CIG FINAL REPORT

Project Title: Impact of Anaerobic Digestion on Air Quality in a Community Anaerobic Digester.

Grantee Name: Washington State University.

Agreement Number: 69-3A75-10-155.

Project Director: Pius Ndegwa, Biological Systems Engineering, L.J. Smith 201, Washington State University, PO Box 646120, Pullman, WA 99164-6120; phone number: 509-335-8167; email: ndegwa@wsu.edu.

Date of submission: June 9, 2015.

Period Covered by Report: 01/01/2010 – 09/30/ 2014

Grant Agreement Deliverables: Document impacts of a community AD technology of dairy manure on air quality and post-digestion manure utilization with respect to:

1. Retention of NH_3 in manure, mitigation of NH_3, odor, and greenhouse gas emissions from manure storage and land applications,
2. Corn silage production using digested manure (i.e. AD effluents).
3. Dissemination of the results to stakeholders (dairy producers, local community, regulators, etc.) and to the scientific community.

Table of Contents

Executive Summary.

Concentrated animal feed operations (CAFOs) are potential sources of odors and other gas emissions that may adversely affect health, lifestyle, property values, and the wellbeing of residents in the vicinities. Reductions of these emissions to legal or acceptable levels are key to sustainability of livestock industry. Although the effectiveness of anaerobic digestion (AD) on the reduction of odor and other gas emissions from animal manure are well known, adoption of AD technology in CAFOs is limited in part due to: inadequate scientifically documented emissions reductions and the view that AD is mainly a technology only for energy production to boost CAFO profits. The specific goals of this project was to evaluate, demonstrate, and document the impacts of anaerobic digestion on: (1) NH_3 and H_2S emissions, (2) greenhouse gas emissions, (3) odor emissions, in a communal anaerobic digester, and (4) corn and wheat silage production. Results from this project are summarized next in this section.

<u>Odor at the AD site:</u> Importing off-farm pre-consumer substrates for co-digestion with dairy manure significantly increased odor concentration at the AD site from the open mixing tank as well as from AD effluent. Similarly, the co-digestion substrates also increased odor intensity and offensiveness of the co-mingled AD feed. The AD process, however, reduced both the intensity and unpleasantness of the AD effluent. Although solids-separation had little effect on odor concentration, it significantly reduced both odor intensity and unpleasantness. The pre-consumer wastes not only increased the total VFA in influent by more than 600% but also changed the proportions of different VFA. Butyric acid, which was probably responsible for increased odor concentration, intensity, and unpleasantness, was the second most dominant VFA (after acetic acid) and accounted for 23% of the total VFA in AD influent and only <6% in raw manures.

<u>Odor issues during post-AD storage:</u> During three months post-AD storage studies, VFA concentrations were significantly lower in the group of AD-treated manure than in the group of non-AD manure demonstrating that AD significantly reduced the potential for generation of VFA during post-AD storage of effluents. Actual odor measurements during the same period confirmed these projections. Consequently, the AD process was effective in reducing odor concentration, intensity, and offensiveness from storage of post-AD dairy manure.

<u>Emissions NH_3, H_2S and GHG during Storage:</u> The AD of dairy manure increased TAN in the effluent, which exacerbated NH_3 emissions from subsequent storage of AD effluents compared to non-AD effluent. Higher emissions of NH_3 were observed in summer compared to the other seasons. Solids separation resulted in significant 64% reduction in NH_3 emissions. The emissions of GHG were significantly higher from the non-AD manure storage than from the AD manure storage. With the exception of N_2O emissions, emissions of GHG were in warmer seasons compared to cooler seasons. The higher emissions of CH_4 and CO_2 observed from non-AD manure than from the AD manure attributed to higher content of easily-degradable organic C in the former compared to the latter. Additional efforts to curb NH_3 emissions may be necessary after AD of dairy manure.

<u>Following Land Application:</u> Regardless of manure application methods, NH_3 emissions were lower when soils received AD manure. On the other hand, manure injection, in general, was more effective in reducing NH_3 emissions than surface application. Emissions of GHG were significantly higher from field plots applied with non-AD than from field plots receiving AD manure. In addition, injection of manure increased further emissions of GHG. Therefore, although slurry injection reduces NH_3 loss, it is necessary to evaluate the gain from NH_3 loss reduction against the potential increase in the greenhouse gases (N_2O and CH_4) emissions from injected manure.

