THE CHARACTERIZATION OF SULFUR FLOWS IN FARM DIGESTERS at EIGHT FARMS

Prepared for

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ABSTRACT

The flow of sulfur through eight dairy farms in New York State, inputs to animals, digester influent and effluent and biogas, were studied from January 2007 to March 2008. Digesters on five farms were traditional plug flow, two were horizontal and mixed and one was vertical with a mixer. Food waste was added to the digester at two dairy farms and there was pre-separation of solids at two farms. On the farms that did not use food waste, 88 percent of the sulfur entering the digester came from the total mixed ration (TMR), 5 percent from drinking water and 7percent from bedding. Where food waste was used 73 percent came from the TMR, 10 percent from food waste, 13 percent from water and 4 percent from bedding. One farm using food waste had a high sulfur content drinking water which shifted these percentages.

The concentration of hydrogen sulfide in the biogas ranged from 1,020 to 6,730 ppm. Digesters with no pretreatment of influent averaged 11.1 pounds of sulfur entering the digester for each 100 cow-days, those with pretreatment averaged 4.8 while those with food waste averaged 13.8. On average, 25 percent of the sulfur entering the digester was removed in the biogas.

Key Words: Digesters, Sulfur, Biogas

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EXECUTIVE SUMMARY

The flow of sulfur in the manure handling system at eight dairy farms in New York State was studied under this contract from January 2007 to March 2008. The sources of sulfur and the mass flow through the various paths the sulfur took through the system including the anaerobic digester were included. The sources/inputs included the total mixed ration (TMR), drinking water, bedding and foot bath. Two farms utilized food waste to increase the production of biogas.

The farms varied considerably in the number of milking cows, dry cows, heifers (big and small) and calves. These animals were combined into a number of "milking cow equivalents". This was done using formulas from American Society of Agricultural and Biological Engineers (ASABE) that calculate the manure produced by each group of animals on a farm whose manure went to the digester. The formulas predict the total solids produced per day (lb TS/day) for an each animal group. Taking the total solids produced per day by all the animals and dividing that total by the pounds of total solids produced by a milking cow on that farm gave an equivalent number of milking cows. The average number of "dairy cows" for the eight dairy farms in the study was 792 with a range from 430 to 1,161 equivalent cows.

Digesters on five farms studied were traditional plug flow type, two were horizontal – mixed and one was a vertical design with mixer. At six farms the digesters were fed manure from the barn and at two farms the digesters were fed separated liquid. On two farms food waste was mixed with the cow manure.

For the 6 farms where the digesters were fed just cow manure, 88% of the sulfur entering the digester came from the total mixed ration. The remainder was in the drinking water and bedding, 5% and 7%, respectively. For the two farms where food waste was added, 73% of sulfur came from TMR, 10% from the food waste, 13% from drinking water and 4% from bedding. One of farms feeding food waste had a high concentration of sulfur in the drinking water.

Drinking water was not a major source of sulfur. However, there was considerable variation in the amount of sulfur contributed via the drinking water. The supply water at the 8 dairy farms ranged from 4.9 mg SO_4 per liter to 972. The highest contribution of sulfur in the drinking water was 3.9 lb of sulfur per 100 cow equivalent –days which was 20% of the total sulfur inputs.

Two farms used copper sulfate in the foot bath. The highest contribution of sulfur from the foot bath was 0.54 lbs S per 100 cow-equivalents, day (4% of the total sulfur at that farm) to a low of 0.09 lbs per 100 cow-equivalents per day. Two farms used separated solids as bedding. This bedding averaged 0.124 percent sulfur while the wood shaving was 0.10 percent S. These values are based on total solids.

To calculate the sulfur "lost" during digestion the mass flow and sulfur concentration of the influent and effluent was needed. Obtaining an accurate measure of these mass flows was impossible at some farms and very difficult at others. A mass balance method (MBM) was developed by writing two mass balance equations, one for the total solids and a second for water. These two equations were solved simultaneously. Data needed to solve these equations included the total solids and sulfur content of the influent and effluent and the production and characteristics of biogas.

