, there is some evidence in the literature that the addition of food wastes into the dairy manure stream may also have an effect on the CH_4 yield of the biogas (Scott and Ma, 2004). Methane has been observed to be as high as 70% when using food-manure mixtures as opposed to 50-60% when using manure alone in the anaerobic digester. Upon completion of lab-scale experiments, setting up the Daniel GC at Ridgeline Dairy (or another dairy utilizing food waste) for continuous stream analysis would provide a thorough evaluation of CH_4 content in this particular biogas stream. It would be valuable to collect consistent analysis of the digester inputs relative to the biogas stream monitoring for comparison. Understanding the digester inputs in relation to the relative biogas output may aid in the optimization of anaerobic digestion processes for financially beneficial energy generation applications.

APPENDIX

Summary of Tedlar® Bag Integrity Study

During the course of H_2S sampling and analysis, the author discovered that the analytical results varied with time despite utilizing the same samples and sampling equipment. H_2S and other sulfur compounds are highly reactive and analytical integrity can be compromised with improper sampling equipment and procedures. Unique properties of Tedlar® PVF film include excellent resistance to weathering, outstanding mechanical properties, and inertness towards a wide variety of chemicals, solvents, and staining agents. Although literature consistently indicates the use of Tedlar® bags for biogas sampling as common practice, no information was found verifying the H_2S absorption characteristics of Tedlar®.

The objective of this small study was to evaluate the effect of storage time on H_2S measurements using 0.5 L Tedlar® bags over a 24 hour period. Using a gas chromatograph, H_2S concentrations between 1000 and 5000 ppm were assessed to suitably cover the range of concentrations typically encountered in H_2S removal in biogas when using biofiltration techniques. Three bags of each concentration (1000, 2500, 5000 ppm H_2S) were analyzed consecutively to ensure that each analysis occurred at the specified time.

After approximately 8 hours, the samples consistently lost measurable concentrations of hydrogen sulfide. The findings are summarized in the figures below.

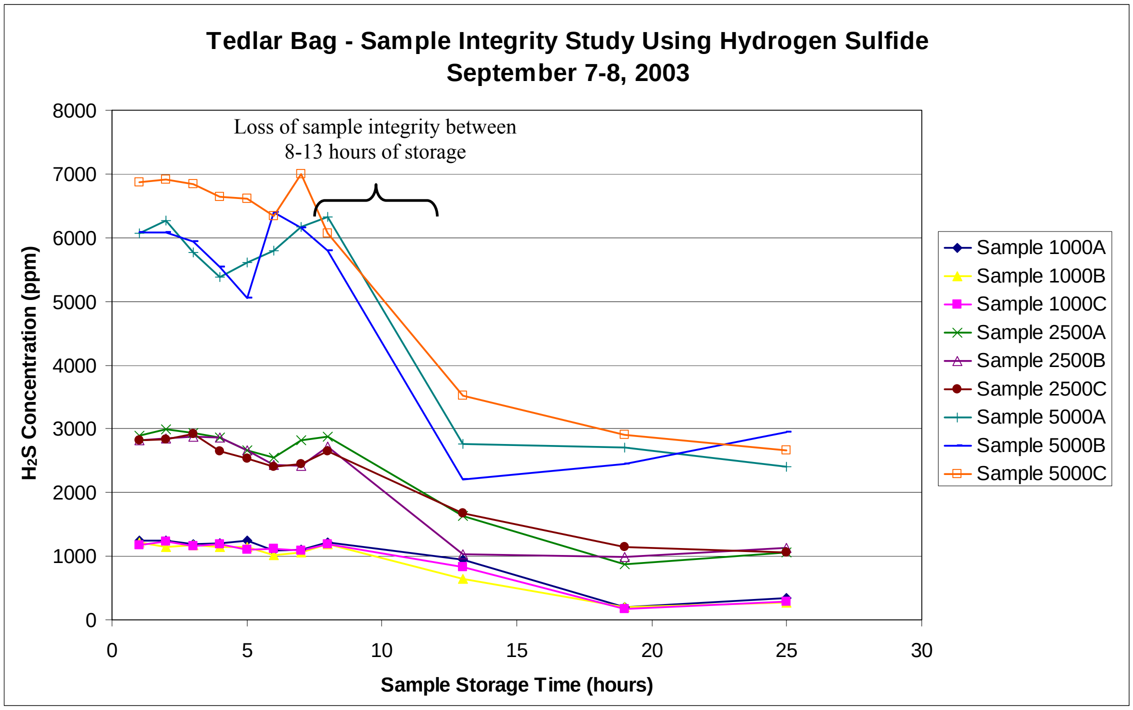

Figure A-1 Rate of decline in sample integrity using Tedlar® gas sampling bags.

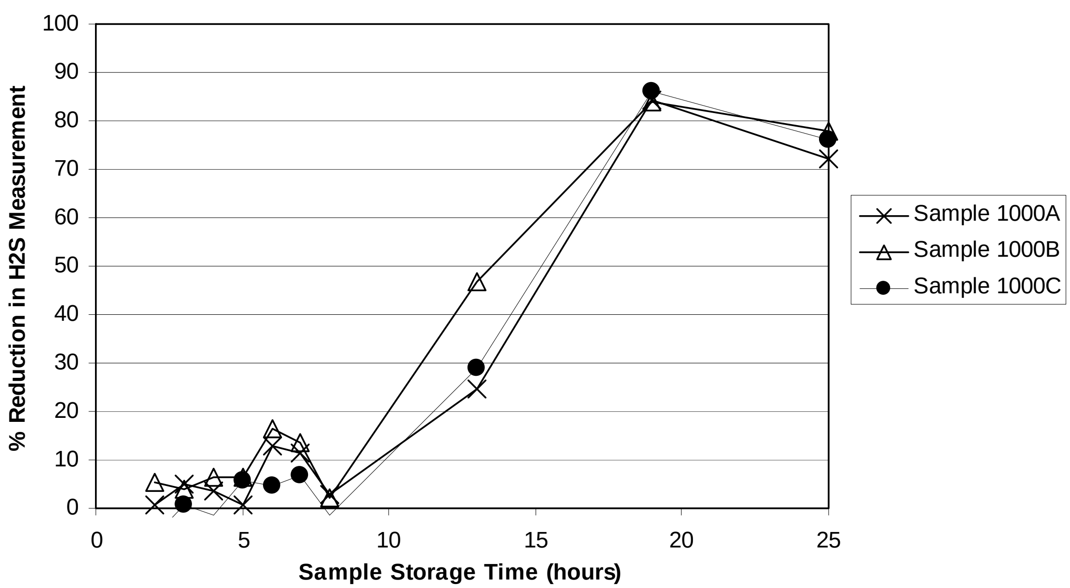

Figure A-2 Percent reduction in H_2S concentration over time at 1000 ppm.

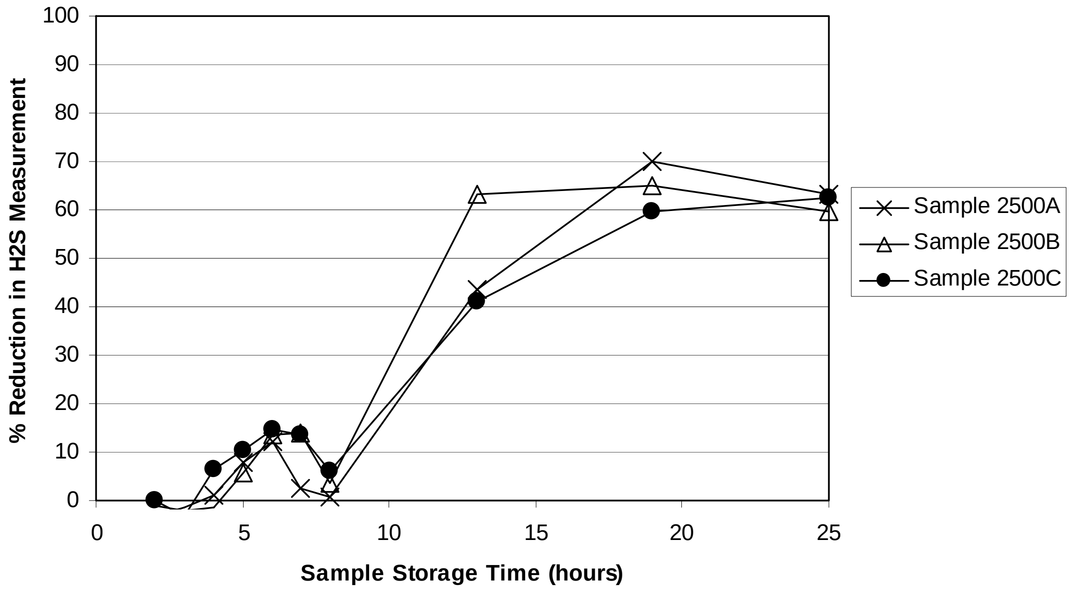

Figure A-3 Percent reduction in H_2S concentration over time at 2500 ppm.

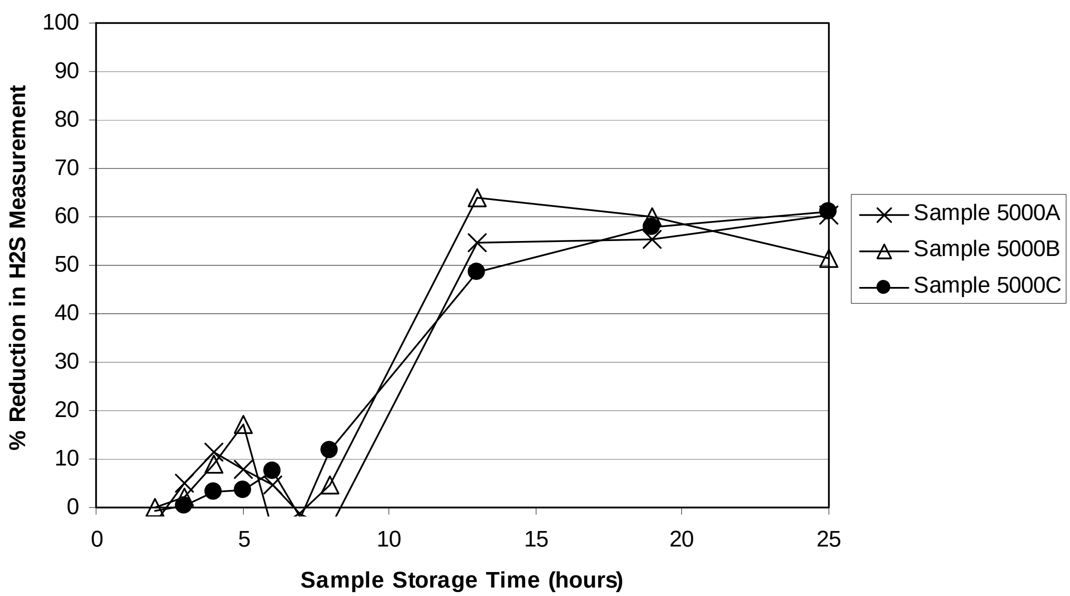

Figure A-4 Percent reduction in H_2S concentration over time at 5000 ppm.

Table A-1 Standard deviation of Tedlar® study samples.

	Standard Deviation (+/- ppm)		
Hour	*1000 ppm*	*2500 ppm*	*5000 ppm*
1	42	41	453
2	50	88	434
3	14	28	572
4	36	125	689
5	73	72	788
6	50	70	334
7	29	227	489
8	15	112	267
13	148	357	664
19	18	136	232
25	44	41	271

Additional Data

Methane Collection at DDI

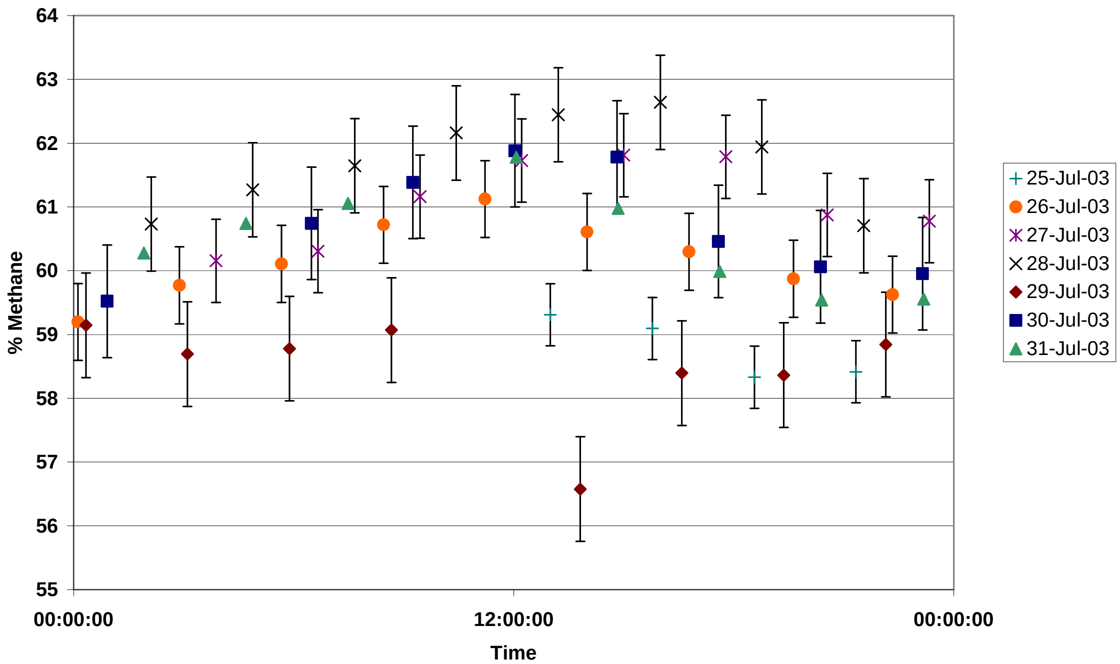

Figure A-5 Methane at DDI for 7 consecutive days (July 25-31, 2003).
Error bars showing standard deviation from the mean in each day of analysis.

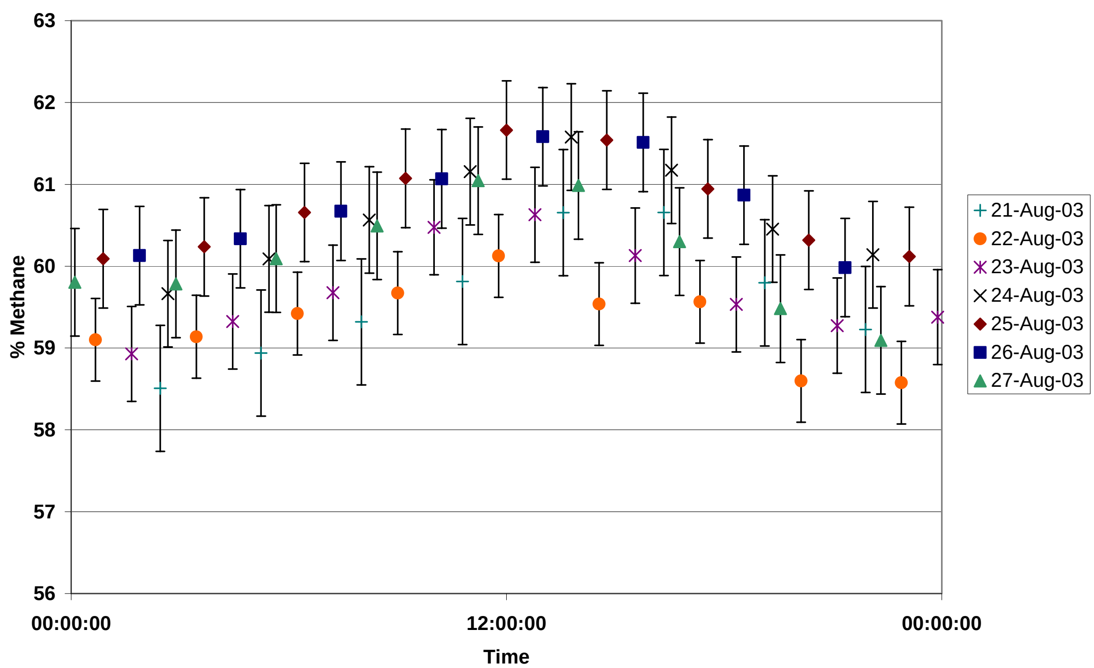

Figure A-6 Methane at DDI for 7 consecutive days (August 21-27, 2003).
Error bars showing standard deviation from the mean in each day of analysis.