<u>Modeling ammonia emissions:</u> Particle size distributions for AD and non-AD manures were substantially different. AD manure indicated significantly higher pH, TAN, ionic strength (IS) and

viscosity than non-AD manure. The K_{oL} and α, under identical conditions (air temperature, liquid temperature, and airflow), were significantly higher for AD manure than for non-AD manure ($p>0.05$). Coupled with significantly higher TAN concentration in the AD manure, these findings suggested that AD of dairy manure significantly exacerbates ammonia volatilization. These results not only agreed with actual measurements from both field and lab studies but elucidated further the reasons behind the increased emissions from AD effluent.

Utilization in Crop Production: AD and Non-AD manure were shown to be equivalent for production of forage yield and nutrient uptake in a double crop system of corn silage-wheat forage. The fall soil NO_3^--N concentration was significantly lower for the non-AD manure as would be expected as this method of manure application would result in more volatile loss of NH_3 at the time of application.

1. Introduction.

Concentrated animal feed operations (CAFOs) are potential sources of odors and other gaseous emissions that may affect (real or perceived) health, lifestyle, property values, and the wellbeing of surrounding residents. Reductions of these emissions to legal or minimal levels are necessary for enhanced sustainability animal agriculture. From ad hoc testimonials and documented scientific literature, anaerobic digestion (AD) has proved successful for significant odor and other gases emissions reduction during storage and land application of treated effluent. Furthermore, AD extracts biogas energy from the manure, while retaining all important nutrients in the digested manures.

Although the effectiveness of AD on the reduction of odor and other gaseous emissions from animal manure is evident, adoption of this technology in CAFOs is still limited probably due to: (i) inadequate scientifically documented emissions reductions in full-scale AD operations, and (ii) the view that AD is mainly a technology for producing biogas energy to boost CAFO profits. More CAFOs would probably consider adopting AD even if the biogas energy is marginal; if respective environmental (abating costly nuisance lawsuits) and nutritional benefits (enhanced manure value), are well demonstrated. The goal of this project was to demonstrate these benefits. The project was conducted at a community AD, a model that brings several CAFOs together to enhance economic viability of the AD system and to lessen concerns from citizens.

The specific goals of this project was to evaluate, demonstrate, and document the impacts of anaerobic digestion on: (i) NH_3 and H_2S emissions, (ii) greenhouse gas emissions (GHG), (iii) odor emissions, (iv) nutrient value of AD effluent for corn silage production, and also to (v) disseminate the project results to stakeholders and the scientific community.

This project was conducted under the collaboration of Washington State University, Purdue State University, Qualco Energy, and the Co-operating Dairy Producers. Qualco Energy and Dairy Producers provided unlimited access to the project site as well as providing other in-kind supports. Purdue University has a well-established odor laboratory and provided expertise and laboratory for all odor analyses. Washington State University provided all other technical expertise and administration of this project. Most of direct financial support was from USDA-NRCS (agreement #: 69-3A75-10-155). Other partial funding (personnel support) were provided by both Purdue and Washington State Universities.

2. Background.

Concentrated animal feed operations are potential sources of offensive odors and other gaseous emissions. The odors and gaseous emissions emanating from CAFOs are, in general, not only annoying but they can also affect health, lifestyles, property values, and wellbeing of nearby residents. Direct and indirect damages to ecosystems from excess NH_3 emissions from CAFOs have been observed in intensive animal production regions. Consequently; it is vital to research and adopt technologies to reduce odors and gas emissions to legal or minimal levels for sustainability of animal agriculture. Several technologies available for addressing these odor and gas emissions, in CAFOs, includes diet modification, manure treatment, capture and treatment of odor and gases, and capture of volatile nitrogen in crops via manure injection, among others.

