Title: Effects of Manure Handling and Application Method on Odor and Gas Emission Potential of Swine Manure – NPB #08-259

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Industry Summary:

This project investigated manure composition and emissions potential of swine manure in opposing contexts of desired and undesired methane generation. In the main study, the full-scale treatment effects of anaerobic digestion on the air emissions potential of swine manure were investigated to improve our understanding of the practical air quality implications of digesting manure. The project also facilitated detailed analysis of swine manure from deep-pit finishing barns across the Midwest in support of a multi-state effort to find a cause behind increased incidence of foam in such facilities. This foam, which consists of methane and other pit gases, has undesirable consequences for facility management and has been implicated in a number of flash fires.

In the first study, manure slurry and digester effluent samples were collected from a pork production facility in eastern Nebraska that utilizes a complete-mix anaerobic digester to treat the manure and produce biogas for generating electricity. Samples were collected from three sites in the manure stream (below-barn pit, digester outlet, and holding pond) over a 15-month period to observe changes in manure composition as a result of manure treatment and over time. When compared for each sampling date, the concentration of manure constituents usually decreased as the manure was digested and stored. This pattern held true on eight of the twelve sampling dates, but for three consecutive sampling events the methane digester was not functioning well and produced little methane. When the digester was operating as designed, chemical oxygen demand was reduced by an average of 45%, odorous volatile fatty acids were reduced by an average of 66%, and ammonia increased by an average of 58%. These results affirm that organic matter is being broken down as desired in the digester. One implication for pork producers is that a functional digester clearly provides a basis for controlling odor during storage of [digested] manure, with subsequent benefits expected for land application as well. The results of this study also reinforced a greater need for conserving nitrogen in digested manure. While digesters improve the plant availability of manure nitrogen by converting organic N into ammonia, much of this fertilizer benefit may be lost through ammonia volatilization during storage and application of the digester effluent.

This project also facilitated extensive analyses of twenty-six manure and foam samples collected from deep-pit pork production facilities in Iowa, Illinois, Minnesota and Nebraska. The analyses included a standard manure analysis (for pH, solids contents, and macro/micronutrient levels); a feed analysis (for protein, fiber and energy composition); and a fat analysis (for levels of 45 different volatile fatty acids). In subsequent statistical analysis by the University of Minnesota, correlations were found between fat content and foam, but no other correlations could be established. While the manure and foam analyses did not identify a specific manageable cause for this facility management problem, they did help narrow down the scope for future study.

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Keywords: Manure analysis, Digester, Foam, Volatile fatty acids

Scientific Abstract:

Manure composition and emissions potential of swine manure were investigated in opposing contexts of desired and undesired methane generation. In the main study, the full-scale treatment effects of anaerobic digestion on the air emissions potential of swine manure were investigated. Manure slurry and digester effluent samples were collected from a pork production facility in eastern Nebraska that utilizes a complete-mix anaerobic digester to treat the manure and produce biogas for use in generating electricity. Samples were collected from three sites in the manure stream (below-barn pit, digester outlet, and holding pond) from 9/22/08 through 12/2/09 in order to observe changes in manure composition as a result of manure treatment and over time. Significant differences were observed in nearly all chemical and odorous compound constituents between the samples collected from the three locations studied at this operation. When compared for each sampling date, the concentration of manure constituents usually decreased as the manure was digested and stored. This pattern held true on eight of the twelve sampling dates, but for three consecutive sampling events the methane digester was not functioning well and produced little methane. When the digester was operating as designed, chemical oxygen demand was reduced by an average of 45%, odorous volatile fatty acids were reduced by an average of 66%, and ammonia increased by an average of 58%. A very clear trend was for odorous compounds to decrease in concentration as the manure slurry moved through the digester and as the effluent was subsequently stored in the basin. Volatile fatty acids (VFA) were consistently detected in all samples with branched-chain VFA comprising $<10\%$ of the total VFA. The proportion of total VFA that were branched-chain VFA was higher in the digester than in the pit when the digester was performing as designed. Aromatic compounds were also detected, but were in lower concentrations compared to VFA. The project also facilitated extensive compositional analyses of twenty-six manure and foam samples that were collected from deep-pit pork production facilities in Iowa, Illinois, Minnesota and Nebraska. The analyses included a standard manure analysis (for pH, solids contents, and macro and micronutrient levels); a feed analysis (for protein, fiber and energy composition); and a fat analysis (for levels of 45 different VFAs). In subsequent statistical analysis by the University of Minnesota, correlations were found between fat content and foam, but no other correlations could be established.