The sulfur in the digester influent where there was no pretreatment averaged 11.1 lbs S per 100 cow-days. Where there was pre-separation of solids the average was reduced to 4.8 lbs S per 100 cow-days. The two farms that added food waste averaged 13.8 lbs S/100 cow-days. The sulfur in the digester effluent for all 8 farms averaged 7.58 lbs S per 100 cow-days giving an average change in sulfur through the digester of 2.61 lbs per 100 cows. These numbers were all calculated using the MBM. The sulfur in the biogas averaged 2.68 lbs S/100 cow-days. This value was based on actual production of biogas and measured concentration of sulfur in the biogas.

The concentration of hydrogen sulfide in the biogas ranged from 1,020 to 6,730 ppm with an average concentration of 3,860 ppm. On average, 25 percent of the sulfur entering the digester was removed in the biogas. The range was 16 to 40 percent.

Section 1
OVERVIEW

The flow of sulfur in the manure handling system at eight dairy farms in New York State was studied under this contract. The sources of sulfur and the mass flow through the various paths the sulfur took through the system including the anaerobic digester were included. The sources/inputs included the total mixed ration (TMR), drinking water, bedding and foot bath. Two farms utilized food waste to increase the production of biogas.

The farms varied considerably in the number of milking cows, dry cows, heifers (big and small) and calves. The number of cows being milked at each farm is given in Table 1-1. These animals were combined into a number of "milking cow" equivalents. This was done using formulas from ASABE (American Society of Agricultural and Biological Engineers) that calculate the manure produced by each group of animals on a farm whose manure went to the digester. The formulas predict the total solids produced per day (lb TS/day) for an each animal group. Taking the total solids produced per day by all the animals and dividing that total by the pounds of total solids produced by a milking cow at that farm gave an equivalent number of milking cows. The average number of "dairy cows" for the eight dairy farms in the study was 800 with a range from 430 to 1,161 equivalent cows.

Digesters on five farms studied were traditional plug flow type, two were horizontal – mixed and one was a vertical design with mixer. See Table 1-1 for details. At six farms the digesters were fed manure from the barn and at two farms the digesters were fed separated liquid. A food waste was mixed with the cow manure on two farms.

Table 1-1. Dairy Farms Studied.

Farm Name	Location	Cow		Digester
		Milking	Equivalent*	
AA Dairy	Candor	430	430	Plug flow,
EL-VI	Newark	900	948	Plug flow, pre-digester separation, partial herd
Emerling	Perry	948	1,049	Plug flow
Noblehurst	Linwood	473	592	Plug flow, twin parallel
Patterson	Auburn	881	1,108	Mixed, food waste
Ridgeline	Clymer	413	518	Mixed, "U" shape, food waste
Sheland	Watertown	473	559	Vertical, pre-digester separation, mixed
Twin Birch	Skaneateles	991	1,161	Plug flow
Average		689	800	

* Equivalent number of milking cows including all animals, based on ASABE formulas and total solids

The concentration of sulfur in the various inputs is given in Table 1-2. The average concentration of sulfur in the TMR among the dairy farms was 0.103% as fed with a standard deviation of only 0.01. The drinking water, however, varied greatly between farms. The average concentration of sulfate in the water was 68.2 mg SO_4/l with a standard deviation of 98.6 and a confidence interval of 68. At one farm a combination of water from a pond (low sulfur) and from a well (high sulfur) was used. Two farms used kiln dried wood shavings/saw dust for bedding with an average sulfur concentration of 0.1%, on a total solids basis. Four farms used separated solids with an average sulfur concentration of 0.124% on a total solids basis or about 25% more sulfur than dry sawdust/shavings.