Amongst the manure treatments methods, AD is reported as successful for treating manure, achieving significant reduction of odor and GHG emissions during post-treatment storage as well as in subsequent land application. Anaerobic digestion is a biological process that degrades and thus bio-stabilizes the manure. Manure that has been properly treated by AD does not undergo significant degradation in subsequent storage or when applied on land and thus results in significantly lower odor emissions than the untreated manure. Moreover, AD extracts valuable biogas energy from the manure but retains important (plant fertilizer) nutrients in the digested manures. Although the effectiveness of AD on the reduction of odor and other gaseous emissions from animal manure is reported, the adoption of this technology in CAFOs is still limited. This is probably because: (i) AD has largely been viewed as a technology only for recovering biogas energy for boosting CAFO profits, (ii) inadequate scientifically documented odor and gaseous emissions reductions in full-scale-CAFO-installed AD systems, and (iii) rapid utilization of NH_3-N and phosphorus for crop production when digested manure is field applied. Majority of CAFOs would probably consider adopting AD if all associated benefits are clearly documented. Our expectations, in this project, were to demonstrate the associated environmental and economic benefits of AD of dairy manure.

In an effort to pool resources to make AD viable, a group of dairy producers in WA teamed up with a local Native American tribe to build a communal anaerobic digester (CAD). The results was reduction in the initial capital cost for individual farms as well as economical maintenance of necessary technical expertise that would be difficult on individual farms. This CAD provides a good example of industry consolidation to tackle common environmental concerns and seems to be the most viable way of enhancing adoption of this technology amongst CAFOs. However numerous questions arise from the public and state environmental agencies on the impact of such endeavors. These concerns include: biosecurity issues; pathogens entering or leaving the respective participating CAFOs, equitable redistribution of nutrients to the participating CAFOs, potential impacts on water quality, and potential impacts on air quality. This project evaluated the impact of the CAD on air quality to demonstrate environmental and economic benefits accruing from such facility.

3. Review of Methods.

The community anaerobic digester (CAD) at which this project was conducted was centrally located amongst four dairies with a total capacity of 3,000 cows. The CAD was approximately 1.5 miles from the nearest of the only participation dairy (during the period of this research) to the North and approximately 2 miles from a fourth dairy in the South (Fig. 3.1). The CAD system was completed in 2008 and consisted of: a 3,000-m^3 plug-flow anaerobic digester; a solid-liquid separator; an in-vessel solids-composting facility; and two lagoons for the liquid AD effluent. Liquid and composted solids were returned to the participating dairy for use as a nutrient source for crop growth. Only one dairy was onboard for the entire duration of this project.

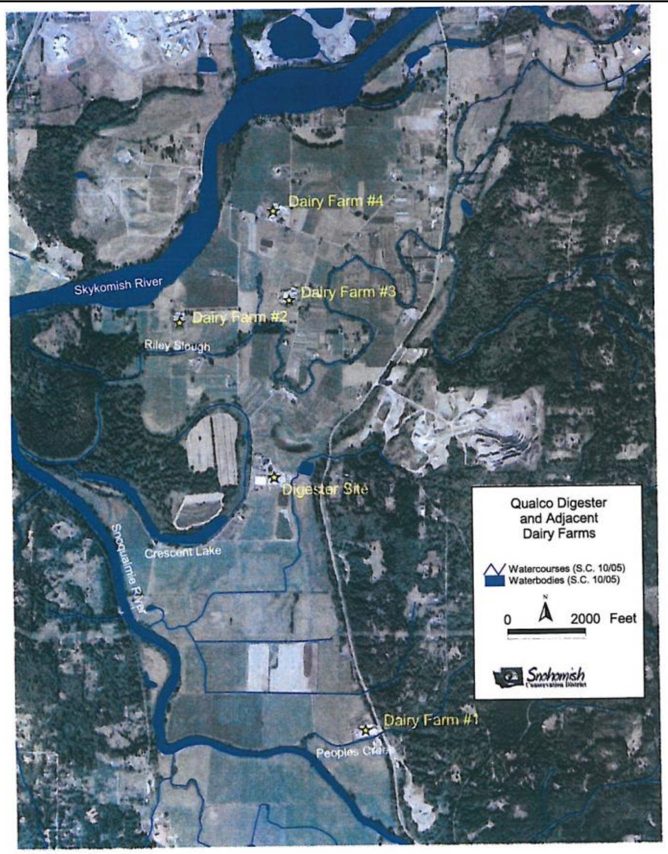

Fig. 3.1. Map of the location of the CAD with respect to the locations of the participating dairies.