Introduction:

Manure is a valuable co-product of pork production due to it being a source of crop nutrients and soil-enhancing organic matter, but environmental concerns associated with manure require continued improvement in understanding and management of manure. One of the main environmental concerns about manure involves the emission of gases and odor during storage, handling, and application. Reducing odor from pork production continues to be an area of emphasis for the industry, as it looks to enhance social and environmental acceptance in rural communities. Air emissions in general have become a focus of attention due to increased scrutiny of animal agriculture by state and federal environmental regulatory agencies, as well as growing concern about climate change and greenhouse gas emissions.

Anaerobic digestion of manure has been posed as way to reduce odor emissions from manure, while reducing greenhouse gas emissions and producing renewable energy. Decomposition of manure normally produces a variety of odorous compounds, which are difficult to control because of their complexity. Anaerobic digestion of manure breaks down organic matter in a controlled process that produces reduced compounds, mainly methane (CH_4) and carbon dioxide (CO_2), which are odorless greenhouse gases. Hydrogen sulfide (H_2S), the main odorous gas produced by digesters is usually removed via a scrubbing process or destroyed along with methane during combustion of the biogas. While several pork production facilities have converted their manure storage facilities to crude digesters by installing impermeable covers, very few full-scale, designed digesters are in operation on U.S. swine farms. A main goal of this project was to obtain field-scale information on the effect of anaerobic digestion on the potential for treated manure to emit gases of concern to the atmosphere, especially odorous gases.

Meanwhile, in pork production facilities across the Midwest, deep pits (below-barn pits 2.5-3 m in depth) are used extensively to store pig manure for intervals of 6 months to a year. An unintended and undesired consequence of these systems is that some anaerobic decomposition of manure occurs, which releases methane and other manure gases. Aside from previously discussed concerns about odor and gas emission to the atmosphere, these gases pose health and safety concerns for the building occupants; concerns that have been successfully managed over the years by providing desired levels of ventilation and sound facility management. In recent years, reports of thick foam building-up on the manure surface and associated problems have increased. The foam contains primarily CH_4, CO_2 and H_2S and can easily build up to depths of 15 cm to 2 m in a matter of days. Foam development has caused problems because it complicates facility and manure management as it fills the pit head space and poses a significant safety risk because disruption of the foam releases a burst of highly flammable and noxious pit gases. Foam has been implicated as a contributing factor in a number of flash fires within Midwest swine facilities during the past few years. As a result of growing concerns about foaming pits, pork producer associations, university researchers, and allied industry representatives from several states have pooled their resources and coordinated activities to determine the underlying cause behind foam in an effort to prevent or at least limit its presence in swine facilities. As part of this overall effort, the Nebraska Pork Producers Association approved the University of Nebraska reallocating some project funds to help conduct an extensive analysis of manure from finishing buildings across the Midwest.

Objectives:

Two related goals in this project were to reduce the potential for swine manure to release odor and gas emissions to the atmosphere and to reduce the presence of hazardous foam building up within deep-pit pork production facilities. These goals were addressed by collecting manure samples from production swine facilities with the following specific objectives:

1) Characterize and compare the relative concentrations of volatile organic compounds by gas chromatography-mass spectroscopy in undigested and digested swine manure.
2) Facilitate detailed compositional analysis of manure samples from deep-pit swine facilities to help identify potential causes of foam development.

(Objectives were modified and approved in fall of 2009)

Methods:

<u>Digester effects on swine manure (Obj. 1).</u>

Sample collection: A total of 100 manure samples were collected from a swine finishing complex that employed a complete-mix anaerobic digester to treat manure slurry (Figure 1). Twelve sampling events occurred during ice-free conditions from 9/22/08 through 12/2/09. During each sampling event, grab samples were collected from three sites on this operation:

i) Annexes to the below-barn pits (where fresh manure accumulated for up to four weeks before draining to the digester);

ii) A sump area at the digester outlet (that received immediate digester effluent); and

iii) An earthen basin (holding pond) that provided long-term storage of the treated effluent.