The mass flow of the various inputs was obtained from the farm operator. These inputs were analyzed for sulfur at Dairy One, Inc. in Ithaca, NY. With this data, the sulfur (pounds per day) for each input was calculated. The sulfur in the manure leaving the barn was assumed to be the pounds of sulfur in the inputs minus the sulfur in the milk. This raw data is presented in Table 1-3 along with data on a per 100 cow basis. On four dairy farms in this study there was no treatment of the manure prior to the digester (AA Dairy, Emerling, Noblehurst and Twin Birch). For these farms the calculated sulfur content in the manure leaving the barn averaged 87.3 lb S/day. Using the "mass balance method", described below, the predicted sulfur in the digester influent for these four farms average 91.1 lb S/day. The difference was only 3.8 lb S/day, a 4.4% difference.

In order to calculate the mass flow of sulfur into and out of the digester, the mass flow (lb/day) of the influent and effluent must be known. Three methods were used to measure/estimate the mass flow of manure to the digester (influent). These included; 1) measuring the change in depth of manure in the pits with an ultrasonic instrument, 2) using equations from ASABE to calculate the manure production for the animals and 3) using a mass balance method (MBM) calculation. At one farm the ultrasonic instrument was used to measure digester effluent. In general there was/is no way to measure the mass flow of the digester effluent.

The "mass balance method" (solving two equations simultaneously) calculates the mass flow of the influent and effluent. The data needed for the mass balance method are 1) concentration (%) of total solids and sulfur in the digester influent and effluent, 2) the production of biogas (cubic feet per day), 3) the concentration of carbon dioxide and 4) biogas temperature. With the mass flow of the influent and effluent and the measured concentration of sulfur, the mass sulfur flow (lb S/day) in the influent and effluent can be calculated. The change in the mass flow of sulfur through the digester should be a good approximation of the sulfur in the biogas. Because the biogas production and its properties are used in the mass balance method one would assume that the computed "loss" of sulfur between the influent and effluent would be equal to the sulfur in the biogas. This is shown in the data in Table 1-8. The average change in sulfur content for the 8 farms was 23.0 lb S/day. The average content of sulfur in the biogas was 23.6 lb/day.

Table 1-2. Concentrations of Sulfur in TMR, Water and Bedding.

	Dairy Farms Studied										
Parameter	AA Dairy	EL-VI	Emerling	Noblehurst	Patterson	Ridgeline	Sheland	Twin Birch	Average	St. Dev	Conf Int.
	Concentration of Sulfur										
TMR, as fed (weighted average) %	0.097	0.092	0.113	0.103	0.12	0.088	0.087	0.12	0.103	0.01	0.01
Drinking Water, mg SO_4/L	4.9	94.6	19.1	6.4	139*	5.9	5.3	12.7	36.0	51.5	35.7
Bedding											
% S of TS, kiln dried **	0.1					0.1			0.10		
%S of TS, separated solids			0.085		0.09		0.2	0.12	0.124	0.05	0.05
Food Waste, as received %					0.01	0.02					
* weighted average (pond and well)											
** from reference, see appendix											

Table 1-3. Summary of Dairy Farms Studied and Flow of Sulfur From Barn and Food Waste.