3.1. Objective 1: Evaluate impacts of dairy manure AD on odor emissions.

3.1.1. Odor Evaluation at the AD Site: Air and liquid samples were collected at four points in the AD-system including: raw or non-AD manure at the point manure was received from the dairy, from the mixing tank, from the AD effluent, and from the liquid immediately after solids separation station (Fig. 3.2). Air samples were collected in 0.05 mm thick, 10-L Tedlar bags using a vacuum air sampling chamber (SKC Vac-U-Chamber, SKC, Inc., Eighty-Four, PA). Liquid samples, collected at the same time in the same locations, were collected in 2-L sample bottles. The samples were immediately shipped to a well-established and collaborating air quality lab at Purdue University (West Lafayette, IN) for odor analyses. The air samples were analyzed by a trained odor panel using a Dynamic Dilution Forced-choice Olfactometer (AC'SCENT International Olfactometer, St. Croix Sensory, Stillwater, MN) following the European olfactometry standard (CEN, 2000). The liquid samples were placed in masked laboratory flasks for evaluations of odor concentration, odor intensity, odor hedonic tone, and odor character by the same team of trained odor panel (ASTM, 1991 and 1992).

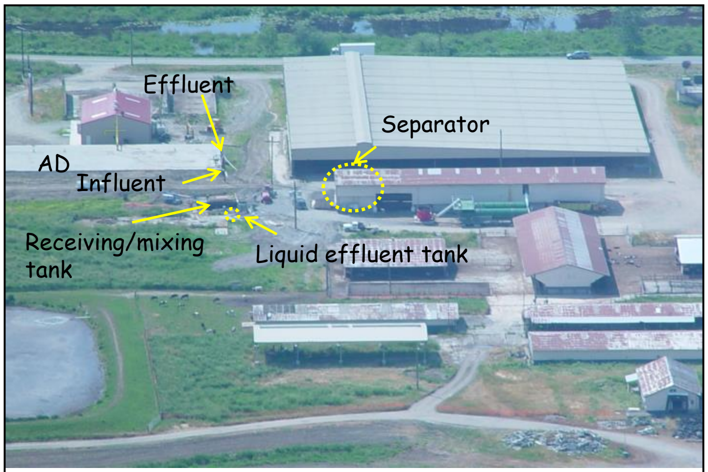

Fig. 3.2. Sampling locations within the community anaerobic digester system.

3.1.2. Odor and Gas Emissions in the Lab-scale Studies: Larger liquid samples (60 L raw and 60 L digested manure) were also collected at the same locations and shipped (in frozen condition) to Purdue University for laboratory evaluation for their potential to generate odor and other gases during subsequent storage periods. Two-three months studies were conducted in 2011 and 2012 to investigate volatile fatty acids (VFA), odor, and gases (ammonia, hydrogen sulfide, and greenhouse gases) emissions and the respective influences of both anaerobic digestion (AD) and manure solids separation under simulated manure storage conditions. The first experiment started on October 5, 2011 and finished on January 20, 2012. The second experiment started on May 25, 2012 and finished on October 3, 2012. Once the frozen manure samples were received at Purdue University, they were kept at ordinary temperature outdoors to thaw completely before pouring into eight manure testing reactors (Fig. 3.3). Manure from each source was tested in two (duplicate) lab-scale reactors that were 61.0 cm high, 38.1 cm diameter, and made of white PVC. The insides of the reactors were lined with Tedlar film, except for the bottoms of the reactors. Each reactor was initially filled with manure to 25.4 cm height. The manure sources in eight reactors for both experiments are listed in **Error! Reference source not found.**.

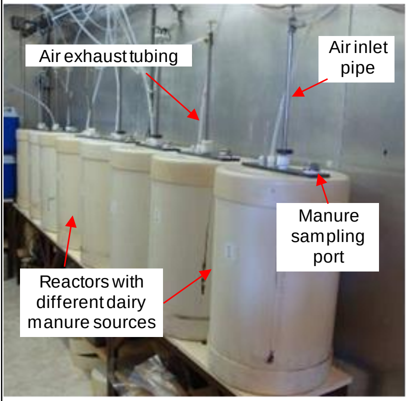

Fig. 3.3. Reactors filled with dairy manure for storage experiment in a temperature-controlled chamber.

Table 3.1. Overview of manure preparation for both studies.