For the first three sampling events, duplicate samples were collected at each location. Triplicate samples were then subsequently collected.

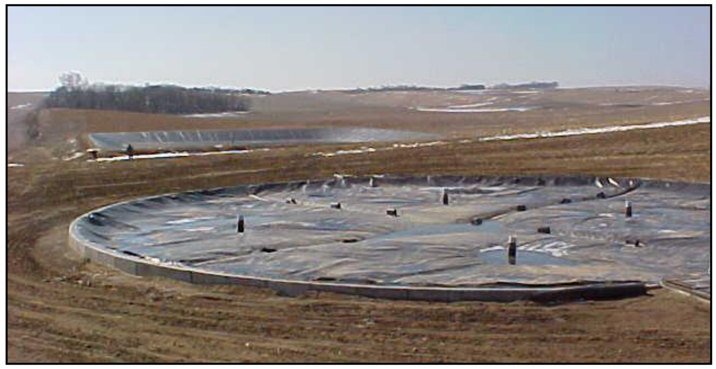

Figure 1. Digester and storage basin on study farm.
(Photo by R. Stowell)

Manure slurry/ characterization: Multiple manure slurry properties (pH, conductivity, total solids, volatile solids, and KCl-extraction for ammonia) were determined within 24 hours of sampling, since these properties may change during storage (even at -20°C). Chemical oxygen demand (COD), nutrient composition (phosphorus), and odor compound composition and concentration do not change (or change very little) when samples are frozen and stored, so those analyses were conducted at the end of the sample collection period to ensure that extraction and incubation conditions were uniform. All analyses were conducted within laboratory facilities at the University of Nebraska using standard methods for wastewater or soil analysis, modified as necessary for manure slurry analysis.

Odorous compound content and relative emission potential: Odorous compound content in all manure slurry / effluent samples was determined directly in the liquid fraction. A single internal standard (ethylbutyrate) was utilized to account for injection volume differences. Odorous compounds were analyzed and detected using gas chromatography and flame ionization methods as described by Miller and Varel (2003). Odorous compounds were categorized as alcohols (propanol, butanol, isobutanol, and pentanol), volatile fatty acids (acetate, propionate, butyrate, isobutyrate, valerate, isovalerate, hexanoate, and isohexanoate), and aromatic compounds (phenol, para-cresol, 4-ethyl phenol, indole, methyl indole, benzoic acid, phenylacetate, and phenylpropionate).

Statistical analyses: Standard ANOVA and repeated ANOVA were used to assess differences between manure sampling sites and between results for individual sites over time. Student's t-tests were used to assess differences ($P < 0.05$) between sites.

Sampling of manure for foam potential.

Sample collection: Twenty-two manure and four foam samples were collected from deep-pit swine buildings during 2010 and early 2011. Composite samples of manure were collected to represent the manure profiles within the pits, while grab samples of foam were collected. An overview of the sampled facilities and manure-foam status is provided in Table 1.

Table 1. Information for collected manure (n=22) and foam (n=4) samples.

Sample ID	State	Facility type	Additives used	DDGS level	Foaming?
S1	IA	Finish	?	None	No
S2	IA	Finish	?	High	No
S3	IA	Finish	?	High	No
S4	IA	Finish	?	High	Yes
IaL	IA	Finish	?	High	Yes
DM	IL	Finish	?	High	No
L1	IL	Finish	microsource	High	Yes
L2	IL	Finish	microsource	High	Yes
T1	MN	Nursery	?	Low	No
T2	MN	Nursery	?	Low	Yes
E1	MN	Finish	?	High	Yes
E2	MN	Finish	?	High	No
E3	MN	Finish	?	High	Yes
F1	MN	Finish	?	High	Yes
F2	MN	Finish	?	High	Yes
NF1	MN	Finish	?	High	No
NF2	MN	Finish	?	High	No
NF1	NE	Finish	MicroAide	High	No
Sum N	NE	Grow-finish	Pit Power	Low	No
Sum S	NE	Grow-finish	BioPlus	Low	No
Cre S	NE	Wean-finish	BioPlus & Pit Power	Low	No
Cre N	NE	Wean-finish	None	Low	No
IaFoam	IA	Finish	?	High	Foam
K1	IA	Finish	?	High	Foam
K2	IA	Finish	?	High	Foam
F2_Foam	MN			High	Foam