	Dairy Farms Studied										
	AA Dairy	EL-VI	Emerling	Noblehurst	Patterson	Ridgeline	Sheland	Twin Birch			
Number of Milking Cows, equivalent	430	948	1,049	592	1,108	518	559	1,161			
(based on ASABE calculations)											
	Pounds of Sulfur per Day										
TMR	44	97.5	134	57.4	146	47.8	72.3	129			
Drinking Water	0.44	19.9	1.2	3.4	41	0.62	0.71	5.0			
Bedding	1.0		2.0		12.5	0.71	3.9	27.9			
Foot Bath		5.1						1.0			
Milk	-7.4	-18.5	-20.2	-9.3	-16.1	-7.8	-9.6	-20.3			
Manure from Barn	38.0	104	117	51.5	183	41.3	67.3	143			
Food Waste					15.3	8.2					
Total	38.0	104	117	51.5	199	49.5	67.3	143			
									Avg	Std Dev	Confid Int
	Inputs - pounds of sulfur per 100 "milking cow"-days (based on conditions at time of study)										
TMR	10.2	10.3	12.8	9.7	13.2	9.2	12.9	11.1	11.2	1.7	1.18
Drinking Water	0.10	2.10	0.11	0.57	3.70	0.12	0.13	0.43	0.98	1.4	0.97
Bedding	0.23		0.19		1.13	0.14	0.70	2.40	0.80	0.87	0.70
Foot Bath		0.54						0.09	0.31		
Total input	10.57	12.92	13.08	10.27	18.01	9.48	13.76	14.03	12.6	2.9	2.00
Milk	-1.72	-1.95	-1.93	-1.57	-1.45	-1.51	-1.72	-1.75	-1.69	0.20	0.14
Manure from Barn	8.85	11.0	11.2	8.70	16.6	7.98	12.0	12.3	10.9	2.9	2.02
Food Waste					1.46	1.58			1.52		
Total	8.85	11.0	11.2	8.70	18.0	9.56	12.0	12.3	11.3	3.20	2.22

Table 1-4. Summary of Sulfur Into Digester.

	Dairy Farms Studied							
Parameter	AA Dairy	EL-VI	Emerling	Noblehurst	Patterson	Ridgeline	Sheland	Twin Birch
Number of Milking Cows, equivalent	430	948	1,049	592	1,049	518	592	1,161
(based on ASABE calculations)								
	Pounds of Sulfur per Day							
Digester Influent (Mass Balance Method)								
no pretreatment	49.5		97.1	56.5				162
pre-separation and partial loading		27.5					45.2	
food waste added					194	46.8		

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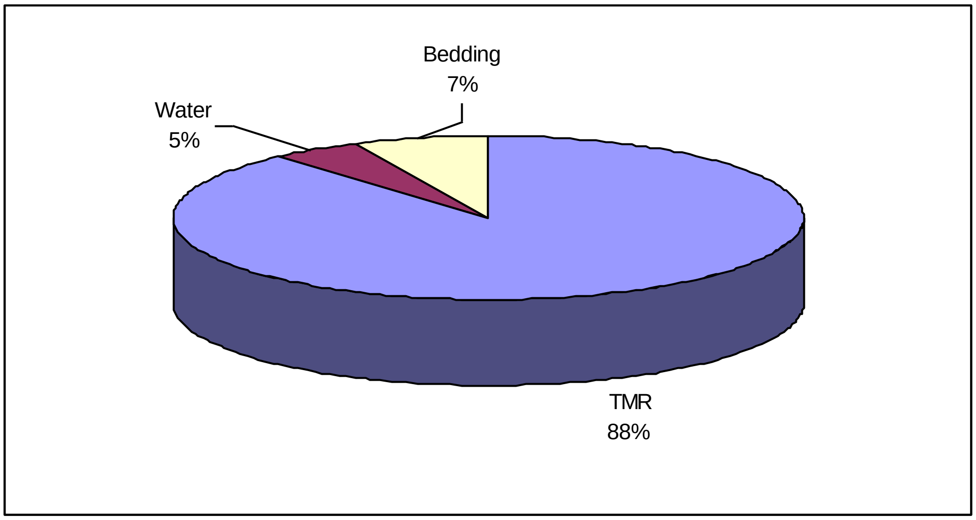
The sources of sulfur in the influent for those farms not using food waste (TMR, water and bedding) are summarized in Tables 1-5. The major source of sulfur is the TMR at 88% as shown in the pie chart in Figure 1-1.

Table 1-5. Sources of Sulfur for Farms Not Using Food Waste.

	Lb Sulfur/100 cow-days							
Parameter	AA Dairy	EL-VI	Emerling	Noblehurst	Twin Birch	Sheland	Average	Percent
TMR	10.23	10.28	12.77	9.70	11.11	12.21	11.05	88.4
Water	0.10	2.10	0.11	0.57	0.43	0.12	0.57	4.6
Bedding	0.23		0.19		2.40	0.66	0.87	7.0

Figure 1-1. Sources of Sulfur for Farms Not Using Food Waste.