Container #	Sampling location	Reactor #	Reactor filling date	
			Experiment 1	Experiment 2
1	Raw manure from dairy barn	1 & 2	10/5/11 (d 0)	5/25/12 (d 0)
2	Influent to AD containing pre-consumer waste	3 & 4	10/5/11 (d 0)	5/25/12 (d 0)
3	Effluent from AD	5 & 6	10/11/11 (d 6)	5/25/12 (d 0)
4	Effluent from AD after separation of solids (output to a lagoon)	7 & 8	10/11/11 (d 6)	5/25/12 (d 0)

Each reactor was continuously ventilated with 6.5 L min^{-1} of fresh air in the manure headspace to simulate manure storage on dairy farms. A compressor continuously supplied fresh ventilation air through an air cleaning and control system consisting of two oil filters, a charcoal filter, two pressure regulators, a drum-shaped manifold, and eight precision orifices. A pressure sensor and a relative humidity (RH/T) sensor were used to monitor the pressure and RH/T inside the air supply manifold (**Fig.3.4**). Exhaust air from all eight reactors was transferred to multiple gas analyzers through 6.35-mm inside diameter Teflon tubing, a set of Teflon filters, a set of 3-way solenoids, a stainless steel mass flow meter, and two Teflon manifolds. A computer system, consisting of a personal computer, data acquisition and control hardware, and data acquisition and control software AirDAC was used to acquire measurement data every second and to schedule air sampling. The data were averaged every 15 s and 1 min and saved into two separate data files.

In the second laboratory experiment, a relay system was designed for automatic monitoring of manure pH in all eight reactors. Two 2-wire pH/ORP transmitters (Model pH 500, Entech Instruments, Vernon Hills, IL) were connected to 16 relays to form an automatic measuring system. A group of eight relays shared a transmitter and each relay was connected to a pH electrode. A total of 16 pH electrodes were used in eight reactors. Each reactor had an electrode to monitor the surface manure pH and another electrode to monitor the bottom manure pH.

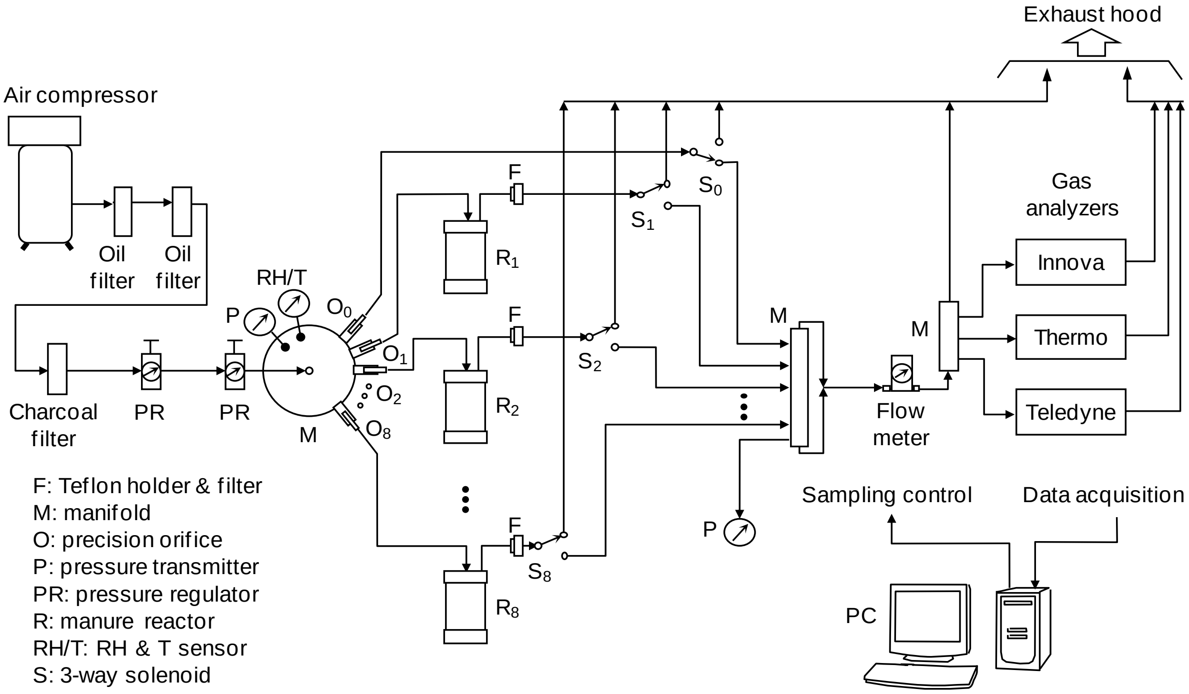

Fig.3.4. Schematic of the experiment setup. Analyzers for gas concentration measurement: “Innova” for CH_4, CO_2, and NH_3; “Thermo” for H_2S; and “Teledyne” for N_2O