All told, manure samples were collected from five finishing facilities in Iowa, three finishing barns in Illinois, nine nursery and finishing facilities in Minnesota, and five finishing barns in Nebraska. Dried distillers grains and solubles (DDGS) were being fed in all but one of these facilities, and some operators reported using feed or pit additives specifically for controlling manure solids in the pit. Nine of the manure samples were collected from facilities that had foam or had recently had foam covering the manure surface. The remaining samples were collected from pits that did not have a history of foaming. Designation of a sample as coming from a 'non-foaming' or 'foam-free' pit is indefinite, at best, as onset of foaming is unpredictable and some non-foaming pits may foam at a later time or imminent foaming may be unknowingly avoided when manure is pumped out of the pit.

Sample analysis: Samples were kept in an insulated container during transit and then either shipped directly or frozen and then shipped for next-day receipt by a commercial laboratory (Midwest Laboratories, Omaha, NE). A complete analysis was done on the manure samples to obtain a fuller assessment of manure composition. The analyses included a standard manure analysis (for pH, solids contents, and macro and micronutrient levels); a feed analysis (for protein, fiber and energy composition); and a fat analysis (for levels of 45 different VFAs). The multi-state team looking into manure foaming was especially interested in obtaining information on volatile fatty acid (VFA) profiles of the samples.

Results and Discussion

Digester effects on swine manure.

Overall digester effects: Significant differences were observed in nearly all chemical and odorous compound constituents between the samples collected from the three locations studied at this operation (Table 2). The exceptions were conductivity and total solids, which either didn't change or were unusually variable during the study.

Table 2. Summary of analysis results for the swine manure slurry and digester effluent.

	Sampling location		
Manure constituents	Below-barn pit	Digester outlet	Storage basin
COD, g/L	77.9[a]	53.9[b]	16.0[c]
pH	7.55[a]	7.54[a]	7.93[b]
Conductivity, µS/cm	23.7	21.7	22.9
Total solids, g/L	25.5	24.3	20.8
Volatile solids, g/L	15.3[a]	13.6[ab]	9.4[b]
NH_3-N, mg N/L	72.0[a]	88.8[a]	27.9[b]
Total phosphorus, mg PO_4/L	316.1[a]	196.3[b]	96.8[c]
Odorous compounds			
Alcohols, µmol/L	236[a]	11[b]	10[b]
Total volatile fatty acid (VFA), mmol/L	106.1[a]	57.3[b]	11.5[c]
Branched-chain VFA, mmol/L	7.4[a]	5.7[a]	0.8[b]
Aromatic compounds, mmol/L	4.4[a]	3.5[b]	1.6[c]

[abc] Values with different superscripts denote that a statistically significant difference existed between sample compositions (no superscripts indicate no statistical differences were found).

Volatile solids (or total organic matter) and COD contents in stored digester effluent showed considerable decreases from contents in the undigested manure collected from the below-barn pit. Loss of volatile solids and COD as the manure moved through the digester and during storage in the basin is consistent with consumption of organic matter and production of methane and other biogases. Interestingly, the ammonia content increased noticeably after digestion, but then dropped during subsequent storage in the basin. These observations are consistent with anticipated ammonia generation during digestion (as organic N is converted to aqueous NH_3) followed by expedited loss of ammonia to the atmosphere as the treated manure is stored for a long period of time in an open structure. Phosphorus contents also decreased in samples as manure moved through the digester and then the effluent was stored within the basin. No real reduction in phosphorus is attributed to digestion of the manure however, as this pattern of lower P contents was likely due to phosphorus settling out of the digested manure profiles and grab sampling under-representing sludge content. Similar to ammonia, phosphorus is liberated from the organic matter as it is digested; but once free, phosphorus may precipitate out and accumulate in the bottom of structures as sludge.

A wide variety of odorous organic compounds were detected in all samples. To facilitate comparisons, the individual compounds were grouped into different odorous compound classes. These classes were alcohols, volatile fatty acids (VFA), branched-chain VFA (isobutyric, isovaleric, and isohexanoic acids) which are a subset of the VFA, and aromatic compounds (specific compounds are listed in the methods section). The concentrations of the odorous compound classes varied considerably between the three locations. A very clear trend was for odorous compounds to decrease in concentration as the manure slurry moved through the digester and as the effluent was subsequently stored in the basin. The VFA were consistently detected in all samples with branched-chain VFA comprising <10% of the total VFA. Aromatic compounds were also detected, but at lower concentrations than VFA.