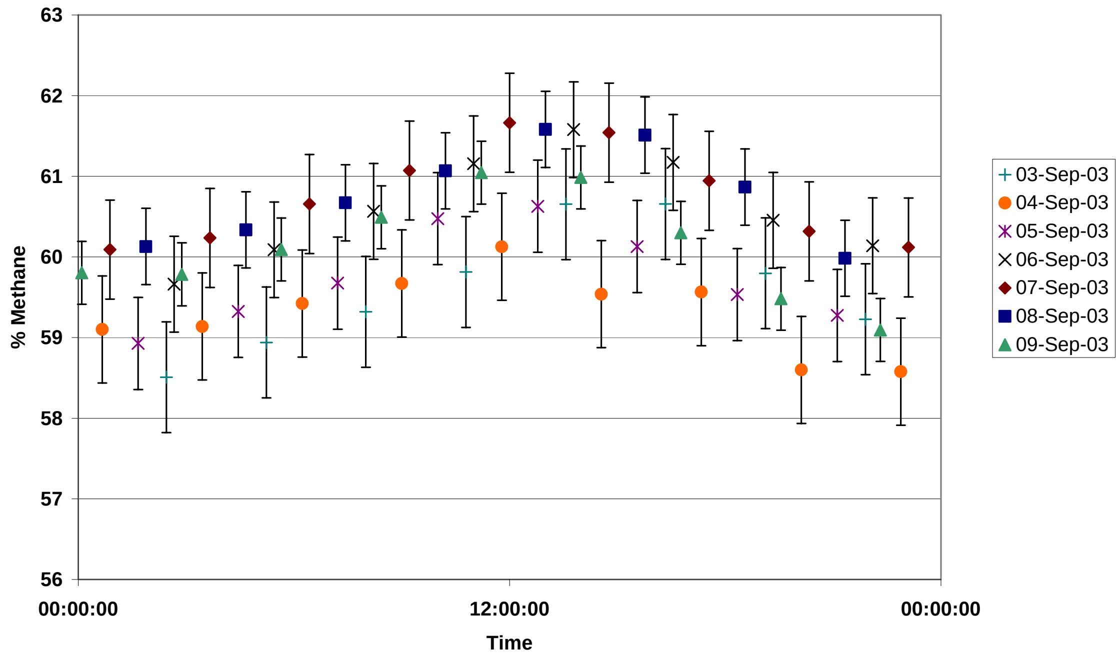

Figure A-7 Methane at DDI for 7 consecutive days (September 3-9, 2003).
Error bars showing standard deviation from the mean in each day of analysis.

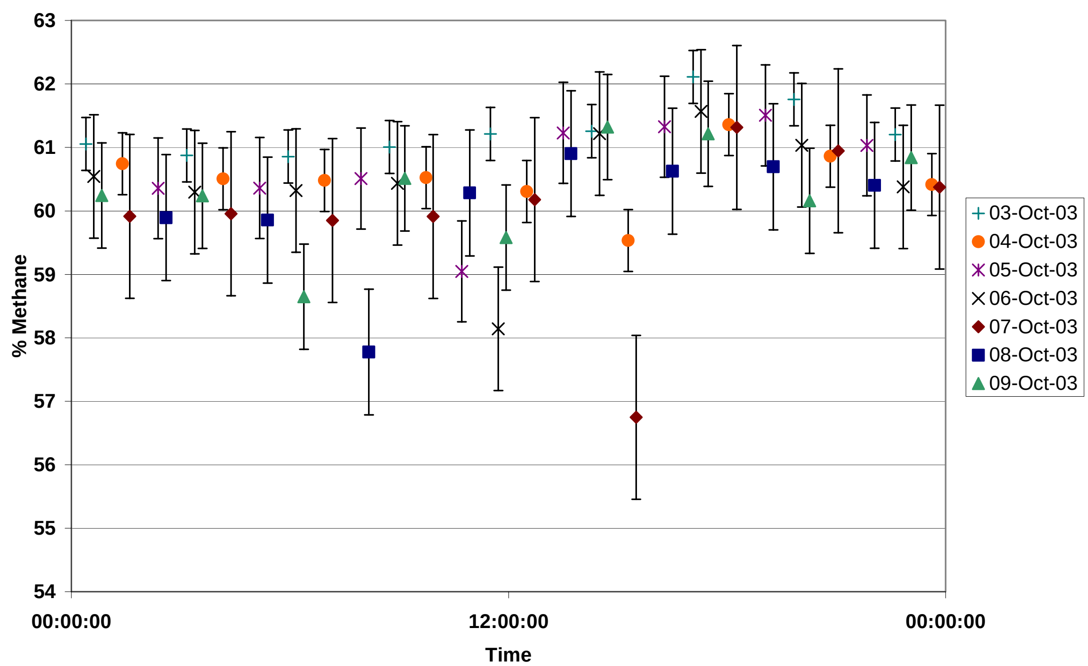

Figure A-8 Methane at DDI for 7 consecutive days (October 3-9, 2003).
Error bars showing standard deviation from the mean in each day of analysis.

Carbon Dioxide Collection at DDI

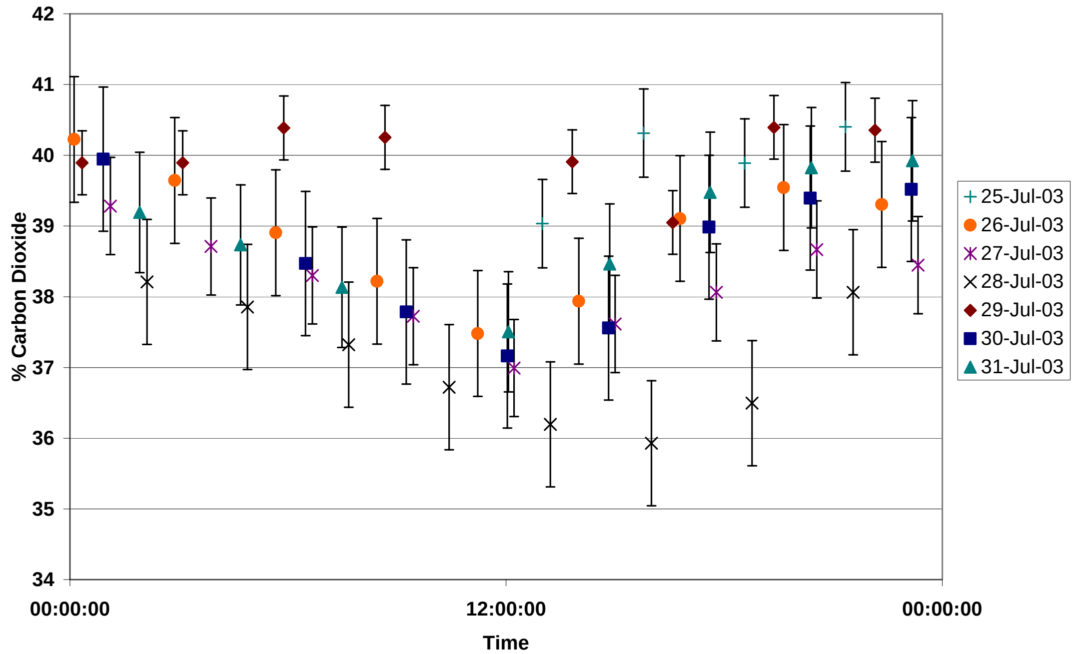

Figure A-9 Carbon dioxide at DDI for 7 consecutive days (July 25-31, 2003).

Error bars showing standard deviation from the mean in each day of analysis.

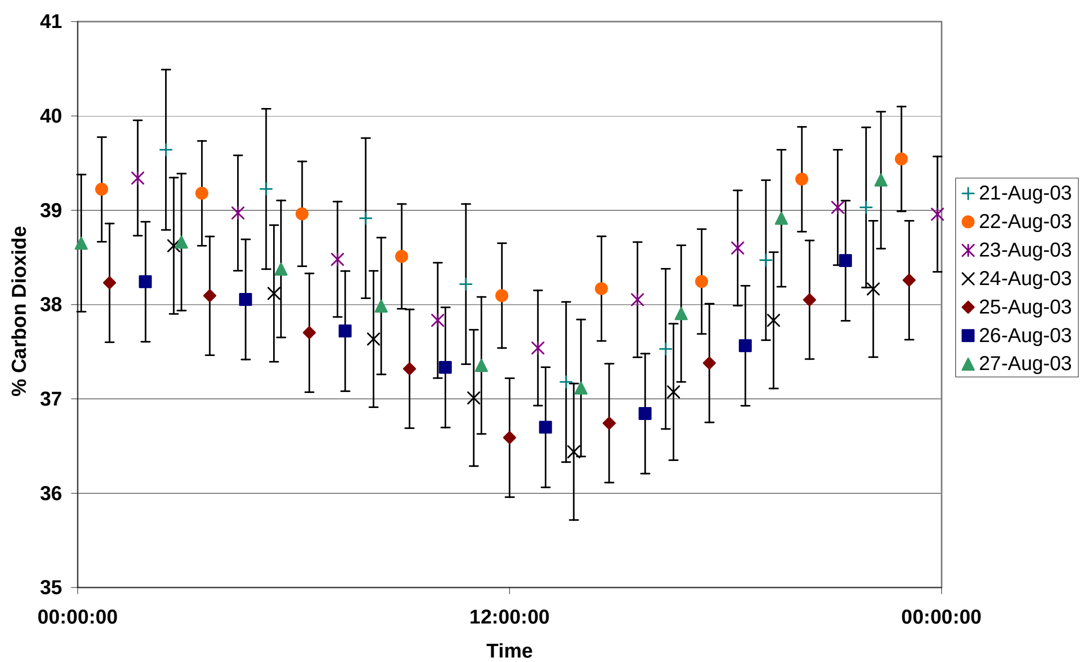

Figure A-10 Carbon dioxide at DDI for 7 consecutive days (August 21-27, 2003).

Error bars showing standard deviation from the mean in each day of analysis.

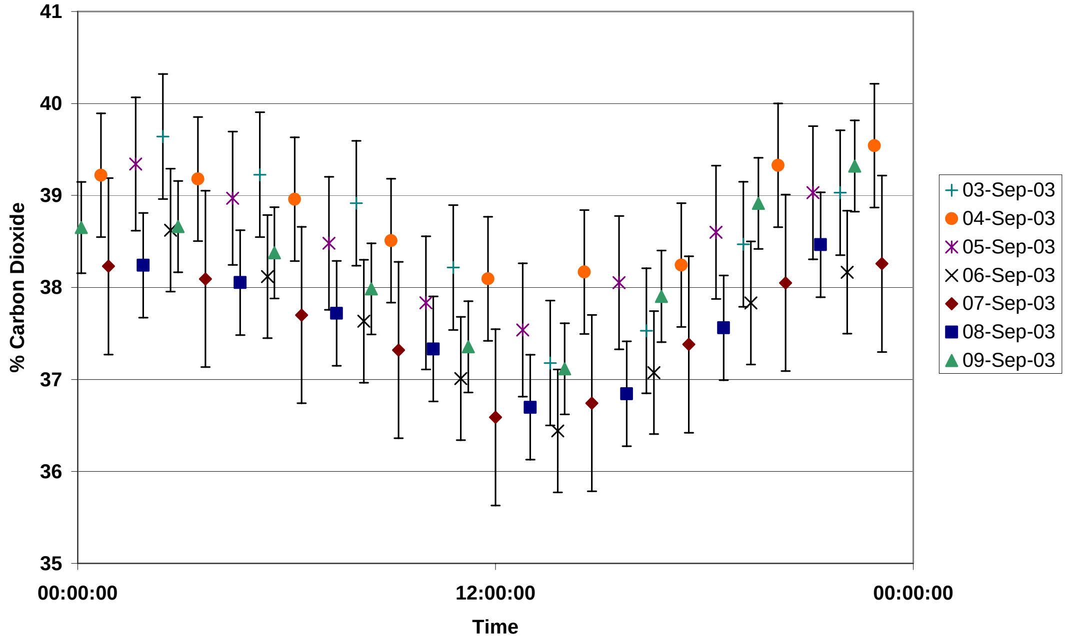

Figure A-11 Carbon dioxide at DDI for 7 consecutive days (September 3-9, 2003).
Error bars showing standard deviation from the mean in each day of analysis.

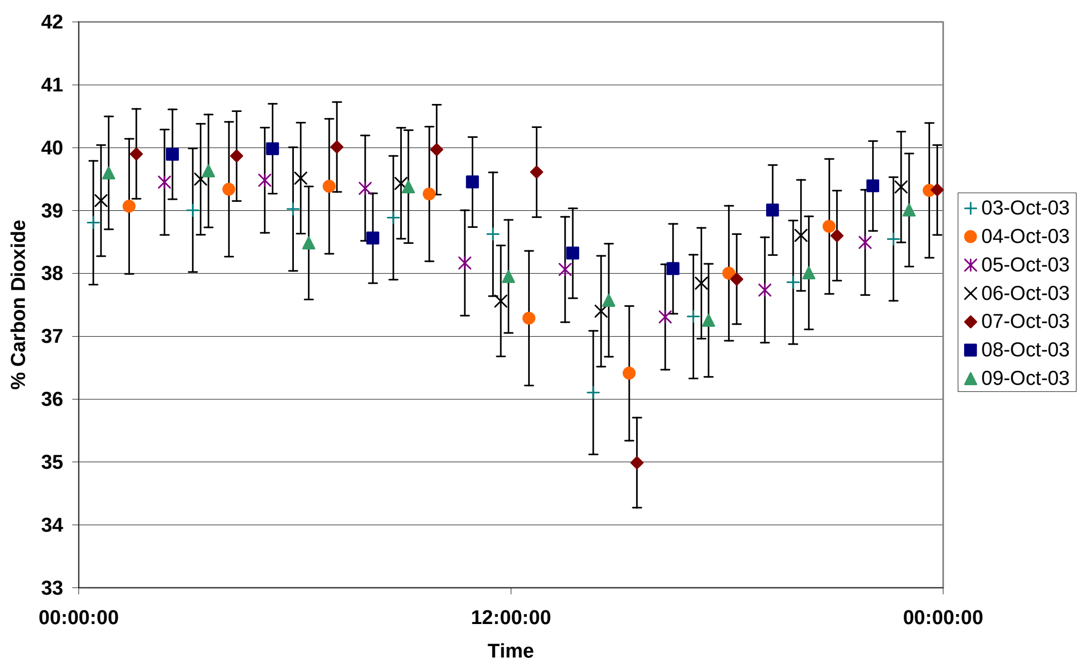

Figure A-12 Carbon dioxide at DDI for 7 consecutive days (October 3-9, 2003).
Error bars showing standard deviation from the mean in each day of analysis.