The concentrations of ammonia (NH_3), hydrogen sulfide (H_2S), and greenhouse gases (GHG), including methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2) in the exhaust air from each bioreactor were measured for 10 min with two INNOVA Model 1412 Photoacoustic Multigas Monitors (for CH_4, CO_2, and NH_3), one Teledyne Model 320EU analyzer (for N_2O), and one Model 450i Pulsed Fluorescence SO_2-H_2S-CS analyzer (for H_2S) (**Error! Reference source not found.**). It took 80 min to measure gas concentrations in exhaust air from eight reactors. Gas concentrations in the reactor inlet air were measured for 20 min after 160 min of sampling air from eight reactors twice.

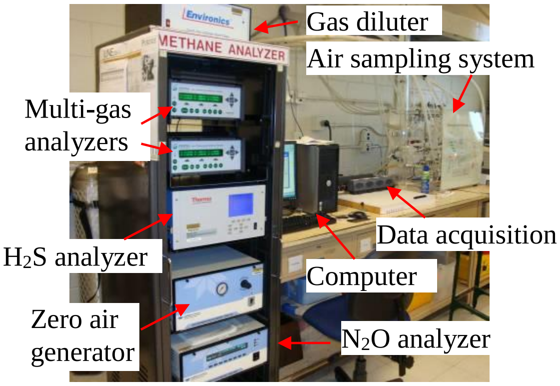

Fig. 3.5. Air sampling instrumentation.

Odor samples were taken weekly or bi-weekly from each reactor. Odor concentration, intensity, and hedonic tone were analyzed at the Purdue Agricultural Air Quality Lab using a dynamic olfactometer and trained odor panelists. A reference odorant of 40 ppm n-butanol was evaluated with the odor samples in each odor measurement session during the three-month tests. Odor detection concentration (ODC) of the n-butanol was calculated using eq. (3.1), which is the concentration at the detection threshold, according to the CEN standard (Comitté Européen de Normalisation, 2000. Air quality - Determination of Odor Concentration by Dynamic Olfactometry. Central Secretariat: Rue de Stassart 36, B-1050, Brussels. Release 00-04-25).

$$\mathrm{ODC_b} = \frac{1000\mathrm{C_b}}{\mathrm{DT_b}} \qquad (3.1)$$

$\mathrm{ODC_b}$= odor detection concentration of n-butanol (ppb), $\mathrm{C_b}$=concentration of n-butanol gas (ppb), $\mathrm{DT_b}$=DT of the n-butanol sample

Given that one European Odor Unit ($\mathrm{OU_E}$)=123µg n-butanol, and 1.0 $\mathrm{OU_E}$ $\mathrm{m^{-3}}$=40 ppb, a normalized odor concentration was calculated with eq. (3.2):

$$\mathrm{OC_E} = \frac{\mathrm{DT}\times\mathrm{ODC_b}}{40} \qquad (3.2)$$

Two different types of manure analysis methods were performed. The first was a regular analysis of the manure, which included total solids, total nitrogen, phosphate, sulfur, calcium, magnesium, sodium, iron, manganese, copper, zinc, pH and ammonium nitrogen. These analyses were conducted for samples collected from each container prior to filling to establish respective initial characteristics. Two samples were taken from each tank after the source manure was completely mixed with a powered mixer. One manure sample was taken from each reactor at the end of the test after the manure was completely mixed with the powered mixer. These manure samples were shipped to the Midwest Laboratories Inc. (Omaha, NE) for analysis with the basic manure and sludge package.

The second series of analyses were to determine VFA concentrations. Two manure samples were taken weekly for VFA concentrations analysis from each reactor: one in the top manure layer within 2.5 cm below the surface and another in the bottom manure layer within 5.0 cm above the reactor bottom (Table 3.2). Analysis of VFA was conducted using HPLC at Purdue University (Laboratory of Renewable Resources Engineering).

Table 3.2. Overview of manure sampling schedule for both studies.