Branched-chain VFA and aromatic compounds are produced during protein fermentation. Comparing the ratio of either of these groups of odorous compounds to total VFA provides insights into the nature of the organic matter undergoing decomposition. Since this ratio increases as manure slurry passes through the digester, it indicates that protein fermentation is an important process in the digester. It may also indicate that metabolism of the branched-chain VFA and aromatic compounds to methane is not as favorable as straight-chain VFA metabolism to methane. In the basin samples, the ratio of aromatic compounds to VFA was proportionately more abundant compared to the pit and digester samples. This may indicate that some aromatic compounds are accumulating in the basin due to their lower volatility.

Changes over time: Two patterns are evident by examining the data over time (Figure 2). First, samples from the below-barn pit and the digester outlet both showed considerable variability in constituent concentrations over time. Digester operation was interrupted for a period of several weeks during the study and very little methane was produced from late September through mid-November 2009, which could be expected to influence resulting effluent constituents. The variations from month to month for several manure constituents (e.g. pH and total solids) were quite large, but the larger swings in concentrations and properties happened during the last half of the study (e.g. volatile solids, ammonia) when the digester was not functioning as well. Second, while the concentrations varied, general trends were that COD and phosphorus concentration decreased with treatment and effluent storage, while ammonia concentration increased some with digestion before decreasing in storage.