Nitrogen Variation at DDI

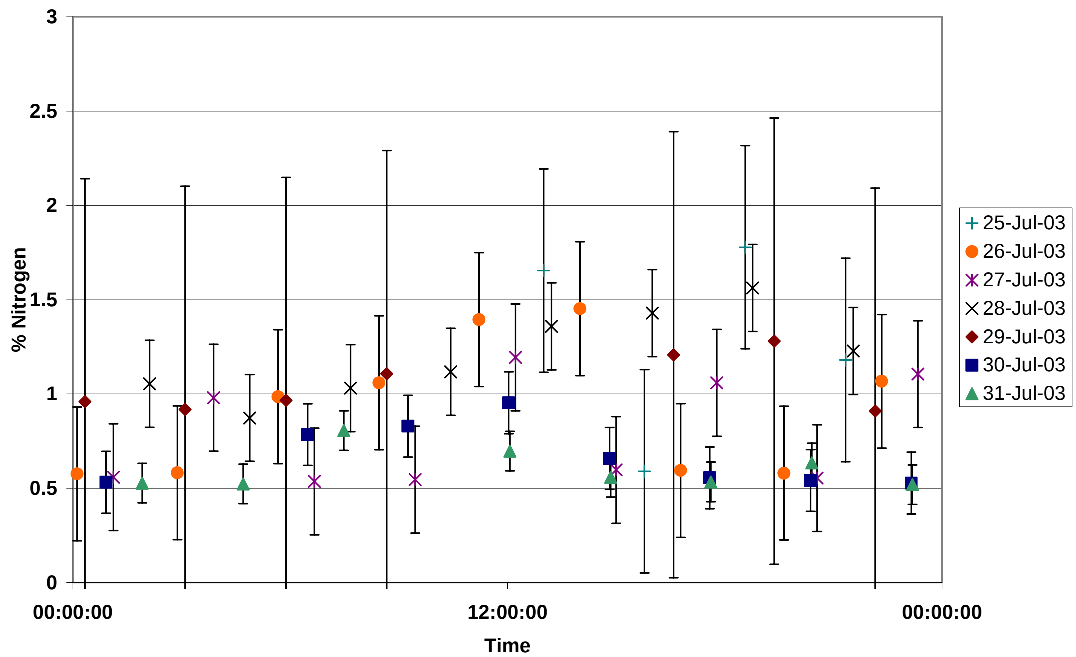

Figure A-13 Nitrogen at DDI for 7 consecutive days (July 25-31, 2003).

Error bars showing standard deviation from the mean in each day of analysis.

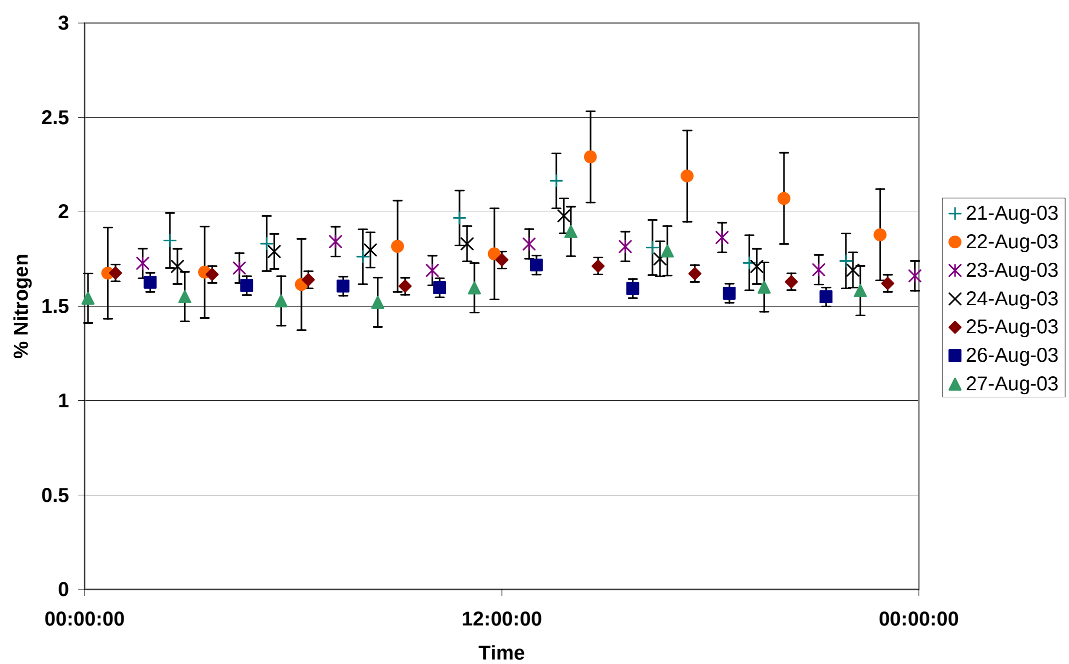

Figure A-14 Nitrogen at DDI for 7 consecutive days (August 21-27, 2003).

Error bars showing standard deviation from the mean in each day of analysis.

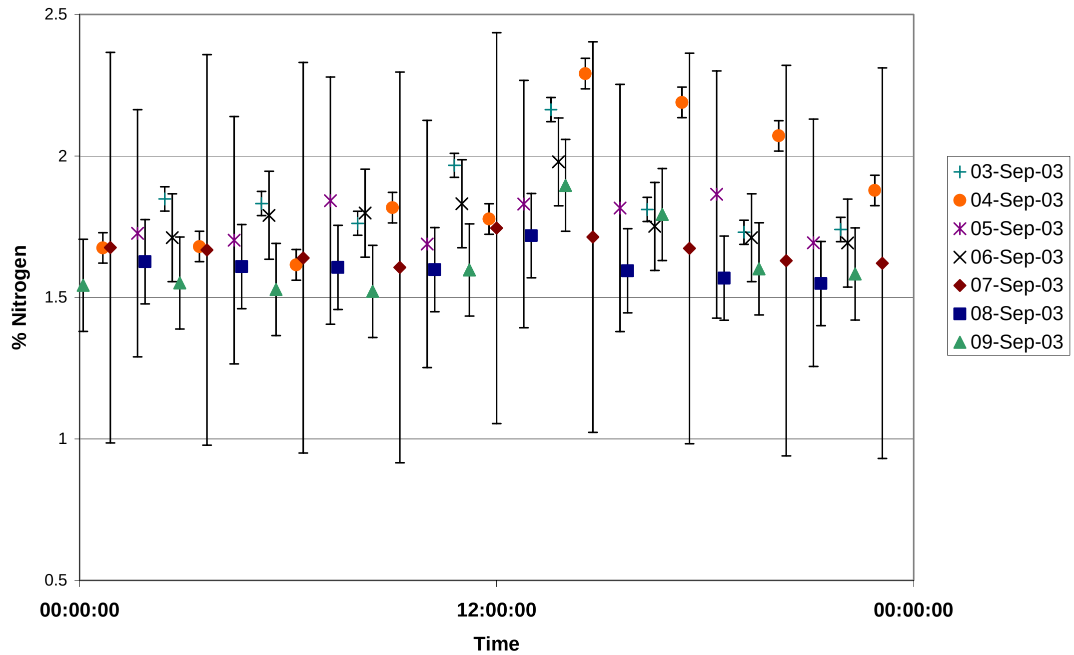

Figure A-15 Nitrogen at DDI for 7 consecutive days (September 3-9, 2003).

Error bars showing standard deviation from the mean in each day of analysis.

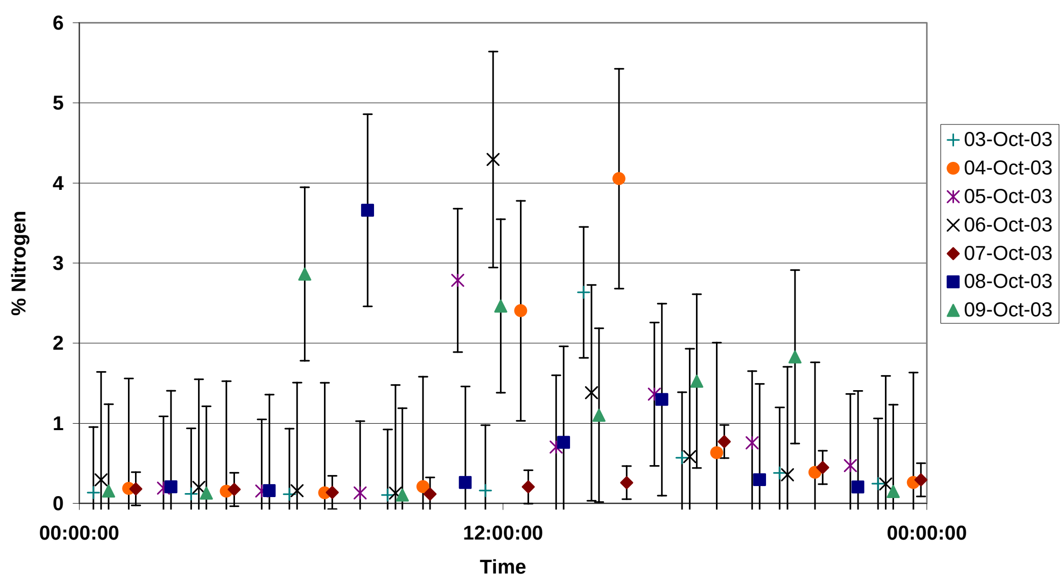

Figure A-16 Nitrogen at DDI for 7 consecutive days (October 3-9, 2003).

Error bars showing standard deviation from the mean in each day of analysis.

BTU Variation at DDI

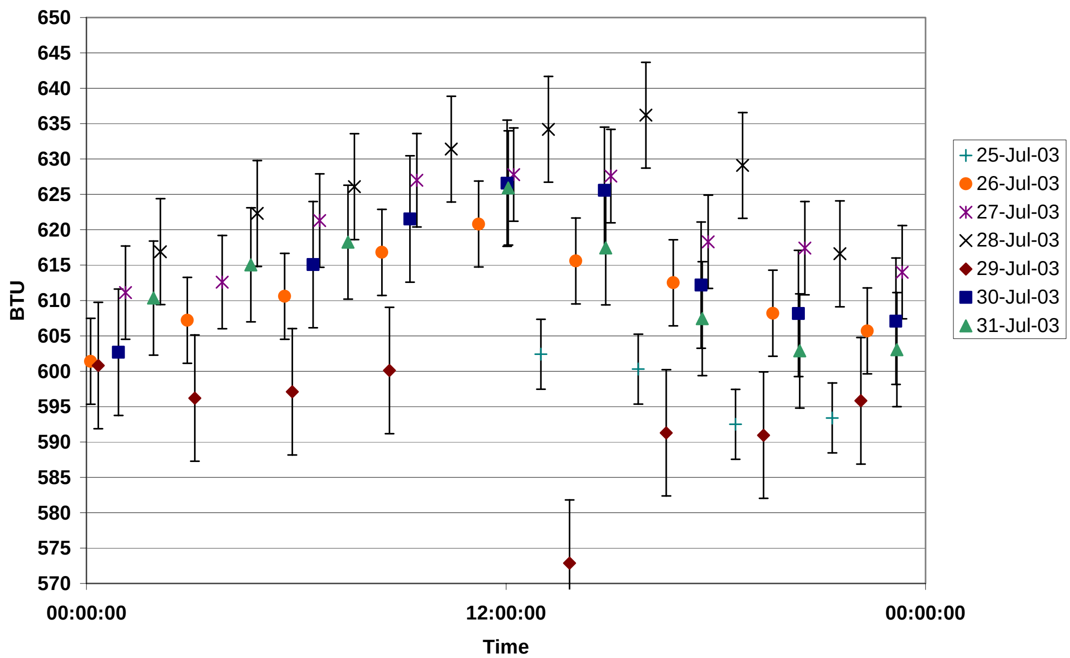

Figure A-17 BTU at DDI for 7 consecutive days (July 25-31, 2003).

Error bars showing standard deviation from the mean in each day of analysis.

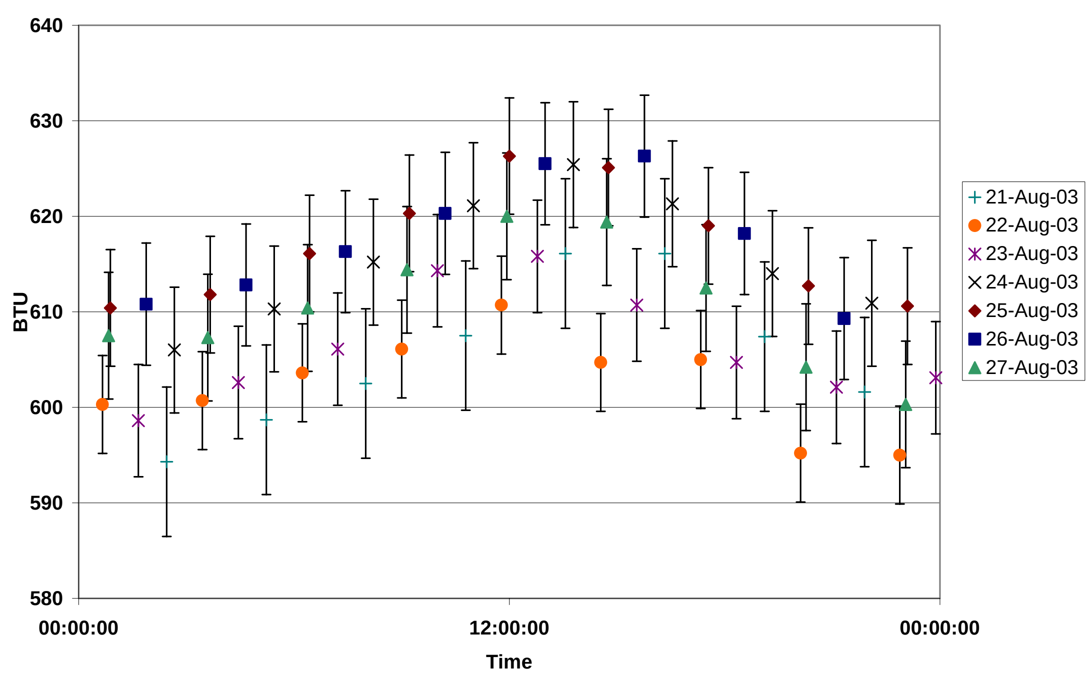

Figure A-18 BTU at DDI for 7 consecutive days (August 21-27, 2003).

Error bars showing standard deviation from the mean in each day of analysis.