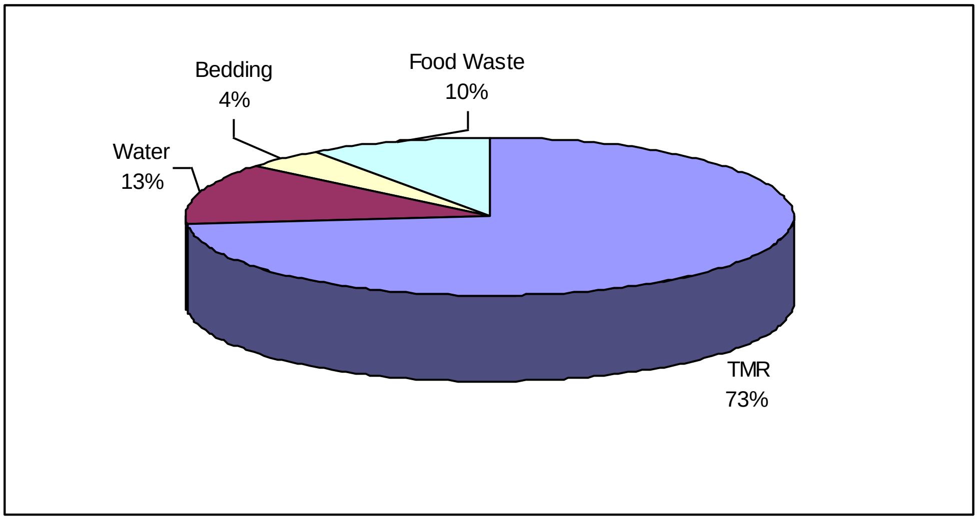


The sources of sulfur for the two farms that added food waste to the dairy manure are shown in Table 1-6. About 10% of the total sulfur entering the digester came from the food waste. This information is also shown in the pie chart in Figure 1-2

Table 1-6. Sources of Sulfur for Farms Adding Food Waste.

	Lb Sulfur/100 cow-days			
Parameter	Patterson	Ridgeline	Average	Percent
TMR	13.92	9.23	11.6	73.4
Water	3.91	0.12	2.01	12.8
Bedding	1.19	0.14	0.66	4.21
Food Waste	1.46	1.58	1.52	9.65

Figure 1-2. Sources of Sulfur for Farms Adding Food Waste.



Reducing the amount of sulfur entering a dairy farm anaerobic digester would appear to start with the total mixed ration as over 70% of the sulfur entering the digester originates in the TMR. However, there is a certain amount of sulfur required for a balanced diet for a dairy cow. Sulfur is present in many of the components used to make up a balanced diet. This study did not investigate sulfur content of the individual ingredients in a "balanced" ration.

Table 1-7. Properties of Biogas.

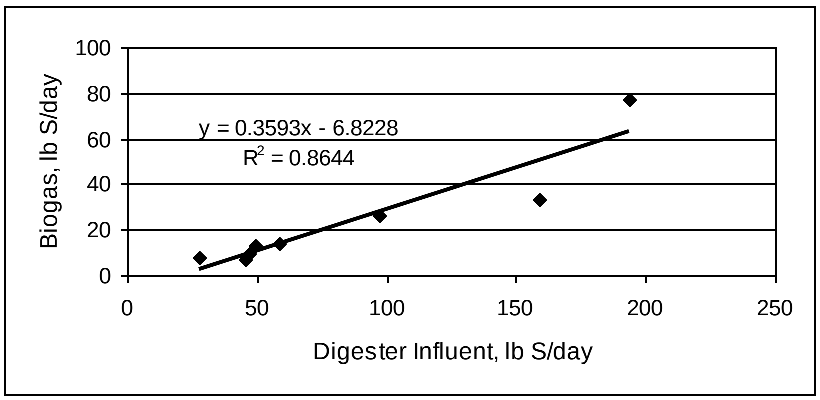
	Dairy Farms Studied										
Parameter	AA Dairy	EL-VI	Emerling	Noblehurst	Patterson	Ridgeline	Sheland	Twin Birch	Average	St. Dev	Conf Int.
Biogas, Hydrogen Sulfide, ppm	4,100	6,730	3,540	3,390	6,180	1,020	2,238	3,700	3,862	1,879	1,302
Biogas, Carbon Dioxide, %	32	32	31	38	38	31	35	36	34.1	3.00	2.08
Biogas, Methane, %	67	67	69	62	62	69	64	64	65.5	2.88	1.99