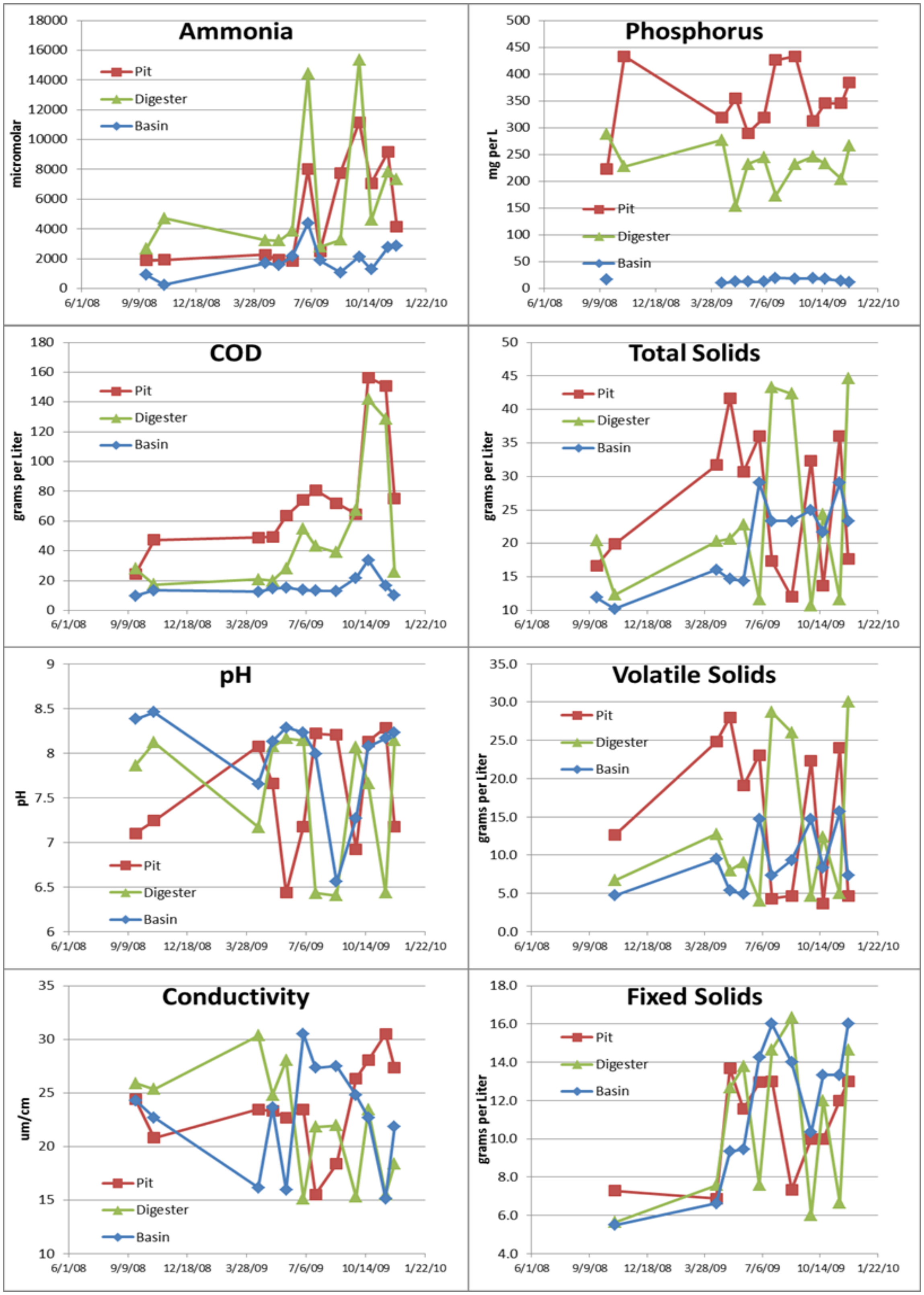

Figure 2. Trends in the constituent concentrations and manure properties of the sampled manure slurry and digester effluent during the study.

The clearest impact of digester performance was evident in the COD data. The COD of the digester effluent during the late-September through mid-November 2009 period was essentially the same as that measured in undigested ‘fresh’ manure slurry (only a 6% reduction). Prior to and immediately after this period, the digester reduced COD by an average of 45%. The effects of poor digester performance on other manure constituents were not obvious and no consistent trends were found. A cursory look at the peaks and valleys in the data shows that major shifts in volatile solids contents corresponded with noticeable pH shifts in the opposite direction. The general volatility in the data during the latter half of the study period is indicative of a system that was ‘upset’ and was reacting to re-achieve balance. While the methane-producing microorganisms in the digester were clearly affected by the state of imbalance, the rest of the anaerobic microbial community may have been unaffected.

Odorous compounds in the manure exhibited temporal patterns with considerable variation in time, but not as much volatility as was observed in the solids contents and pH data. Similar to COD concentration, odorous compound concentrations were generally highest in the manure sampled from the below-barn pit and lowest in the stored effluent (Figure 3). Very high alcohol concentrations were measured in the pit slurry on two occasions (4/17/09 and 6/3/09). Factoring out those two dates, the concentration of total alcohols in the pit samples averaged 15.9 µM, which was significantly greater than the concentration of the effluent in the storage basin, but not statistically different from that of the immediate digester effluent.