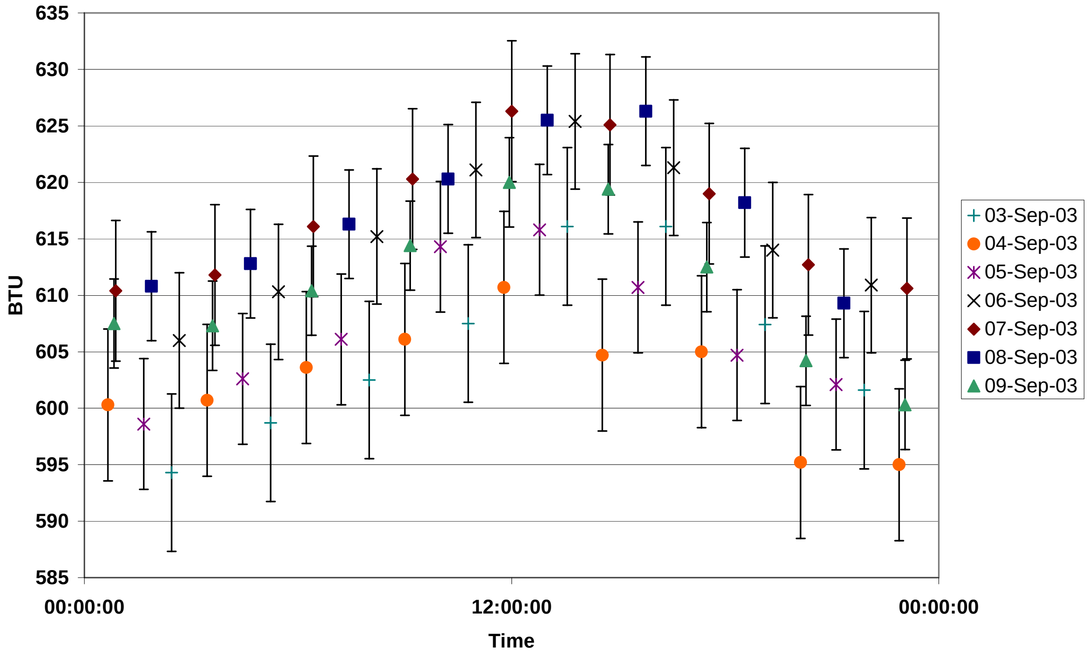

Figure A-19 BTU at DDI for 7 consecutive days (September 3-9, 2003).

Error bars showing standard deviation from the mean in each day of analysis.

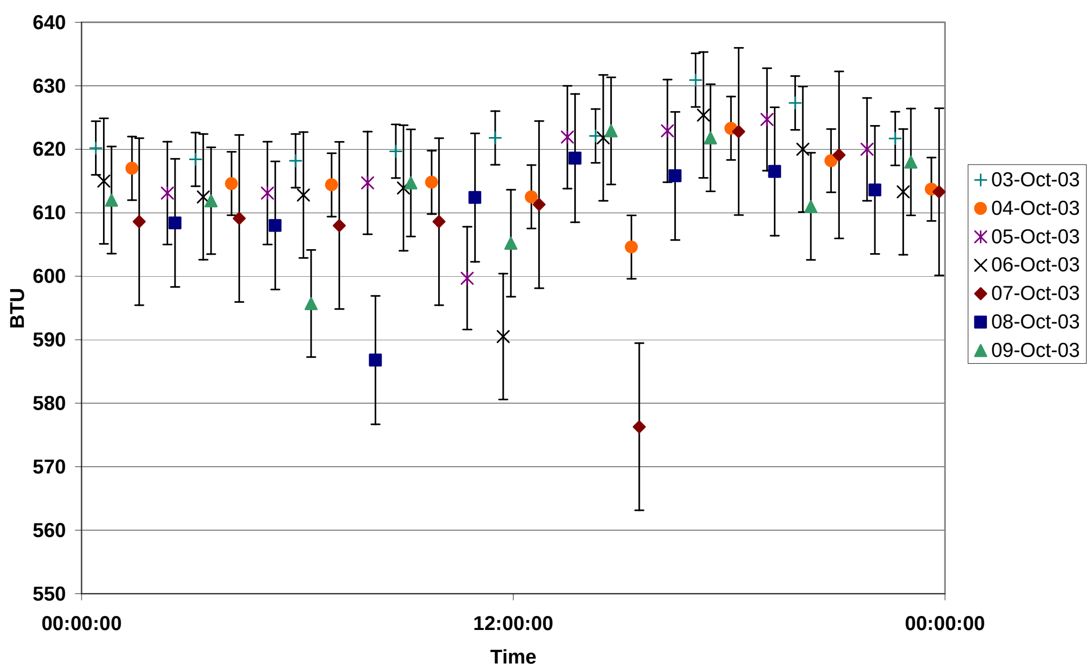

Figure A-20 BTU at DDI for 7 consecutive days (October 3-9, 2003).

Error bars showing standard deviation from the mean in each day of analysis.

Raw Data

Table A-2 Long-term analysis at DDI July-November 2003.

		Component				
Date	Time	%CH4	%N2	%CO2	BTU	Sum of Components (%)
25/07/03	13:00	59.309	1.654	39.034	602.4	99.997
25/07/03	15:47	59.094	0.59	40.313	600.3	99.997
25/07/03	18:34	58.33	1.778	39.889	592.5	99.997
25/07/03	21:20	58.415	1.18	40.402	593.4	99.997
26/07/03	0:07	59.197	0.576	40.224	601.4	99.997
26/07/03	2:53	59.771	0.582	39.644	607.2	99.997
26/07/03	5:40	60.107	0.985	38.905	610.6	99.997
26/07/03	8:27	60.719	1.059	38.219	616.8	99.997
26/07/03	11:13	61.123	1.394	37.48	620.8	99.997
26/07/03	14:00	60.608	1.452	37.937	615.6	99.997
26/07/03	16:47	60.297	0.594	39.106	612.5	99.997
26/07/03	19:38	59.873	0.58	39.544	608.2	99.997
26/07/03	22:20	59.626	1.067	39.304	605.7	99.997
27/07/03	1:07	60.156	0.559	39.282	611.1	99.997
27/07/03	3:53	60.306	0.98	38.711	612.6	99.997
27/07/03	6:40	61.161	0.536	38.3	621.3	99.997
27/07/03	9:27	61.727	0.546	37.724	627	99.997
27/07/03	12:13	61.812	1.194	36.991	627.8	99.997
27/07/03	15:00	61.786	0.597	37.614	627.6	99.997
27/07/03	17:47	60.875	1.059	38.063	618.3	99.997
27/07/03	20:33	60.776	0.554	38.667	617.4	99.997
27/07/03	23:20	60.445	1.105	38.447	614	99.997
28/07/03	2:07	60.733	1.054	38.21	616.9	99.997
28/07/03	4:53	61.268	0.873	37.856	622.3	99.997
28/07/03	7:40	61.645	1.031	37.321	626.1	99.997
28/07/03	10:26	62.16	1.117	36.72	631.4	99.997
28/07/03	13:13	62.444	1.358	36.195	634.2	99.997
28/07/03	16:00	62.639	1.429	35.929	636.2	99.997
28/07/03	18:46	61.94	1.562	36.495	629.1	99.997
28/07/03	21:33	60.706	1.228	38.063	616.6	99.997
29/07/03	0:20	59.144	0.959	39.894	600.8	99.997
29/07/03	3:06	58.693	0.918	40.386	596.2	99.997
29/07/03	5:53	58.778	0.966	40.253	597.1	99.997
29/07/03	8:40	59.07	1.108	39.909	600.1	100.087
29/07/03	13:49	56.575	4.372	39.05	572.87	99.997
29/07/03	16:35	58.394	1.208	40.395	591.28	99.997
29/07/03	19:22	58.362	1.28	40.355	590.96	99.997
29/07/03	22:09	58.842	0.909	40.246	595.82	99.997
30/07/03	0:55	59.521	0.532	39.944	602.69	99.997
30/07/03	6:29	60.743	0.784	38.47	615.06	99.997
30/07/03	9:15	61.383	0.829	37.785	621.54	99.997
30/07/03	12:02	61.882	0.953	37.162	626.59	99.997
30/07/03	14:49	61.782	0.658	37.557	625.58	99.997

30/07/03	17:35	60.459	0.555	38.983	612.19	99.997
30/07/03	20:22	60.061	0.541	39.395	608.16	99.997
30/07/03	23:09	59.953	0.527	39.517	607.06	99.997
31/07/03	1:55	60.277	0.527	39.193	610.34	99.997
31/07/03	4:42	60.741	0.523	38.733	615.04	99.997
31/07/03	7:29	61.057	0.806	38.134	618.24	99.997
31/07/03	12:04	61.782	0.697	37.505	625.91	99.984
31/07/03	14:51	60.977	0.558	38.462	617.43	99.997
31/07/03	17:37	59.989	0.5333	39.475	607.43	99.997
31/07/03	20:24	59.539	0.634	39.824	602.87	99.997
31/07/03	23:11	59.557	0.519	39.921	603.05	99.997
01/08/03	1:57	59.949	0.523	39.525	607.02	99.997
01/08/03	4:44	60.493	0.519	38.985	612.53	99.997
01/08/03	7:31	61.026	0.62	38.351	617.92	99.997
01/08/03	10:17	61.811	0.56	37.626	625.87	99.997
01/08/03	13:04	61.658	0.773	37.566	624.32	99.997
01/08/03	15:51	61.243	0.694	38.06	620.12	99.997
04/08/03	13:25	61.79	3.18	34.86	628.82	99.830
04/08/03	16:12	62.006	0.29	37.701	627.85	99.997
04/08/03	18:58	60.56	0.138	39.299	613.21	99.997
04/08/03	21:45	59.909	0.09	39.998	606.62	99.997
05/08/03	0:32	59.846	0.069	40.082	605.98	99.997
05/08/03	3:18	60.091	0.064	39.842	608.46	99.997
05/08/03	6:05	60.621	0.054	39.322	613.82	99.997
08/08/03	12:56	58.233	6.952	34.812	589.65	99.997
08/08/03	15:42	60.426	2.576	36.995	611.85	99.997
08/08/03	18:29	59.769	2.663	37.538	605.47	99.970
08/08/03	21:16	59.104	2.521	38.372	598.47	99.997
09/08/03	0:02	58.807	2.55	38.64	595.46	99.997
09/08/03	2:49	58.959	2.527	38.511	597	99.997
09/08/03	5:36	59.325	2.49	38.153	600.98	99.968
09/08/03	8:22	59.918	2.439	37.64	606.71	99.997
09/08/03	11:09	60.245	2.55	37.202	610.02	99.997
8/10/2003						0.000
8/11/2003						0.000
8/12/2003						0.000
8/13/2003						0.000
8/14/2003						0.000
8/15/2003						0.000
8/16/2003						0.000
8/17/2003						0.000
8/18/2003						0.000
19/08/03	11:34	59.346	3.67	36.981	602.7	99.997
19/08/03	14:21	59.136	2.459	38.402	600.7	99.997
19/08/03	17:07	58.77	2.189	39.038	597	99.997
19/08/03	19:54	58.146	2.06	39.791	590.6	99.997
19/08/03	22:41	58.001	1.889	40.107	589.2	99.997
20/08/03	1:27	58.143	1.889	39.965	590.6	99.997
20/08/03	4:14	58.5	1.883	39.614	594.2	99.997
20/08/03	7:00	58.976	1.874	39.147	599.1	99.997
20/08/03	9:47	59.535	1.939	38.523	604.7	99.997

20/08/03	12:34	59.223	2.794	37.98	601.5	99.997
20/08/03	15:20	58.831	2.379	38.787	597.6	99.997
20/08/03	18:07	58.432	1.987	39.578	593.5	99.997
20/08/03	20:54	58.069	1.899	40.029	589.9	99.997
20/08/03	23:40	58.206	1.845	39.946	591.3	99.997
21/08/03	2:27	58.508	1.848	39.641	594.3	99.997
21/08/03	5:14	58.939	1.832	39.226	598.7	99.997
21/08/03	8:00	59.319	1.762	38.916	602.5	99.997
21/08/03	10:47	59.813	1.967	38.217	607.5	99.997
21/08/03	13:34	60.654	2.164	37.179	616.1	99.997
21/08/03	16:20	60.656	1.811	37.53	616.1	99.997
21/08/03	19:07	59.797	1.73	38.47	607.4	99.997
21/08/03	21:54	59.227	1.74	39.03	601.6	99.997
22/08/03	0:40	59.101	1.675	39.221	600.3	99.997
22/08/03	3:27	59.138	1.68	39.179	600.7	99.997
22/08/03	6:14	59.422	1.615	38.96	603.6	99.997
22/08/03	9:00	59.671	1.817	38.509	606.1	99.997
22/08/03	11:47	60.126	1.777	38.094	610.7	99.997
22/08/03	14:33	59.538	2.291	38.168	604.7	99.997
22/08/03	17:20	59.564	2.189	38.244	605	99.997
22/08/03	20:07	58.598	2.071	39.328	595.2	99.997
22/08/03	22:53	58.577	1.878	39.542	595	99.997
23/08/03	1:40	58.928	1.727	39.342	598.6	99.997
23/08/03	4:27	59.324	1.702	38.971	602.6	99.997
23/08/03	7:13	59.675	1.842	38.48	606.1	99.997
23/08/03	10:00	60.475	1.689	37.833	614.3	99.997
23/08/03	12:47	60.628	1.83	37.539	615.8	99.997
23/08/03	15:33	60.129	1.816	38.052	610.7	99.997
23/08/03	18:20	59.533	1.864	38.6	604.7	99.997
23/08/03	21:07	59.274	16:37	39.03	602.1	99.997
23/08/03	23:53	59.378	1.661	38.958	603.1	99.997
24/08/03	2:40	59.663	1.711	38.623	606	99.997
24/08/03	5:27	60.089	1.79	38.118	610.3	99.997
24/08/03	8:13	60.565	1.798	37.634	615.2	99.997
24/08/03	11:00	61.155	1.831	37.011	621.1	99.997
24/08/03	13:47	61.578	1.979	36.44	625.4	99.997
24/08/03	16:33	61.172	1.751	37.074	621.3	99.997
24/08/03	19:20	60.454	1.711	37.832	614	99.997
24/08/03	22:06	60.139	1.692	38.166	610.9	99.997
25/08/03	0:53	60.091	1.676	38.23	610.4	99.997
25/08/03	3:40	60.236	1.668	38.093	611.8	99.997
25/08/03	6:26	60.656	1.64	37.701	616.1	99.997
25/08/03	9:13	61.072	1.606	37.319	620.3	99.997
25/08/03	12:00	61.663	1.745	36.589	626.3	99.997
25/08/03	14:46	61.541	1.713	36.743	625.1	99.997
25/08/03	17:33	60.944	1.673	37.38	619	99.997
25/08/03	20:20	60.317	1.63	38.05	612.7	99.997
25/08/03	23:06	60.118	1.621	38.258	610.6	99.997
26/08/03	1:53	60.129	1.626	38.242	610.8	99.997
26/08/03	4:40	60.335	1.609	38.053	612.8	99.997
26/08/03	7:26	60.672	1.606	37.719	616.3	99.997