Test days		Regular sample		VFA samples		Operation
Ex. 1	Ex. 2	Ex. 1	Ex. 2	Ex. 1	Ex. 2	
0	0	4	8	0	8	Test 1: Regular sampling in containers 1 and 2 (2/container). Test 2: Regular and VFA sampling in containers 1, 2, 3 and 4 (2/container).
6		4				Test 1: Regular sampling in containers 3 and 4 (2/container)
7–98	5–110			224	272	Both tests: Weekly VFA sampling in reactors (2/reactor)
107	131	8			16	Test 1: Last regular sampling event (1/reactor). Test 2: VFA sampling at the end of test (2/reactor).

3.2. Objectives 2 & 3: Evaluate impacts of dairy manure AD on NH_3, H_2S, and GHG emissions.

3.2.1. Field Measurements of Ammonia (NH_3), H_2S, And GHG Emissions During Land Application of Digested and Undigested Manure: Gaseous emissions of ammonia (NH_3) and GHG (CO_2, CH_4, and N_2O) from twelve plots receiving two different dairy (AD and non-AD) manures (Fig. 3.4) were monitored by a photoacoustic IR multigas monitor (INNOVA, Model 1412, Innova AirTech Instruments, Ballerup, Denmark) using the standard 8-inch closed chamber (Fig. 3.5). Standard static chambers have two vents. However, we used a modified static chamber method, after the first year. In the original static chamber, air samples were collected using syringes and transferred to air-evacuated sample vials for later determination of concentrations in the lab using gas chromatograph. In the modified method, however, one vent was connected to the inlet of a photoacoustic gas analyzer that drew air from the headspace of the chamber using an internal pump, while the other port was connected to the outlet of the analyzer and returned the sampled air to the headspace of the chamber. The analyzer thus continuously determined the cumulative concentrations of the respective gases in the headspace with time. Measurements were stopped at saturation of gases in the headspace, which was indicated by concentration plateaus. In most cases, measurements were completed within 10 minutes of sampling. The respective gas fluxes were determined from linear segments of the concentration versus time plots in each case, the chamber volumes, and the emitting-surface-areas.

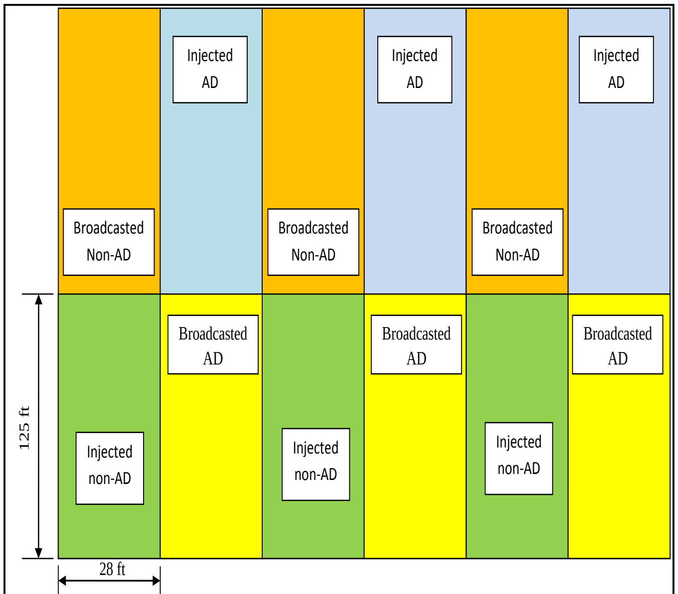

Fig. 3.4. A color coded schematic of the layout of the 12 field plots in which manure application tests were conducted.

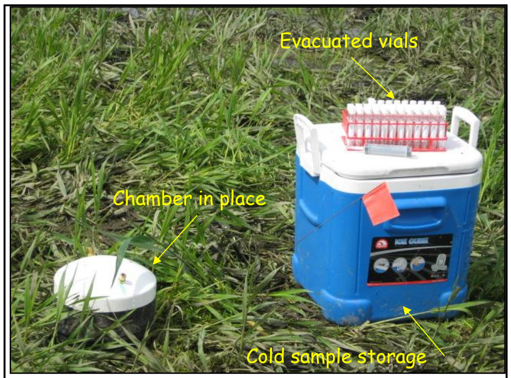

Fig. 3.5. Instrumentation used to collected gas samples after manures were applied on the field plots.