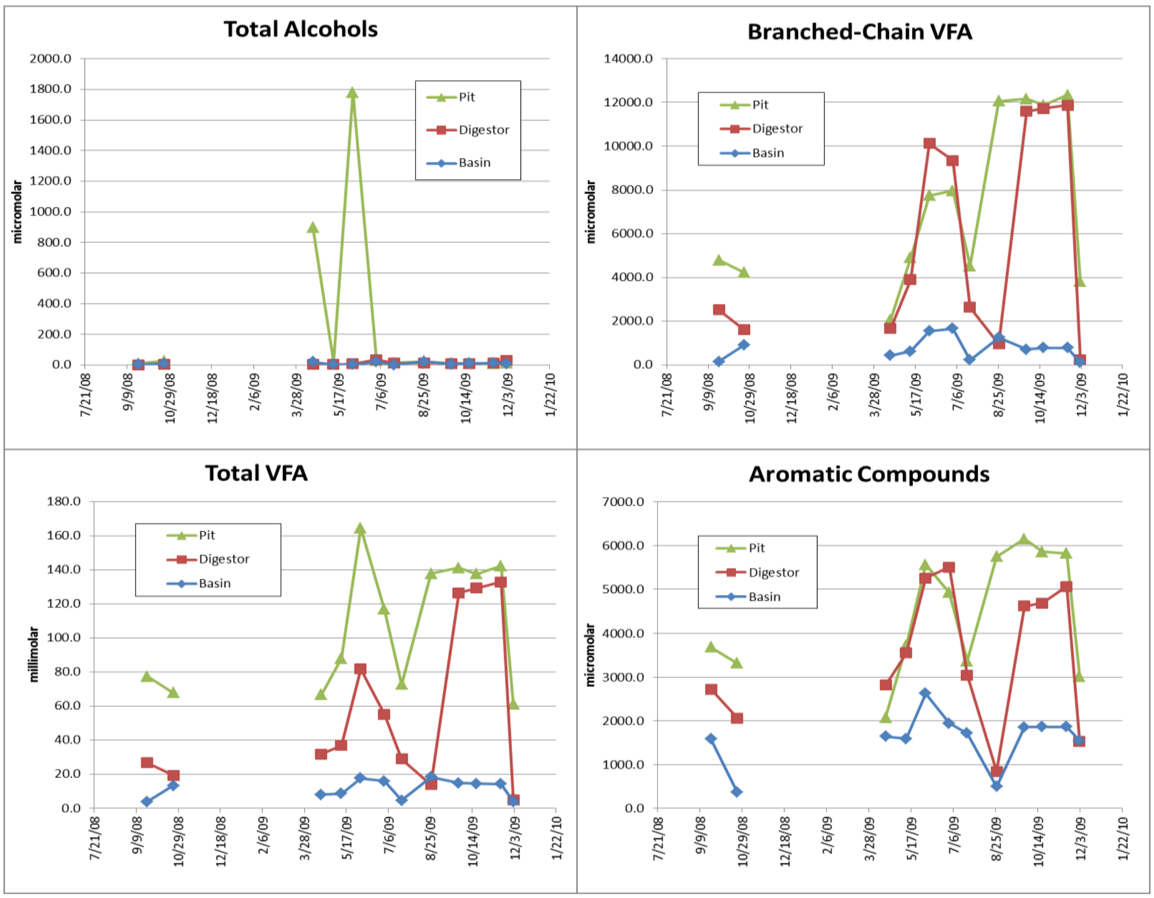

Figure 3. Trends in the concentrations of odorous compounds in the sampled manure slurry and digester effluent during the study.

Examining the concentrations of total VFA, the branched-chain VFA subset, and aromatic compounds over time helps to clarify how manure solids were utilized by microbes and how well the digester was performing (Figure 3). When the digester was operating as designed, the total VFA was reduced by an average of 66%, but on individual sampling dates, total VFA concentrations showed reductions of up to 90%. When the digester was not performing well, VFA concentrations were reduced by only 8%, which was remarkably consistent with the COD data. Digestion of swine manure resulted in much less consistent reductions in branched-chain VFA and aromatic compounds, though the general trend was the same as for total VFA. There were noticeable periods of time when digestion resulted in no reduction in branched-chain VFA and/or aromatic compound concentrations relative to pit slurry. It was interesting to note that when the digester was not performing well, aromatic compounds appeared to have been reduced more than were VFA.

Additional evidence and insight can be gleaned by examining the ratios of branched-chain VFA and aromatic compounds to total VFA. When the digester was performing as designed, the proportion of total VFA that were branched-chain VFA was higher in the digester effluent than in the pit slurry (Figure 4). This trend is even clearer when looking at the ratio of aromatic compounds to total VFA. Both proteins and carbohydrates can be converted to VFA; straight-chain VFA are produced by conversion of carbohydrates, while branched-chain VFA and aromatic compounds are produced during protein fermentation. Since total VFA content was reduced more relative to protein fermentation products (refer back to Figure 3), the VFA fraction coming from carbohydrates (straight-chain VFA) in the manure was being converted to methane more efficiently than was the VFA fraction coming from protein (branched-chain VFA). When the digester was not producing methane as designed, the ratios were identical, indicating that methanogenesis was no longer consuming the carbohydrate fraction of the VFA. One implication for enhancing methane production would be to develop microbial communities in the digester that were 'trained' to utilize carbohydrate and protein fermentation products equally.