26/08/03	10:13	61.067	1.598	37.332	620.3	99.997
26/08/03	13:00	61.581	1.718	36.698	625.5	99.997
26/08/03	15:46	61.511	1.594	36.845	626.3	99.950
26/08/03	18:33	60.867	1.568	37.562	618.2	99.997
26/08/03	21:20	59.983	1.549	38.465	609.3	99.997
27/08/03	0:06	59.803	1.543	38.651	607.5	99.997
27/08/03	2:53	59.784	1.551	38.662	607.3	99.997
27/08/03	5:39	60.092	1.528	38.377	610.4	99.997
27/08/03	8:26	60.492	1.521	37.984	614.4	99.997
27/08/03	11:13	61.045	1.597	37.355	620	99.997
27/08/03	13:59	60.986	1.896	37.115	619.4	99.997
27/08/03	16:46	60.3	1.793	37.904	612.5	99.997
27/08/03	19:33	59.481	1.601	38.915	604.2	99.997
27/08/03	22:19	59.094	1.583	39.32	600.3	99.997
28/08/03	1:06	58.983	1.578	39.436	599.1	99.997
28/08/03	3:53	59.093	1.612	39.292	600.3	99.997
28/08/03	6:39	59.422	1.692	38.883	603.6	99.997
28/08/03	9:26	59.868	1.632	38.497	608.1	99.997
28/08/03	12:13	60.165	1.749	38.083	611.1	99.997
28/08/03	14:59	59.942	1.801	38.254	608.9	99.997
28/08/03	17:46	59.322	1.724	38.951	602.6	99.997
28/08/03	20:33	58.898	1.602	39.497	598.3	99.997
28/08/03	23:19	58.893	1.577	39.527	598.2	99.997
29/08/03	2:06	59.017	1.613	39.367	599.5	99.997
29/08/03	4:53	59.359	1.603	39.035	603	99.997
29/08/03	7:39	59.936	1.564	38.497	608.8	99.997
29/08/03	10:26	60.319	1.71	37.968	612.7	99.997
29/08/03	13:12	60.478	1.696	37.754	616.6	99.928
30/08/03						0.000
01/09/03	17:50	59.281	2.752	37.964	602.1	99.997
01/09/03	20:37	59.076	2.461	38.46	600.1	99.997
01/09/03	23:24	58.814	2.353	38.83	597.4	99.997
02/09/03	2:11	58.864	2.328	38.805	597.9	99.997
02/09/03	4:57	59.084	2.417	38.496	600.1	99.997
02/09/03	7:44	59.344	2.392	38.261	602.8	99.997
02/09/03	10:30	59.813	2.349	37.835	607.5	99.997
02/09/03	13:17	59.803	2.538	37.656	607.4	99.997
02/09/03	16:04	59.307	2.483	38.207	602.4	99.997
02/09/03	18:50	58.406	2.455	39.136	593.2	99.997
02/09/03	21:37	58.051	2.465	39.481	589.7	99.997
03/09/03	0:24	57.98	2.435	39.582	588.9	99.997
03/09/03	3:10	58.323	2.378	39.296	592.4	99.997
03/09/03	5:57	58.674	2.334	38.989	596	99.997
03/09/03	8:44	59.061	2.413	38.523	599.9	99.997
03/09/03	11:30	59.589	2.315	38.093	605.3	99.997
03/09/03	14:17	59.86	2.358	37.779	608	99.997
03/09/03	17:04	59.39	2.339	38.268	603.2	99.997
03/09/03	19:50	58.565	2.334	39.098	594.9	99.997
03/09/03	22:37	57.995	2.305	39.697	589.1	99.997
04/09/03	1:24	57.895	2.274	39.828	588.1	99.997
04/09/03	4:10	57.926	2.434	39.637	588.4	99.997

04/09/03	6:57	58.274	2.389	39.334	591.9	99.997
04/09/03	9:44	58.801	2.296	38.9	597.3	99.997
04/09/03	12:30	59.166	2.423	38.408	601	99.997
04/09/03	15:17	59.055	2.39	38.552	599.8	99.997
04/09/03	18:03	58.207	2.362	39.428	591.3	99.997
04/09/03	20:50	57.523	2.393	40.081	584.3	99.997
04/09/03	23:37	57.262	2.352	40.383	581.7	99.997
05/09/03	2:23	57.248	2.394	40.355	581.5	99.997
05/09/03	5:10	57.521	2.336	40.14	584.3	99.997
05/09/03	7:57	57.976	2.308	39.713	588.9	99.997
05/09/03	10:43	58.438	2.388	39.171	593.6	99.997
05/09/03	13:30	57.955	3.474	38.568	588.7	99.997
05/09/03	16:17	57.447	3.182	39.368	583.5	99.997
05/09/03	19:03	56.92	2.759	40.318	578.2	99.997
05/09/03	21:50	56.741	2.521	40.735	576.4	99.997
06/09/03	0:37	56.936	2.492	40.569	578.4	99.997
06/09/03	3:23	57.243	2.529	40.225	581.5	99.997
06/09/03	6:10	57.619	2.531	39.847	585.3	99.997
06/09/03	8:57	58.285	2.438	39.274	592	99.997
06/09/03	11:43	58.825	2.545	38.627	597.5	99.997
06/09/03	14:30	58.393	2.909	38.695	593.1	99.997
06/09/03	17:17	58.129	2.775	39.093	590.4	99.997
06/09/03	20:03	57.769	2.576	39.652	586.8	99.997
06/09/03	22:50	57.639	2.464	39.894	585.5	99.997
07/09/03	1:36	57.847	2.432	39.718	587.6	99.997
07/09/03	4:23	58.166	2.385	39.446	590.8	99.997
07/09/03	7:10	58.598	2.406	38.993	595.2	99.997
07/09/03	9:56	59.086	2.506	38.487	600.2	100.079
07/09/03	12:43	59.631	2.498	37.868	605.7	99.997
07/09/03	15:30	58.826	4.54	36.631	597.4	99.997
07/09/03	18:16	59.594	2.791	37.612	605.3	99.997
07/09/03	21:03	59.348	2.591	38.058	602.8	99.997
07/09/03	23:50	59.03	2.42	38.547	599.6	99.997
08/09/03	2:36	59.103	2.344	38.55	600.3	99.997
08/09/03	5:23	59.27	2.34	38.387	602	99.997
08/09/03	8:10	59.641	2.29	38.066	605.8	99.997
08/09/03	10:56	60.023	2.345	37.629	609.7	99.997
08/09/03	13:43	60.245	2.537	37.215	611.9	99.997
08/09/03	16:30	60.212	2.74	37.045	611.6	99.997
08/09/03	19:16	59.697	2.51	37.79	606.3	99.997
08/09/03	22:03	59.094	2.454	38.449	600.2	99.997
09/09/03	0:50	58.758	2.529	38.71	596.8	99.997
09/09/03	3:36	58.763	2.407	38.827	596.9	99.997
09/09/03	6:23	58.984	2.361	38.652	599.1	99.997
09/09/03	9:09	59.257	2.331	38.409	601.9	99.997
09/09/03	11:56	59.741	2.484	37.772	606.8	99.997
09/09/03	14:43	59.811	2.863	37.323	607.5	99.997
09/09/03	17:29	59.568	2.477	37.952	605	99.997
09/09/03	20:16	59.227	2.411	38.359	601.6	99.997
09/09/03	23:03	59.162	2.348	38.487	600.9	99.997
10/09/03	1:49	59.211	2.365	38.421	601.4	99.997

10/09/03	4:36	59.413	2.333	38.251	603.5	99.997
10/09/03	7:23	59.79	2.324	37.883	607.3	99.997
10/09/03	10:09	60.298	2.334	37.365	612.4	99.997
10/09/03	13:20	61.192	5.5	33.279	621.8	99.971
10/09/03	16:06	59.007	5.893	35.097	599.2	99.997
10/09/03	18:53	59.472	3.905	36.35	606.7	99.727
10/09/03	21:40	57.749	6.446	35.802	586.5	99.997
11/09/03	0:26	61.417	0.141	38.439	623.9	99.997
11/09/03	3:13	57.474	6.397	36.126	583.7	99.997
11/09/03	6:00	61.546	0.116	38.335	625.2	99.997
11/09/03	8:46	61.867	0.112	38.018	628.4	99.997
11/09/03	11:33	59.365	4.794	35.838	602.9	99.997
11/09/03	14:20	59.213	6.265	34.519	601.3	99.997
11/09/03	17:06	60.461	3.699	35.837	614	99.997
11/09/03	19:53	61.701	0.642	37.654	626.7	99.997
11/09/03	22:40	61.315	0.344	38.338	622.8	99.997
12/09/03	1:26	60.719	0.239	39.039	616.8	99.997
12/09/03	4:13	58.246	3.492	38.259	591.6	99.997
12/09/03	7:00	56.841	5.612	37.544	577.3	99.997
12/09/03	9:46	60.283	0.163	39.551	612.4	99.997
12/09/03	12:33	57.051	6.003	36.943	579.4	99.997
12/09/03	15:20	56.481	6.743	36.773	573.6	99.997
12/09/03	18:06	56.119	6.891	36.987	569.9	99.997
12/09/03	20:53	56.516	6.097	37.384	574	99.997
12/09/03	23:39	60.362	0.495	39.14	613.2	99.997
13/09/03	2:26	60.534	0.123	39.34	614.9	99.997
13/09/03	5:13	61.025	0.139	38.833	619.9	99.997
13/09/03	7:59	61.549	0.112		625.2	61.661
13/09/03	10:46	61.994	0.18	37.823	629.7	99.997
13/09/03	13:33	62.423	0.291	37.283	634.1	99.997
13/09/03	16:19	62.128	0.236	37.633	631.1	99.997
13/09/03	19:06	60.073	2.641	37.283	610.1	99.997
13/09/03	21:53	58.628	4.354	37.015	595.4	99.997
14/09/03	0:39	57.037	6.77	36.19	579.2	99.997
14/09/03	3:26	57.497	6.198	36.302	583.9	99.997
14/09/03	6:13	57.652	6.398	35.947	585.5	99.997
14/09/03	8:59	58.173	6.173	35.651	590.8	99.997
14/09/03	11:46	58.838	5.666	35.493	597.5	99.997
14/09/03	14:33	58.346	7	34.651	592.5	99.997
14/09/03	17:19	62.159	0.261	37.577	631.4	99.997
14/09/03	20:06	61.17	0.196	38.631	621.4	99.997
14/09/03	22:53	60.532	0.155	39.31	614.9	99.997
15/09/03	1:39	60.226	0.137	39.634	611.8	99.997
15/09/03	4:26	57.913	3.936	38.148	588.2	99.997
15/09/03	7:12	60.47	0.121	39.406	614.3	99.997
15/09/03	9:59	60.8	0.221	38.976	617.6	99.997
15/09/03	12:46	61.127	0.318	38.552	620.9	99.997
15/09/03	15:32	61.268	0.387	38.342	622.4	99.997
15/09/03	18:19	60.672	0.24	39.085	616.3	99.997
15/09/03	21:06	60.262	0.181	39.554	612.2	99.997
15/09/03	23:52	60.176	0.148	39.673	611.3	99.997

16/09/03	2:39	57.834	4.088	38.075	587.4	99.997
16/09/03	5:26	56.738	6.197	37.062	576.2	99.997
16/09/03	8:12	60.954	0.15	38.893	619.2	99.997
16/09/03	10:59	61.14	0.107	38.75	621.1	99.997
16/09/03	13:46	56.848	7.853	35.296	577.3	99.997
16/09/03	16:32	57.275	7.725	34.997	581.6	99.997
16/09/03	19:19	61.234	0.347	38.416	622	99.997
16/09/03	22:06	56.875	6.773	36.349	577.6	99.997
17/09/03	0:52	60.588	0.183	39.226	615.5	99.997
17/09/03	3:39	60.214	0.702	39.081	611.7	99.997
17/09/03	6:26	60.739	0.141	39.117	617	99.997
17/09/03	9:12	60.909	0.14	38.948	618.7	99.997
17/09/03	11:59	60.469	1.725	37.803	614.2	99.997
17/09/03	14:45	57.097	8.009	34.891	579.8	99.997
17/09/03	17:32	58.77	5.134	36.093	596.8	99.997
17/09/03	20:19	61.42	1.086	37.491	623.9	99.997
17/09/03	23:05	60.764	0.222	39.011	617.2	99.997
18/09/03	1:52	60.759	0.172	39.066	617.2	99.997
18/09/03	4:39	60.797	0.146	39.054	617.6	99.997
18/09/03	7:25	58.238	4.542	37.217	591.5	99.997
9/19/2003						0.000
9/20/2003	20:32	60.852	0.205	38.94	618.1	99.997
9/21/2003						0.000
9/22/2003						0.000
9/23/2003						0.000
9/24/2003						0.000
9/25/2003	15:38	60.066	0.115	39.816	610.2	99.997
9/25/2003	17:11	56.484	6.542	36.971	573.6	99.997
9/25/2003	19:58	60.875	0.5	38.622	618.4	99.997
9/25/2003	22:44	61.737	0.336	37.924	627.1	99.997
9/26/2003	1:31	61.686	0.252	38.059	626.6	99.997
9/26/2003	4:18	57.98	5.446	36.571	588.8	99.997
9/26/2003	7:04	60.811	0.152	39.034	617.7	99.997
9/26/2003	9:51	60.634	0.131	39.232	615.9	99.997
9/26/2003	12:38	61.259	0.296	38.442	622.3	99.997
9/26/2003	15:24	59.341	2.283	38.373	602.7	99.997
9/26/2003	18:11	60.51	1.269	38.218	614.6	99.997
9/26/2003	20:57	60.202	1.623	38.172	611.5	99.997
9/26/2003	23:44	59.652	2.408	37.937	605.9	99.997
9/27/2003	2:31	59.117	3.383	37.497	600.4	99.997
9/27/2003	5:17	59.472	3.043	37.482	604	99.997
9/27/2003	8:04	60.824	1.275	37.898	617.8	99.997
9/27/2003	10:51	61.202	0.125	38.67	621.7	99.997
9/27/2003	13:37	61.536	0.219	38.242	625.1	99.997
9/27/2003	16:24	60.627	2.398	36.972	615.8	99.997
9/27/2003	19:11	61.199	1.099	37.699	621.6	99.997
9/27/2003	21:57	60.263	1.626	38.108	612.1	99.997
9/28/2003	0:44	56.54	7.26	36.197	574.2	99.997
9/28/2003	3:31	58.884	3.15	37.963	598.1	99.997
9/28/2003	6:17	60.712	0.132	39.153	616.7	99.997
9/28/2003	9:04	60.873	0.125	38.999	618.4	99.997