The relationship between the sulfur in the digester influent and the sulfur in the biogas was analyzed. Table 1-8 shows the pounds of sulfur in the influent and the pounds of sulfur in the biogas (lb S/day). The percent removed in the biogas is also given. On average, 25.6% of the influent sulfur was removed in the biogas. The two sulfur mass flows are plotted against each other in Figure 1-3. The slope of the linear trend line is 36.5% which predicts that 36.5% of the influent sulfur will be removed in the biogas. The R^2 value for the linear fit was 0.86, higher value than for either power or exponential tend lines.

Table 1-8. Sulfur Removed in the Biogas.

Farm	Influent*	Effluent*	Change	Biogas	Discrepancy	Percent S in Biogas Removed
	lb S/day					
AA Dairy	49.5	38.6	10.9	13.5	2.6	27.3
EL-VI	27.5	20.5	7	8.3	1.3	30.2
Emerling	97.1	80.7	16.4	26	9.6	26.8
Noblehurst	58.9	48.5	10.4	13.8	3.4	23.4
Patterson	194	104	90	77	-13	39.7
Ridgeline	47.2	35.1	12.1	9.8	-2.3	20.8
Sheland	45.2	42.6	2.6	7.2	4.6	15.9
Twin Birch	159	124	35	33.6	-1.4	21.1
					Average	25.6
* based on mass balance method						

Figure 1-3. Relationship between Influent Sulfur and Biogas Sulfur.



The results of the mass balance analysis are given in Table 1-9. The farms were divided into three groups, 1) no pretreatment of the influent, 2) pre-separation of solids and 3) food waste was added. The average pounds of sulfur in the influent and effluent are given. Because of the wide divergence in the operation of the two digesters using separation and the two farms where food waste is added, the average values are meaningless as well as the standard deviations and confidence intervals.

Table 1-9. Summary of Sulfur Flow Through Digesters.

Parameters	Number of Farms	Pounds of Sulfur per 100 cow-days		
		Average	Standard Deviation	Confidence interval (5%)
Influent – no pretreatment*	4	11.1	2.0	1.73
Influent – separation*	2	4.8	2.7+	+
Food waste added*	2	13.8	6.6+	+
Digester Effluent*	8	7.58	2.6	2.32
Change in Digester	8	2.61	2.6	
Biogas	8	2.68	2.1	
Discrepancy	8	0.07		

* Based on Mass Balance Method
+ With only 2 farms in this sample the standard deviation and confidence interval may not be useful.

The change in mass flow of sulfur through the digester based on the mass flow method averaged 2.61 lb S per 100 cow-days for eight digesters. The sulfur in the biogas, computed with biogas flow and the concentration of sulfur in the biogas, average 2.68 lb S per 100 cow-days.

The relationship between the production of biogas and the volatile solids destroyed was analyzed and eventually the production of biogas per milking cow. The total solids entering the digester (manure plus bedding and food waste, where applicable) was taken from the results of the mass balance method (MBM). The results are shown in Table 1-10. Using the pounds of total solids produced by a milking cow on that farm, as predicted by the ASABE equations, the number of "milking cows equivalent" based on these total solids was calculated. This number is shown on line 3 in Table 1-10. The numbers of equivalent cows, based on just manure production, are given on line 4 for comparison. At the EL-VI farm the "milk cow equivalents" based on the digester influent was 204 while the ASABE equivalent was 1,050. Roughly 20% of the total solids leaving the barn were entering the digester. The two "equivalents" at Sheland Farm were closer than expected because of the pre-separation of solids. More investigation needs to be done to explain these differences.