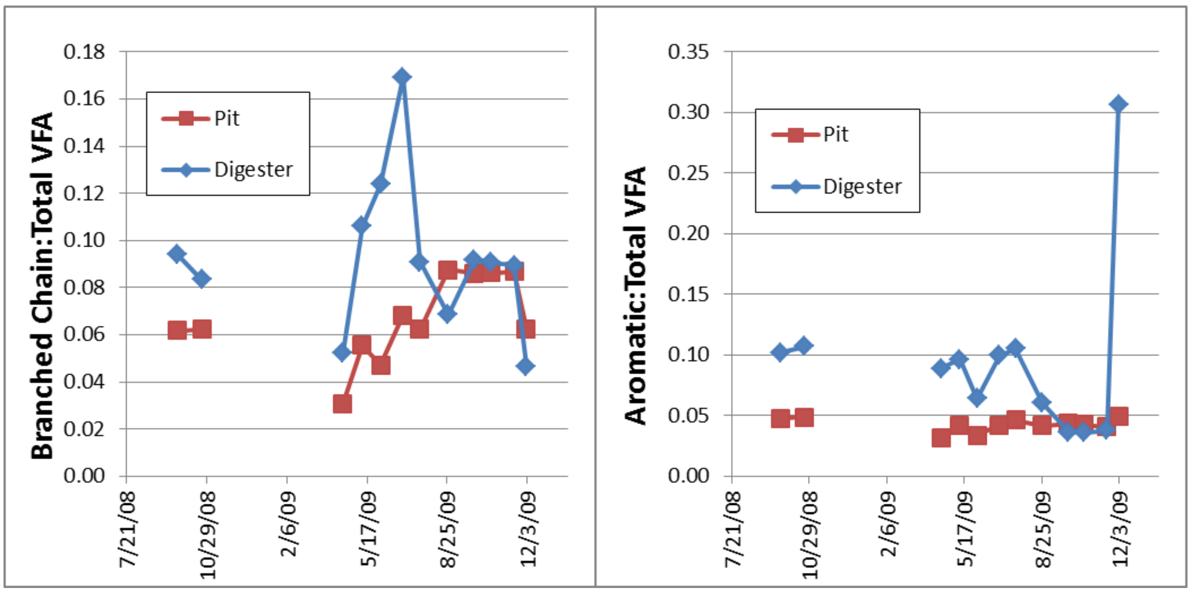

Figure 4. Ratios of branched-chain VFA to total VFA and of aromatic compounds to total VFA in the manure slurry and digester effluent samples during the study period.

Sampling of manure for foam potential.

This project facilitated extensive compositional analyses of twenty-six samples (22 manure and 4 foam) collected from swine production facilities in Iowa, Illinois, Minnesota and Nebraska. The analyses included a standard manure analysis (for pH, solids contents, and macro and micronutrient levels); a feed analysis (for protein, fiber and energy composition); and a fat analysis (for levels of 45 different VFAs). The laboratory analysis results were provided to the University of Minnesota (c/o David Schmidt, Biological Systems and BioProducts Engineering), where the data was analyzed to determine if any manure characteristics correlated with foaming. The data and fuller results of this analysis are to be reported separately by the University of Minnesota, along with producer survey results and results of related studies. Briefly, correlations were found between fat content and foam, but no other correlations could be established.

Summary and Conclusions

Two manure-analysis campaigns were conducted in this project.

A study was conducted on a swine finishing operation to assess the effects of anaerobic digestion on the gas- and odor-forming constituents of swine manure. Samples collected from three locations (below-barn manure pits, digester outlet, and the effluent storage basin) confirmed that the composition of manure changed both as it traveled through the manure management system and over time. An unforeseen failure in the digester system provided a unique opportunity to contrast the system's performance and indicated that methane production from carbohydrate was the predominant methane formation pathway. The primary conclusion drawn from the study was that anaerobic digestion of swine manure has a pronounced impact on odorous compound content and other wastewater parameters. When the digester was operating as designed, odorous volatile fatty acids were reduced by an average of 66% and chemical oxygen demand was reduced by an average of 45%. Another conclusion was that digesters increase the availability of nitrogen in manure (ammonia increased by an average of 58%), which unfortunately may also increase losses of this valuable plant nutrient via ammonia volatilization.

This project also facilitated extensive compositional analyses of manure and foam samples collected from deep-pit swine production facilities in Iowa, Illinois, Minnesota and Nebraska. The analyses included a standard manure analysis, a feed analysis, and a fat analysis. In subsequent statistical analysis by the University of Minnesota, correlations were found between fat content and foam, but no other correlations could be established. Future sampling and analysis work is being directed toward the microbial communities that are associated with foaming manure.

Reference cited:

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