9/28/2003	11:51	56.908	6.73	36.359	577.9	99.997
9/28/2003	14:37	61.29	0.286	38.421	622.6	99.997
9/28/2003	17:24	61.517	0.263	38.217	624.9	99.997
9/28/2003	20:11	61.045	0.187	38.765	620.1	99.997
9/28/2003	22:57	60.564	0.155	39.278	615.2	99.997
9/29/2003	1:44	60.341	0.138	39.518	613	99.997
9/29/2003	4:30	60.313	0.128	39.556	612.7	99.997
9/29/2003	7:17	60.454	0.123	39.42	614.1	99.997
9/29/2003	10:04	58.599	3.478	37.92	595.2	99.997
9/29/2003	12:50	59.427	2.759	37.811	603.6	99.997
9/29/2003	15:37	59.936	2.541	37.52	608.8	99.997
9/29/2003	18:24	62.097	0.419	37.481	630.7	99.997
9/29/2003	21:10	62.074	0.355	37.568	630.5	99.997
9/29/2003	23:57	61.645	0.276	38.076	626.2	99.997
9/30/2003	2:44	60.274	1.719	38.004	612.2	99.997
9/30/2003	5:30	57.814	5.433	36.75	587.2	99.997
9/30/2003	8:17	57.77	5.431	36.796	586.7	99.997
9/30/2003	11:04	60.137	1.959	37.901	610.8	99.997
9/30/2003	13:50	61.298	0.151	38.548	622.7	99.997
9/30/2003	16:37	60.67	1.552	37.775	616.2	99.997
9/30/2003	19:24	59.25	5.184	35.563	601.7	99.997
9/30/2003	22:10	62.254	0.643	37.1	632.3	99.997
10/1/2003	0:57	61.798	0.4	37.799	627.7	99.997
10/1/2003	3:44	61.23	0.281	38.486	622	99.997
10/1/2003	6:30	60.8	0.214	38.983	617.6	99.997
10/1/2003	9:17	60.594	0.176	39.227	615.5	99.997
10/1/2003	12:03	60.621	0.23	39.146	615.8	99.997
10/1/2003	14:50	60.657	1.765	37.575	616.1	99.997
10/1/2003	17:37	61.197	0.655	38.145	621.6	99.997
10/1/2003	20:23	60.941	0.406	38.65	619	99.997
10/1/2003	23:10	60.791	0.272	38.934	617.5	99.997
10/2/2003	1:57	60.704	0.195	39.098	616.6	99.997
10/2/2003	4:43	60.727	0.158	39.112	616.9	99.997
10/2/2003	7:30	60.207	1.213	38.577	611.6	99.997
10/2/2003	10:17	60.938	0.207	38.852	619	99.997
10/2/2003	13:03	61.832	0.38	37.785	628.1	99.997
10/2/2003	15:50	61.215	1.984	36.798	621.7	99.997
10/2/2003	18:37	59.643	3.814	36.54	605.7	99.997
10/2/2003	21:23	61.394	0.167	38.436	623.6	99.997
10/3/2003	0:10	61.054	0.135	38.808	620.2	99.997
10/3/2003	2:57	60.873	0.119	39.005	618.4	99.997
10/3/2003	5:43	60.857	0.115	39.025	618.2	99.997
10/3/2003	8:30	61.006	0.105	38.886	619.7	99.997
10/3/2003	11:17	61.212	0.161	38.624	621.8	99.997
10/3/2003	14:03	61.256	2.635	36.106	622.1	99.997
10/3/2003	16:50	62.111	0.571	37.315	630.9	99.997
10/3/2003	19:36	61.757	0.38	37.86	627.3	99.997
10/3/2003	22:23	61.204	0.245	38.548	621.7	99.997
10/4/2003	1:10	60.743	0.187	39.067	617	99.997
10/4/2003	3:56	60.505	0.152	39.34	614.6	99.997
10/4/2003	6:43	60.479	0.132	39.386	614.4	99.997

10/4/2003	9:30	60.524	0.209	39.264	614.8	99.997
10/4/2003	12:16	60.305	2.404	37.288	612.5	99.997
10/4/2003	15:03	59.533	4.053	36.411	604.6	99.997
10/4/2003	17:50	61.36	0.633	38.004	623.3	99.997
10/4/2003	20:36	60.862	0.387	38.748	618.2	99.997
10/4/2003	23:23	60.415	0.261	39.321	613.7	99.997
10/5/2003	2:10	60.355	0.191	39.451	613.1	99.997
10/5/2003	4:56	60.359	0.154	39.484	613.1	99.997
10/5/2003	7:43	60.509	0.132	39.356	614.7	99.997
10/5/2003	10:30	59.047	2.785	38.165	599.7	99.997
10/5/2003	13:16	61.229	0.705	38.063	621.9	99.997
10/5/2003	16:03	61.325	1.364	37.308	622.9	99.997
10/5/2003	18:50	61.505	0.756	37.736	624.7	99.997
10/5/2003	21:36	61.032	0.472	38.493	620	99.997
10/6/2003	0:23	60.544	0.294	39.159	615	99.997
10/6/2003	3:09	60.296	0.202	39.499	612.5	99.997
10/6/2003	5:56	60.321	0.159	39.517	612.8	99.997
10/6/2003	8:43	60.433	0.129	39.435	613.9	99.997
10/6/2003	11:29	58.141	4.293	37.563	590.5	99.997
10/6/2003	14:16	61.217	1.38	37.4	621.8	99.997
10/6/2003	17:03	61.569	0.583	37.845	625.4	99.997
10/6/2003	19:49	61.035	0.357	38.605	620	99.997
10/6/2003	22:36	60.377	0.244	39.376	613.3	99.997
10/7/2003	1:23	59.914	0.182	39.901	608.6	99.997
10/7/2003	4:09	59.956	0.173	39.868	609.1	99.997
10/7/2003	6:56	59.849	0.136	40.012	608	99.997
10/7/2003	9:43	59.911	0.116	39.97	608.6	99.997
10/7/2003	12:29	60.178	0.206	39.613	611.3	99.997
10/7/2003	15:16	56.749	8.259	34.989	576.3	99.997
10/7/2003	18:03	61.315	0.772	37.91	622.8	99.997
10/7/2003	20:49	60.947	0.449	38.601	619.1	99.997
10/7/2003	23:36	60.375	0.294	39.328	613.3	99.997
10/8/2003	2:23	59.894	0.207	39.896	608.4	99.997
10/8/2003	5:09	59.854	0.159	39.984	608	99.997
10/8/2003	7:56	57.776	3.66	38.561	586.8	99.997
10/8/2003	10:42	60.282	0.26	39.455	612.4	99.997
10/8/2003	13:29	60.903	0.762	38.322	618.6	99.987
10/8/2003	16:16	60.625	1.296	38.076	615.8	99.997
10/8/2003	19:02	60.695	0.294	39.008	616.5	99.997
10/8/2003	21:49	60.402	0.203	39.392	613.6	99.997
10/9/2003	0:36	60.244	0.153	39.6	612	99.997
10/9/2003	3:22	60.236	0.129	39.632	611.9	99.997
10/9/2003	6:09	58.648	2.863	38.486	595.7	99.997
10/9/2003	8:56	60.512	0.104	39.381	614.7	99.997
10/9/2003	11:42	59.58	2.464	37.953	605.2	99.997
10/9/2003	14:29	61.321	1.102	37.574	622.9	99.997
10/9/2003	17:16	61.216	1.526	37.255	621.8	99.997
10/9/2003	20:02	60.158	1.829	38.01	611	99.997
10/9/2003	22:49	60.839	0.149	39.009	618	99.997
10/10/2003	1:36	60.666	0.129	39.202	616.3	99.997
10/10/2003	4:22	60.184	0.889	38.924	611.3	99.997

10/10/2003	7:09	60.726	0.119	39.152	616.9	99.997
10/10/2003	9:56	60.203	1.253	38.541	611.5	99.997
10/10/2003	12:42	61.408	0.383	38.206	623.8	99.997
10/10/2003	15:29	60.81	2.498	36.689	617.6	99.997
10/10/2003	18:15	60.138	2.493	37.366	610.8	99.997
10/10/2003	21:02	60.398	0.426	39.173	613.5	99.997
10/10/2003	23:49	59.098	1.744	39.155	600.3	99.997
10/11/2003	2:35	59.696	0.215	40.086	606.4	99.997
10/11/2003	5:22	59.703	0.17	40.124	606.5	99.997
10/11/2003	8:09	58.894	1.696	39.407	598.2	99.997
10/11/2003	10:55	60.191	0.25	39.556	611.4	99.997
10/11/2003	13:42	59.443	2.746	37.808	603.8	99.997
10/11/2003	16:29	60.925	0.653	38.419	618.9	99.997
10/11/2003	19:15	60.375	0.334	39.288	613.3	99.997
10/11/2003	22:02	60.187	0.215	39.595	611.4	99.997
10/12/2003	0:49	59.75	0.175	40.072	607	99.997
10/12/2003	3:35	59.749	0.143	40.105	607	99.997
10/12/2003	6:22	59.958	0.385	39.654	609.1	99.997
10/12/2003	9:09	60.146	0.118	39.733	611	99.997
10/12/2003	11:55	59.593	1.514	38.89	605.3	99.997
10/12/2003	14:42	60.971	0.445	38.581	619.3	99.997
10/12/2003	17:29	61.52	0.689	37.788	624.9	99.997
10/12/2003	20:15	59.991	2.219	37.787	609.3	99.997
10/12/2003	23:02	60.597	0.241	39.159	615.6	99.997
10/13/2003	1:48	60.206	0.176	39.615	611.6	99.997
10/13/2003	4:35	60.116	0.14	39.741	610.7	99.997
10/13/2003	7:22	60.171	0.126	39.7	611.2	99.997
10/13/2003	10:08	60.481	0.245	39.271	614.4	99.997
10/13/2003	12:55	60.586	1.932	37.479	615.4	99.997
10/13/2003	15:42	61.006	0.913	38.078	619.7	99.997
10/13/2003	18:28	59.543	2.396	38.058	604.8	99.997
10/13/2003	21:15	60.294	0.321	39.382	612.5	99.997
10/14/2003	0:02	60.22	0.218	39.559	611.7	99.997
10/14/2003	2:48	60.212	0.161	39.624	611.7	99.997
10/14/2003	5:35	60.351	0.133	39.513	613.1	99.997
10/14/2003	8:22	60.575	0.116	39.306	615.3	99.997
10/14/2003	11:08	60.773	0.226	38.998	617.3	99.997
10/14/2003	13:55	61.175	0.811	38.011	621.4	99.997
10/14/2003	16:42	61.896	0.915	37.186	628.7	99.997
10/14/2003	19:28	61.727	0.461	37.809	627	99.997
10/14/2003	22:15	61.082	0.286	38.609	621.1	99.977
10/15/2003	1:02	60.608	0.199	39.19	615.7	99.997
10/15/2003	3:48	60.333	0.15	39.514	612.9	99.997
10/15/2003	6:35	60.423	0.214	39.36	613.8	99.997
10/15/2003	9:21	60.41	0.116	39.471	613.7	99.997
10/15/2003	12:08	61.067	0.346	38.584	620.3	99.997
10/15/2003	14:55	62.145	0.438	37.414	631.2	99.997
10/15/2003	17:41	62.429	0.278	37.29	634.1	99.997
10/15/2003	20:28	61.626	0.96	37.411	626	99.997
10/15/2003	23:15	61.822	0.156	38.019	628	99.997
10/16/2003	2:01	61.608	0.13	38.259	625.8	99.997

10/16/2003	4:48	61.458	0.118	38.421	624.3	99.997
10/16/2003	7:35	61.528	0.115	38.354	625	99.997
10/16/2003	10:21	61.65	0.234	38.113	626.2	99.997
10/16/2003	13:08	60.686	3.705	35.606	616.3	99.997
10/16/2003	15:55	62.328	1.569	36.1	633	99.997
10/16/2003	18:41	62.371	1.104	36.522	633.5	99.997
10/16/2003	21:28	61.398	1.924	36.675	623.6	99.997
10/17/2003	0:15	62.178	0.212	37.607	631.6	99.997
10/17/2003	3:01	60.923	1.669	37.405	618.8	99.997
10/17/2003	5:48	60.755	1.853	37.389	617.1	99.997
10/17/2003	8:35	61.925	0.118	37.954	629	99.997
10/17/2003	11:21	61.08	1.601	37.316	620.4	99.997
10/17/2003	14:08	61.048	2.059	36.89	620.1	99.997
10/17/2003	16:54	61.937	2.635	35.425	629	99.997
10/17/2003	19:41	63.242	0.479	36.276	642.3	99.997
10/17/2003	22:28	62.742	0.317	36.938	637.3	99.997
10/18/2003	1:14	62.133	0.227	37.637	631.1	99.997
10/18/2003	4:01	61.68	0.175	38.142	626.5	99.997
10/18/2003	6:48	61.389	0.141	38.467	623.6	99.997
10/18/2003	9:34	61.185	0.258	38.554	621.5	99.997
10/18/2003	12:21	61.194	1.621	37.182	621.5	99.997
10/18/2003	15:08	62.082	0.628	37.287	630.6	99.997
10/18/2003	17:54	62.035	0.431	37.531	630.1	99.997
10/18/2003	20:41	61.577	0.297	38.123	625.5	99.997
10/18/2003	23:28	60.996	0.206	38.795	619.6	99.997
10/19/2003	2:14	60.613	0.159	39.225	615.7	99.997
10/19/2003	5:01	59.695	1.355	38.947	606.4	99.997
10/19/2003	7:48	60.436	0.12	39.441	613.9	99.997
10/19/2003	10:34	59.959	1.099	38.939	609.1	99.997
10/19/2003	13:21	61.183	0.346	38.468	621.5	99.997
10/19/2003	16:08	62.211	0.363	37.423	631.9	99.997
10/19/2003	18:54	62.398	0.27	37.329	633.8	99.997
10/19/2003	21:41	62.091	0.197	37.709	630.7	99.997
10/20/2003	0:27	61.599	0.162	38.236	625.7	99.997
10/20/2003	3:14	61.315	0.137	38.545	622.8	99.997
10/20/2003	6:01	61.122	0.125	38.75	620.9	99.997
10/20/2003	8:47	61.141	0.114	38.742	621.1	99.997
10/20/2003	11:34	61.519	0.292	38.186	624.9	99.997
10/20/2003	14:21	62.084	1.171	36.742	630.6	99.997
10/20/2003	17:07	62.781	0.7	36.516	637.7	99.997
10/20/2003	19:54	62.218	0.42	37.359	632	99.997
10/20/2003	22:41	60.949	1.253	37.795	619.1	99.997
10/21/2003	1:27	61.055	0.203	38.739	620.2	99.997
10/21/2003	4:14	60.666	0.156	39.175	616.3	99.997
10/21/2003	7:01	60.492	0.133	39.372	614.5	99.997
10/21/2003	9:47	60.564	0.262	39.171	615.2	99.997
10/21/2003	12:34	61.717	0.433	37.847	626.9	99.997
10/21/2003	15:21	62.452	0.352	37.193	634.3	99.997
10/21/2003	18:07	62.331	0.228	37.438	633.1	99.997
10/21/2003	20:54	61.892	0.179	37.926	628.7	99.997
10/21/2003	23:41	61.501	0.152	38.344	624.7	99.997