The average biogas production at the farms is given on line 5. Dividing the cubic feet of biogas per day by the number of milking cow equivalents (line 3) gave the biogas production per milking cow equivalent (line 6). The average biogas production per milking cow equivalent where food waste was not added to the manure was 65.4 ft^3/cow-equivalent with a standard deviation of 5.6 and a confidence interval of ± 3.9. The average biogas production on the two farms feeding food waste was 107cuft/cow-equivalent based on total solids lost (volatile solids) – some 60% greater than where no food waste was fed.

Reports for the eight dairy farms are attached.

Table 1-10. Analysis of Total Solids Entering Digester and Production of Biogas.

Analysis of Total Solids Entering Digester and Production of Biogas								
	Dairy Farms Studied							
	AA Dairy	EL-VI	Emerling	Noblehurst	Patterson	Ridgeline	Sheland	Twin Birch
Total solids to digester per day from MBM, lbs 1	10,270	3,620	25,920	13,170	30,650	14,780	10,490	28,050
Total solids per milking cow-day (ASABE) 2	16.7	17.7	17.8	17.4	17.2	16.5	17.4	17.7
Equivalent number of milking cows, digester* (1) / (2) = 3	615	205	1,456	757	1,782	896	603	1,585
Equivalent number of milking cows on farm (ASABE) 4	430	948	1,049	592	1,108	518	559	1,161
Cows being milked	430	900	948	473	881	413	473	991
Production of Biogas, cuft/day (wet, 60F) 5	39,700	15,000	88,200	44,640	151,700	115,600	39,180	111,200
Biogas, cuft/cow equivalent digester-day, (5) / (3) = 6	64.6	73.3	60.6	59.0	85.1	129.1	65.0	70.2
Average biogas production on farms not feeding food waste		65.4	cuft/cow-day					
Standard Deviation		5.5						
Confidence Interval		3.8						
* equivalent based on total solids entering digester								
1) MBM = mass balance method This number would include TS from bedding and food waste where appropriate.								
2) Predicted pounds of total solids produced per milking cow at given RHA using ASABE equations.								
3) Equivalent number of milking cows based on the TS from MBM and the TS per milking cow (ASABE)								

* Assumes the density of raw manure and separated liquid to be 8.34 lbs/gal

APPENDIX
References and Equations

Equations

Standard Deviation (*s*):

$$s = \sqrt{\frac{\sum (x - m)}{n - 1}^{2}} \quad \text{where } \sum = \text{sum, } x = \textit{total scores, } m = \textit{mean, } n = \textit{number of scores}$$

Confidence Interval (C.I.) (assume 95% confidence)

If a statistic is normally distributed and the standard error of the statistic is known, then a confidence interval for that statistic can be computed as follows:

statistic ± *(z)* (σ_{stat}) where σ_{stat} *is the standard error of the statistic*

Dixon Q-test: Detection of a single outlier: www.chem.uoa.gr/applets/Applet**Qtest**/Text_**Qtest**2.htm

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Cow Equivalent:
Proposal for ASAE D384-2, Manure Production and Characteristics. Section 5.0: Equations for As-Excreted Manure Characteristics Estimates for Dairy Cattle. July 2005.

Sulfur Content in Wood:
http://ncp.fi/koulutusohjelmat/metsa/5Eurese/WoodEnergyEcology/emmisions.htm
http://bioenergy.ornl.gov/papers/bioen96/mclaugh.html
www.fpl.fs.fed.us/documnts/pdf1983/baker83a.pdf
http://64.233.169.104/search?q=cache:2z8U4UDr28YJ:leeds-faculty.colorado.edu/lawrence/sys..

Sulfur Content in Milk:
http://www.traceminerals.com/inorganic.html