10/22/2003	2:27	61.195	0.133	38.669	621.6	99.997
10/22/2003	5:14	60.64	0.844	38.513	616	99.997
10/22/2003	8:00	61.126	0.119	38.752	620.9	99.997
10/22/2003	10:47	61.209	0.505	38.283	621.7	99.997
10/22/2003	13:34	61.934	1.075	36.988	629.1	99.997
10/22/2003	16:20	62.986	0.553	36.458	639.8	99.997
10/22/2003	19:07	62.787	0.352	36.858	637.7	99.997
10/22/2003	21:54	62.327	0.259	37.411	633.1	99.997
10/23/2003	0:40	61.788	0.209	38	627.6	99.997
10/23/2003	3:27	61.351	0.166	38.48	623.2	99.997
10/23/2003	6:14	61.067	0.154	38.776	620.3	99.997
10/23/2003	9:00	61.01	0.133	38.854	619.7	99.997
10/23/2003	11:47	61.086	0.133	38.778	620.5	99.997
10/23/2003	14:34	61.404	0.281	38.312	623.7	99.997
10/23/2003	17:20	62.548	0.425	37.024	635.3	99.997
10/23/2003	20:07	63.093	0.359	36.545	640.8	99.997
10/23/2003	22:54	62.978	0.286	36.733	639.7	99.997
10/24/2003	1:40	62.515	0.21	37.272	635	99.997
10/24/2003	4:27	62.195	0.179	37.632	631.8	100.006
10/24/2003	7:14	61.905	0.16	37.932	628.8	99.997
10/24/2003	10:00	61.696	0.144	38.157	626.7	99.997
10/24/2003	12:47	61.532	0.479	37.986	625	99.997
10/24/2003	15:33	61.48	2.88	35.637	624.4	99.997
10/24/2003	18:20	62.862	0.995	36.14	638.5	99.997
10/24/2003	21:07	62.681	0.67	36.646	636.7	99.997
10/24/2003	23:53	62.266	0.455	37.276	632.5	99.997
10/25/2003	2:40	61.707	0.324	37.966	626.8	99.997
10/25/2003	5:27	61.361	0.252	38.384	623.3	99.997
10/25/2003	8:13	61.314	0.24	38.443	622.8	99.997
10/25/2003	11:00	61.439	0.48	38.078	624.1	99.997
10/25/2003	13:47	61.819	1.408	36.77	627.9	99.997
10/25/2003	16:33	62.532	0.884	36.581	635.1	99.997
10/25/2003	19:20	62.066	0.824	37.107	630.4	99.997
10/25/2003	22:07	61.49	0.592	37.915	624.6	99.997
10/26/2003	0:53	61.139	0.352	38.506	621	99.997
10/26/2003	3:40	60.615	0.544	38.838	615.7	99.997
10/26/2003	6:27	60.578	0.274	39.145	615.4	99.997
10/26/2003	9:13	60.572	0.398	39.027	615.3	99.997
10/26/2003	12:00	60.187	0.649	39.161	611.4	99.997
10/26/2003	14:47	60.776	0.229	38.992	617.4	99.997
10/26/2003	17:33	61.141	0.214	38.642	621.1	99.997
10/26/2003	20:20	61.257	0.202	38.538	622.2	99.997
10/26/2003	23:06	61.388	0.403	38.206	623.6	99.997
10/27/2003	1:53	61.988	0.311	37.698	629.6	99.997
10/27/2003	4:40	62.215	0.21	37.572	632	99.997
10/27/2003	7:26	62.006	0.785	37.206	629.8	99.997
10/27/2003	10:13	62.648	0.207	37.142	636.3	99.997
10/27/2003	13:00	63.03	0.534	36.433	640.2	99.997
10/27/2003	15:46	63.776	0.711	35.51	647.7	99.997
10/27/2003	18:33	64.398	0.912	34.687	654	99.997
10/27/2003	21:20	64.682	0.835	34.48	656.9	99.997

10/28/2003	0:06	64.182	0.474	35.341	651.9	99.997
10/28/2003	2:53	62.969	0.341	36.687	639.6	99.997
10/28/2003	5:40	61.487	0.763	37.747	624.6	99.997
10/28/2003	8:26	61.521	0.544	37.932	624.9	99.997
10/28/2003	11:13	61.162	0.444	38.391	621.3	99.997
10/28/2003	14:00	60.919	0.808	38.27	618.8	99.997
10/28/2003	16:46	61.568	0.888	37.541	625.4	99.997
10/28/2003	19:33	62.058	0.825	37.114	630.3	99.997
10/28/2003	22:20	61.28	0.672	38.045	622.5	99.997
10/29/2003	1:06	60.406	0.61	38.981	613.6	99.997
10/29/2003	3:53	59.889	0.555	39.553	608.4	99.997
10/29/2003	6:39	59.58	0.534	39.883	605.2	99.997
10/29/2003	9:26	58.695	0.355	40.947	596.3	99.997
10/29/2003	12:13	59.212	0.4	40.385	601.5	99.997
10/29/2003	14:59	59.727	0.732	39.538	606.7	99.997
10/29/2003	17:46	60.673	0.902	38.422	616.3	99.997
10/29/2003	20:33	61.894	0.766	37.337	628.7	99.997
10/29/2003	23:19	61.862	0.589	37.546	628.4	99.997
10/30/2003	2:06	60.539	0.237	39.221	615	99.997
10/30/2003	4:53	60.585	0.342	39.07	615.4	99.997
10/30/2003	7:39	60.329	0.348	39.32	612.8	99.997
10/30/2003	10:26	59.655	0.295	40.047	606	99.997
10/30/2003	13:13	59.898	0.373	39.726	608.5	99.997
10/30/2003	15:59	60.624	0.826	38.547	615.8	99.997
10/30/2003	18:46	61.606	0.962	37.429	625.8	99.997
10/30/2003	21:33	62.081	0.859	37.057	630.6	99.997
10/31/2003	0:19	61.66	0.724	37.613	626.3	99.997
10/31/2003	3:06	60.83	0.668	38.499	617.9	99.997
10/31/2003	5:53	60.53	0.65	38.817	614.9	99.997
10/31/2003	8:39	60.443	0.644	38.91	614	99.997
10/31/2003	11:26	59.962	0.606	39.429	609.1	99.997
10/31/2003	14:12	59.895	0.711	39.391	608.4	99.997
10/31/2003	16:59	60.322	0.984	38.691	612.7	99.997
10/31/2003	19:46	60.858	1.288	37.751	618.2	99.897
10/31/2003	22:32	61.551	1.808	36.638	625.2	99.997
11/1/2003	1:19	62.208	1.964	35.825	631.8	99.997
11/1/2003	4:06	62.882	2.05	35.065	638.6	99.997
11/1/2003	6:52	63.482	2.187	34.328	644.7	99.997
11/1/2003	9:39	63.748	2.22	34.029	647.4	99.997
11/1/2003	12:26	63.617	2.23	34.15	646.1	99.997
11/1/2003	15:12	63.414	2.153	34.43	644	99.997
11/1/2003	17:59	63.268	2.153	34.576	642.5	99.997
11/1/2003	20:46	63.3	2.088	34.609	642.9	99.997
11/1/2003	23:32	62.808	1.501	35.688	637.9	99.997
11/2/2003	2:19	62.193	1.146	36.658	631.7	99.997
11/2/2003	5:06	61.808	0.998	37.191	627.8	99.997
11/2/2003	7:52	61.321	0.883	37.793	622.9	99.997
11/2/2003	10:39	60.358	0.559	39.08	613.1	99.997
11/2/2003	13:26	60.535	0.581	38.881	614.9	99.997
11/2/2003	16:12	60.829	0.743	38.425	617.9	99.997
11/2/2003	18:59	61.574	1.043	37.38	625.4	99.997

11/2/2003	21:45	62.399	1.137	36.461	633.8	99.997
11/3/2003	0:32	62.922	1.176	35.899	639.1	99.997
11/3/2003	3:19	63.006	1.187	35.804	639.9	99.997
11/3/2003	6:05	62.634	1.099	36.264	636.2	99.997
11/3/2003	8:52	62.641	1.179	36.177	636.2	99.997
11/3/2003	11:39	62.593	1.253	36.151	635.7	99.997
11/3/2003	14:25	62.71	1.367	35.92	636.9	99.997
11/3/2003	17:12	62.708	1.675	35.614	636.9	99.997

*Data collected using the Daniel Danalyzer 520 in-line gas chromatograph.
Note: At times, breaks in sampling are present. This is due to either equipment failure or biogas stream interruptions as a result of digester malfunctions or chromatograph calibrations.

Sample Daniel GC Data Output

```
                                    ANALYSIS

DATE: 09/08/03            ANALYSIS TIME:    235           STREAM SEQUENCE:
       1
TIME:     16:30           CYCLE TIME:      9999           STREAM#:     1
GCID#:            1       MODE:          REMOTE           CYCLE START TIME:
 16:25

COMP NAME COMP CODE          MOLE %         WEIGHT %            B.T.U.*
 REL DEN*

METHANE       100           60.2120           36.129            609.53
    0.3335
C6+           108           0.00300            0.011              0.16
    0.0001
PROPANE       102           0.00000            0.000              0.00
    0.0000
I-BUTANE      103           0.00000            0.000              0.00
    0.0000
N-BUTANE      104           0.00000            0.000              0.00
    0.0000
NEO-C5        107           0.00000            0.000              0.00
    0.0000
IPENTANE      105           0.00000            0.000              0.00
    0.0000
NPENTANE      106           0.00000            0.000              0.00
    0.0000
NITROGEN      114           2.74000            2.871              0.00
    0.0265
C O 2         117           37.0450           60.989              0.00
    0.5629
ETHANE        101           0.00000            0.000              0.00
    0.0000

TOTALS                     100.000          100.000             609.68
    0.9231

* @ 14.730 PSIA DRY & UNCORRECTED FOR COMPRESSIBILITY

[illegible] 60 DEG. F

COMPRESSIBILITY FACTOR (1/Z)                                        =   1.0031
ACT B.T.U. @  14.730 PSIA & 60 DEG. F CORRECTED FOR (1/Z) =    611.6
DRY B.T.U. @  14.730 PSIA & 60 DEG. F CORRECTED FOR (1/Z) =    611.6
SAT B.T.U. @  14.730 PSIA & 60 DEG. F CORRECTED FOR (1/Z) =    601.1
REAL RELATIVE DENSITY                                               =   0.9255
[illegible] @ 14.730 PSIA                                           =    624.9
UNNORMALIZED TOTAL MOLE %                                           =    98.08

ACTIVE ALARMS

NONE
```

Dairy One Analytical Procedures

Dairy One Forage Lab Analytical Procedures - 12/04

730 Warren Road, Ithaca, NY 14850
ph: 1.800.496.3344, 607.257.1272
fax: 1.607.257.6808

I. Dry Matter

A. 60ºC for 4 hours (forced air).
B. 135ºC for 2 hours - AOAC 930.15.
C. Near Infrared Reflectance Spectroscopy (NIRS) - AOAC 991.03.

II. Protein

A. Crude Protein

1. Kjeldahl - AOAC 984.13. 10.5g of catalyst (ratio of 10g K2SO4 to 0.3g CuS04) is used. A Boric acid receiving solution contains methyl red-methylene blue indicator.

2. Block Digestion and Tecator Kjeltec Auto 1030 or 2400 Analyzer - Modified Kjeldahl procedure with automatic distillation and titration.

a. AOAC 976.06 (G) and (H).
b. FOSS Tecator, Application Note AN 300, pp. 1-12, 1987 "The Determination of Nitrogen according to Kjeldahl using Block Digestion and Steam Distillation".

3. Leco FP-528 Combustion analyzer

a. AOAC 990.03
b. Leco Application Note "Nitrogen/Protein in Animal Feeds" Form 203-821-146, 2000.

4. NIRS - AOAC 989.03. Used for grass, grass-legume mixtures, legume hays, haylages, fresh forages and pastures; corn silage and corn stalks (fresh and fermented); corn silage and haylage mixtures; shelled, ear, and snaplage corn; hays, fresh forages, pastures and silages for barley, wheat, oats, triticale, peavine, soybean and triticale and peas; fresh forages and silages for rye, sorghum, sorghum-sudan and sudangrass; barley, oats, triticale and wheat grains; brewers grains.

B. Soluble Protein (Insoluble Protein - ISP)

1. Cornell Sodium Borate-Sodium Phosphate Buffer Procedure. Soy products incubated at 39°C. All other samples incubated at ambient temperature. Cornell Nutrition Conference Proceedings, 1990, pp. 85-86.

2. NIRS - ISP as in Crude Protein NIRS (II. A. 4.).

C. Degradable Protein (Undegradable Intake Protein - UIP)

1. Cornell Streptomyces griseus (SGP) enzymatic digestion. Enzyme concentration held constant.

a. Concentrates incubated for 18 hrs. Cornell Nutrition Conference Proceedings, 1990. pp. 81-88.

b. Forage samples incubated for 2 hrs at higher SGP concentration. J. Dairy Sci. 1999. 82: 343-354.

2. NIRS - UIP as in Crude Protein NIRS (II. A. 4.).

D. Acid Detergent or Neutral Detergent Insoluble Crude Protein (ADI-CP, NDI-CP).

1. ADF or NDF residue is subjected to Kjeldahl or Kjeltec analysis to determine the protein fraction bound to the fiber. Sodium Sulfite not used for NDI-CP.

2. a. NIRS - ADI-CP - Used on fermented haycrop forages only.

b. NIRS - NDI-CP as in Crude Protein NIRS (II. A. 4.).

E. Non Protein Nitrogen (NPN)

1. Urea and Ammoniacal Nitrogen - AOAC 941.04.

2. Urea - AOAC 967.07.

III. Fiber

A. Acid Detergent Fiber (ADF)

1. ANKOM A200 Filter Bag Technique (FBT). ANKOM Application Note 01/02 "Method for Determining Acid Detergent Fiber". Solutions same as AOAC 973.18 (C). Samples individually weighed into filter bags and digested as a group of 24 in 2L of ADF solution in ANKOM A200 Digestion Unit. FBT eliminates filter steps. Samples are rinsed three times with boiling water in filter bags followed by an acetone rinse and drying at 100ºC for 2 hours.

2. Liquid samples - AOAC 973.18 (C). Whatman 541 filter paper and buchner funnels.

3. NIRS - ADF as in Crude Protein NIRS (II. A. 4.) - AOAC 989.03.

B. Neutral Detergent Fiber (NDF)

1. ANKOM A200 Filter Bag Technique (FBT). ANKOM Application Note 01/02 "Method for Determining Neutral Detergent Fiber (aNDF)". Solutions same as Journal of Dairy Science 74:3583 - 3597. Samples individually weighed into filter bags and digested as a group of 24 in 2L of NDF solution in ANKOM A200 Digestion Unit. Four ml of Alpha Amylase and 20g sodium sulfite are added at the start of digestion. FBT eliminates filter steps. Samples are rinsed three times with boiling water. Alpha Amylase is added to the first 2 rinses. Water rinses are followed by an acetone rinse and drying at 100ºC for 2 hours.

2. Liquid samples - Journal of Dairy Science 74:3583 - 3597, 10/91.

3. NIRS - NDF as in Crude Protein NIRS (II. A. 4.).

C. Crude Fiber - AOAC 962.09. Samples filtered through bingham linen after first boil and through Whatman AH-934 glass membrane filter paper after second boil.

D. Lignin

1. ANKOM A200 Filter Bag Technique (FBT). ANKOM Application Note 01/02 "Method for Determining Acid Detergent Lignin in DaisyII Incubator". Solution same as AOAC 973.18(D). ADF performed as in III.A.1. ADF residue digested as a group of 24 in 72% w/w sulfuric acid for 3 hours in ANKOM DaisyII Incubator at ambient temperature.

2. Liquid samples - AOAC 973.18(D). No asbestos.

3. NIRS - Lignin as in Crude Protein NIRS (II. A. 4.).

E. In-Vitro True Digestibility (Indigestible residue - IDR)

1. ANKOM DaisyII Filter Bag Technique (FBT). ANKOM Application Note 11/00 "In Vitro True Digestibility using the DaisyII Incubator". Rumen fluid collected from TMR fed, high producing lactating cow. Feed samples incubated in Van Soest buffer/rumen fluid mixture for 6, 24, 30, or 48 hours under anaerobic conditions at 39ºC. After incubation, samples extracted using NDF procedure to remove bacterial contamination. Residue is undigested fibrous material and is used to calculate digestibility.

2. NIRS - IDR 24, 30, or 48 as in Crude Protein NIRS (II. A. 4.).

IV. Minerals

A. Elements including Ca, P, Mg, K, Na, Fe, Zn, Cu, Mn, Mo, Co analyzed using a Thermo Jarrell Ash IRIS Advantage Inductively Coupled Plasma (ICP)

Radial Spectrometer.

1. General Feeds and Forage Types - Thermo Jarrell Ash "The Spectroscopist" Dec. 1994, Vol. 3. No. 1. pp 6-9. Samples ashed in muffle furnace at 500ºC for 4 hours. Three ml of 6N HCl are added to ash residue and evaporated to dryness on a 100º - 120ºC hot plate. Minerals extracted with acid solution (1.5N HNO_3 + 0.5N HCl) and determined using an IRIS Advantage.

2. Grain and Mineral Mixes - High Organic Matter (OM) mixes ashed 2 hours at 500ºC. Low OM samples not ashed. 10 ml Mineral Mix extracting solution (1.8N HCl + 0.3N HNO_3) added to sample and digested on 100º - 120ºC hot plate. Filtered through Whatman 4 filter paper into volumetric flasks using 1.5N HNO_3 + 0.5N HCl and minerals determined using an IRIS Advantage.

3. NIRS Ca, P, Mg, K as in Crude Protein NIRS (II. A. 4.).

B. Sulfur

1. Leco Model SC-432. Leco Application Note "Sulfur in Plant Tissue" Form 203-601-229, 08/92. Samples combusted in oxygen rich atmosphere at 1350°C. Sulfur bearing compounds break down freeing sulfur, then oxidized to form SO_2. Gases flow through an infrared detection cell which measures the concentration of SO_2. The instrument converts that value and reports a percent sulfur.

2. NIRS - S as in Crude Protein NIRS (II. A. 4.).

C. Chloride Ion - Potentiometric titration with $AgNO_3$ using Brinkman Metrohm 716 Titrino Titration Unit with silver electrode.

1. Metrohm Application Bulletin No. 130 by Metrohm Ltd., C-H-9101 Herisau, Switzerland distributed in the US by Brinkmann Instruments Inc., One Cantiaque Road, PO Box 1019, Westbury, NY 11590-0207, phone 1-800-645-30502.

2. The method by Metrohm is similar to the concepts found in: Cantliffe, D.J., MacDonald, G.E. and Peck, N.H. 1970. The potentiometric determination of nitrate and chloride in plant tissue. New York's Food and Life Sciences Bulletin. No.3, September 1970. Plant Sciences. Vegetable Crops Geneva. No. 1: 5-7.

V. Supplemental Services

A. Fat

1. Ether Extraction AOAC 2003.05 Crude Fat in Feeds, Cereal Grains, and

Forages

Extraction by Soxtec HT6 System using anhydrous diethyl ether. Crude fat residue determined gravimetrically after drying

2. Acid Hydrolysis - AOAC 954.02 - Crude Fat in Pet Food.

3. Dried Milk - AOAC 932.06 A (b) and 932.06 B (Roese-Gottlieb Method).

4. NIRS - Fat as in Crude Protein NIRS (II.A.4.)

B. Ash

1. AOAC Method 942.05.

2. NIRS - Ash as in Crude Protein NIRS (II. A. 4.).

C. Mycotoxins - Neogen Veratox Quantitative Test for Aflatoxin, Vomitoxin, Zearalenone, Fumonisin, T-2 Toxin, and Ochratoxin.

Each toxin test is a non-competitive or direct competitive enzyme-linked immunosorbent assay (ELISA). Free toxins or mycotoxin-enzyme conjugates bind to immobilized antibodies. A substrate is added and color develops as a result of the presence of bound conjugate. The color intensity formed is inversely related to toxin concentration. Optical density readings of samples are compared to controls and ppm or ppb are calculated. Sample optical densities are measured using a BioTek EL 301 instrument. Aflatoxin is approved for use by USDA's Federal Grain Inspection Service (FGIS). Vomitoxin is FGIS (Federal Grain Inspection Service) and GIPSA (USDA Grain Inspection, Packers and Stockyards Administration) approved and AOAC - Research Institute Performance Tested. Fumonisin is GIPSA (2001-102) and AOAC (2001.06) approved.

D. Nitrates

1. RQflex® Reflectometer Method - Nov. 2004 - present

EMD Application Note "Nitrates in Plant Sap", NITRA18.emd; 07/99; extraction modified.
EMD Chemicals Inc., 480 S. Democrat Road, Gibbstown, NJ 08027

1g of dried, ground sample is extracted in 50ml deionized water for 20 minutes by shaking at 280 oscillations/minute. Samples are filtered through Whatman 934-AH (1.5um) filter paper, then analyzed by RQflex® Reflectometer using Relectoquant® Nitrate test strips.

When a test strip is immersed in a sample, a reducing agent reduces nitrate ions to nitrite ions. In the presence of an acidic buffer, the nitrite ions react with an aromatic amine to form a diazonium salt. The salt reacts with N-(1-naphthyl)-ethyelene-diamine to form a red-violet azo dye that is measured reflectometrically. Nitrate concentration is proportional to the color reaction.

Each strip contains two reaction zones generating dual replicate analyses per sample. The RQflex® Reflectometer's double optic system measures the analyte concentration based on the light reflected from the dual reaction zones. Barcode-controlled software calculates the mean of those two measurements.

2. Cadmium Reduction Method - 1988 - Nov. 2004

Cadmium reduction reaction using Chromotropic Acid followed by colorimetric analysis utilizing Milton Roy MV 21 Spectrometer.

Hach Method - Hach Company, Loveland, Colorado.

Plant Tissue and Sap Analysis Manual. Literature Code #3118.
Extraction - pp. 130-131, no charcoal, shake 0.200g in 100ml water for 1 hour.
Analysis - pp. 132-133, NitraVer 5 substituted by NitraVer 6 and 3.

E. pH - Corning General Purpose Combination Electrode and Corning pH/ion meter 150.

F. Starch

1. YSI 2700 SELECT Biochemistry Analyzer - YSI Incorporated, Application Note Number 319.
Samples are pre-extracted for sugar by incubation in water bath and filtration on Whatman 41 filter paper. Residues are thermally solubilized using an autoclave, then incubated with glucoamylase enzyme to hydrolyze starch to produce dextrose. Samples injected into sample chamber of YSI Analyzer where dextrose diffuses into a membrane containing glucose oxidase. The dextrose is immediately oxidized to hydrogen peroxide and D-glucono-4-lactone. The hydrogen peroxide is detected amperometrically at the platinum electrode surface. The current flow at the electrode is directly proportional to the hydrogen peroxide concentration, and hence to the dextrose concentration. Starch is determined by multiplying dextrose by 0.9.

2. NIRS - Starch as in Crude Protein NIRS (II. A. 4.).

G. Sugar

1. West Virginia University Procedure by W.H. Hoover and T.K. Miller Webster. Determination of Nonstructural Carbohydrates.

This water soluble sugar method is described in the following paper:Hall, M.B., W.H. Hoover, J.P. Jennings and T.K. Miller Webster. 1999. A method for partitioning neutral detergent soluble carbohydrates. J. Sci. Food Agric. 79:2079-2086.

2. NIRS - Sugar as in Crude Protein NIRS (II. A. 4.).

H. Volatile Fatty Acids
Extraction - Samples blended for 2 min. in deionized water, filtered through cheesecloth, then filtered through disposable syringe filter. Adapted from Personal Communication, L.E. Chase, Ph.D., Cornell University.Analysis -

1. Acetic, Propionic, Butyric, Iso-butyric acids - Aliquot of extract mixed 1:1 ratio with 0.06M Oxalic acid containing 100ppm Trimethylacetic acid (internal standard). Samples injected into a Perkin Elmer Autosystem XL Gas Chrmatograph containing a Supelco packed column with the following specifications: 2m x 2mm Tightspec ID, 4% Carbowax 20M on 80/120 B-DA.

Procedure based upon:
"GC Separation of VFA C2-C5" Supelco GC Bulletin 749F, 1975.
"Analyzing Fatty Acids by Packed Column Gas Chromatography" Supelco GC Bulletin 856A, 1990.
"Volatile Fatty Acid SOP" W.H. Miner Institute, Chazy, NY.

2. Lactic acid - Aliquot of extract analyzed for L-Lactate using a YSI 2700 SELECT Biochemistry Analyzer equipped with an L-Lactate membrane. YSI User's Manual, page 4-7.

Samples injected into sample chamber of YSI Analyzer where L-Lactate diffuses into a membrane containing L-Lactate oxidase. The L-Lactate is immediately oxidized to hydrogen peroxide and pyruvate. The hydrogen peroxide is detected amperometrically at the platinum electrode surface. The current flow at the electrode is directly proportional to the hydrogen peroxide concentration, and hence to the L-Lactate concentration. Total Lactic acid is determined by multiplying L-Lactate by 2.0.

VI. Manure

All results corrected for density except total solids.

A. Total Solids

1. Liquid or solid; no bedding
    - Oven - 100°C for 16 hours (gravity).
2. Liquid or solid with bedding
    - Oven - 60°C for 6-8 hours (forced air).
    - Near Infrared Reflectance Spectroscopy - AOAC 991.03

B. Nitrogen, total

1. Kjeldahl - AOAC 984.13 - for wet samples or as-is basis (primary).
2. Kjeltec - AOAC 2001.11 - for wet samples or as-is basis (secondary).
3. Combustion by Leco FP-528 - AOAC 990.03 - for pre-dried samples.

C. Ammonia-Nitrogen

1. Distillation - AOAC 941.04.

D. Organic Nitrogen

1. by difference (Total N - Ammonia-N).

E. Minerals

1. Ca, P, Mg, K, Na, Fe, Zn, Cu, Mn, Mo, Co
    - Weigh 1g dried, ground or 3g wet sample. Dry ash at 500°C for 4 hours, followed by wet ash with 1:1 HCl on 100 - 120°C hot plate. Final extraction and dilution in 1.5N HCl + 0.5N HNO_3.
    - Analysis by Thermo IRIS Advantage DX Inductively Coupled Plasma (ICP) Radial Spectrometer..
2. Sulfur (S)
    - Combustion by Leco Model SC-432. 200mg dried sample burned in oxygen rich atmosphere at 1350°C. Sulfur bearing compounds are broken down freeing sulfur, then oxidized to form SO_2. Infrared detection cell measures SO_2 concentration and instrument converts and reports %sulfur
3. Chloride (Cl)
    - Weigh 0.5g dried, ground or 5g wet sample. Extract in 50ml 0.1N HNO_3 followed by potentiometric titration with $AgNO_3$ using Brinkmann Metrohm 716 Titrino Titration Unit with silver

electrode.

F. Ash

1. AOAC 942.05

G. pH

1. AOAC 973.04 (Technique similar to pH of peat).

35ml liquid sample poured into 50ml beaker. 15g solid or semi-solid sample weighed into 200 ml deionized water, stirred, and allowed to stabilize five minutes. Analyzed using Thermo Orion Posi-pHlo SympHony Electrode and Thermo Orion 410 A meter.

H. Nitrates

1. RQflex Reflectometer Method.

Weigh 1g of dried, ground or 10g wet sample. Extract in 50ml deionized water for 20 minutes by shaking at 280 oscillations/minute. Filter through Whatman 934-AH (1.5um) filter paper, then analyze by RQflex® Reflectometer using Relectoquant® Nitrate test strips.

I. Density

1. Standard Vial Method

Samples weighed into fixed volume vessel. Density calculated and expressed in kg/l, lbs./ft3, and lbs./gal.

VII. Water

A. Coliform and *E. coli* (presence/absence in 100ml)

Colilert® - IDEXX Laboratories, Inc., One IDEXX Drive, Westbrook, Maine 04092,

Colilert® uses the patented Defined Substrate Technology® (DST®) to simultaneously detect total coliforms and E. coli. Two nutrient-indicators, ONPG and MUG, are the major sources of carbon in Colilert® and can be metabolized by the coliform enzyme ß-galactosidase and the E. coli enzyme ß-glucuronidase, respectively.

As coliforms grow in Colilert®, they use ß-galactosidase to metabolize ONPG and change it from colorless to yellow to indicate presence.

E. coli use ß-glucuronidase to metabolize MUG and create fluorescence to indicate presence. Since most non-coliforms do not have these enzymes, they are unable to grow and interfere.

Colilert® is US FDA Approved for Dairy Waters.

Milk Laboratory Evaluation Form FDA 2400m (3/01)

Colilert® is also US EPA-approved for drinking water presence/absence(P/A) and Most Probable Number (MPN) and for source water. Pertinent references:

June 29, 1989 US EPA Federal Register Colilert® coliform approval
June 10, 1992 US EPA Federal Register Colilert® E. coli approval

Colilert® detects total coliforms and E. coli at 1 organism/100 ml.

B. Standard Plate Count (colonies per ml)

US FDA Milk Laboratory Evaluation Form FDA 2400a (1/01)

Petrifilm Aerobic Count Method - Deposit 1ml of sample onto petrifilm and cover. Distribute sample with spreader and allow gel to solidify for 1 minute. Incubate 48 hours at 32°C. Count colonies when incubation time is complete.

C. pH

AOAC 973.41

Analyzed using Thermo Orion Posi-pHlo SympHony Electrode and Thermo Orion 410 A meter. Calibrated with buffers referenced to NIST SRMs. pH 4 buffer contains potassium hydrogen phthalate and pH 7 buffer contains sodium phosphate dibasic and potassium phosphate monobasic.

D. Nitrates (ppm NO3 and ppm NO3-N)

RQflex Reflectometer Method. Nitrate in Waste Water. NITRA12.emd; 12/95.
EMD Chemicals Inc., 480 S. Democrat Road, Gibbstown, NJ 08027

Reflectometric determination after reduction to nitrite and reaction with Griess reagent. Reflectoquant® Nitrate test strip immersed in water, allowed to react for specified time, then analyzed by RQflex® Reflectometer.

Nitrate-Nitrogen (NO3-N) calculated as Nitrates (NO3) divided by 4.427.

E. Sulfates (ppm SO4 and SO4-S)

Turbidimetric Method. 957-13-3. (Based upon principles in AOAC 973.57).
Orbeco Analytical Systems, Inc., 185 Marine Street, Farmingdale, NY 11735, 1-800-922-5242.

Conditioning reagent containing glycerol, alcohol, sodium chloride and hydrochloric acid added to water. BaCl2 crystal added resulting in precipitation of sulfate as $BaSO_4$. Suspension is measured photometrically at 420nm and sulfate concentration determined from a standard conversion table.

Sulfate-sulfur (SO_4-S) calculated as sulfates (SO_4) divided by 2.996.

F. Total Dissolved Solids (ppm TDS)

Conductivity Method. ES&D Model 76 Conductivity meter.

The total quantity of free ions is determined by ability of the sample to conduct an electrical current. Immerse electrode in water while gently stirring. Measure temperature of water, set temperature knob, allow meter to stabilize 15 seconds, then record reading.

G. Minerals

1. ppm Ca, P, Mg, K, Na, Fe, Zn, Cu, Mn, Mo

   Analyzed directly with no sample preparation by Thermo IRIS Advantage HX Inductively Coupled Plasma (ICP) Radial Spectrometer.

   ppm Hardness as $CaCO_3$ equivalent calculated as (Ca x 2.5) + (Mg x 4.1).

2. ppm Chloride (Cl)

   25ml 0.2N HNO_3 added to 25ml of water followed by potentiometric titration with $AgNO_3$ using Brinkmann Metrohm 716 Titrino Titration Unit with silver electrode.

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