Measurements were conducted, every day, for between 6 and 14 d during planting seasons, every year. Both AD and non-AD dairy manure were plowed-in approximately two days after application and the plots harrowed about two days after plowing. All treatments (AD versus non-AD, broadcasting versus sub-surface manure injections) were studied in triplicates.

3.2.2. Field Measurements 0f Ammonia (NH_3), H_2S, And GHG Emissions during Storage of Digested and Undigested Manure: Emissions from manure storages were measured following a similar protocol to the one described above for the field plots. The only differences were the designs of the chambers, sampling procedure, and time of sampling. The volumes of the three floating-chambers (22,229 cm^3) used for measurements at the manure storages were approximately three times more than of the chambers used in the field measurements and covered approximately twice the emitting-surface-area (729 cm^2). These chambers also had two vents and required foam-platform to ensure they stayed partly immersed and afloat (Fig. 3.6). One vent was connected to the inlet of a photoacoustic gas analyzer (INNOVA model 1412) that drew air from the headspace of each chamber using an internal pump, while the other port was connected to the outlet of the analyzer and returned the sampled air to the headspace of the chamber, after the analysis. Six measurements were carried out during each season every year during the project period.

Fig. 3.6. A photograph view of a floating chamber used to measure emissions from manure storages or lagoons.

Ammonia fluxes from the same manure storages were also determined from measurements of NH_3 concentration downwind of the manure storages using an open path ultra-violet differential optical absorption spectroscopy (UV-DOAS), meteorological conditions, and a backward Lagrangian stochastic (bLS) inverse-dispersion model. Six events for the same periods as those lagoon measurements were conducted. Mostly, the UV-DOAS measurements were performed in north area of the lagoon for downwind, because wind direction of Monroe city in Washington State is mainly from south. The spectroscopy was installed at least 40-m apart from the lagoon storage and continuously monitored for more than 22 hours for both downwind and upwind (background).

3.2.3. Laboratory Measurements of Ammonia Emissions from Storage and Land Application (Lab-Scale): Another set of laboratory tests were conducted at Washington State University to identify the effects of AD and solids-liquid separation on ammonia emissions during subsequent AD effluent storage and land application. For these studies, lab manure storage tests were simulated for 21 d in plastic containers with open surface areas of 386 cm^2 filled with 2.5 L manure samples obtained at the following four points in an AD system: raw manure (RM) feed substrate, raw manure supplemented with other substrates (AD influent), AD effluent, and AD effluent after solids-liquid separation (AD liquid effluent). A photographic view of these experiments setups are shown in Figure 3.7.

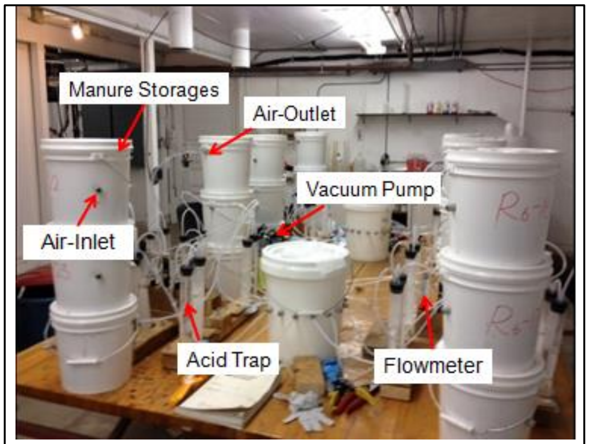

Fig. 3.7. A photographic view of the lab simulation of both manure storage and land application.

3.2.4. Modeling NH3 Emissions: The manure samples for this study were sourced from a commercial flush dairy located in Outlook, Washington, operating a mixed-plug-flow mesophilic anaerobic digester (Mixed Plug-Flow^{TM}, DVO Inc., Chilton, WI). Samples of raw liquid dairy manure were collected in 20 L sealable plastic buckets from the manure-receiving tank. Similarly, samples of anaerobically digested manure were collected from the digester-effluent tank. The AD and UD manure samples both collected as single batches to run the entire study. The samples were transported back to the lab and stored in a cold room at 5°C until commencement of studies and analysis. The composition of the feed rations, on this dairy, dating four weeks prior to the manure sampling date are presented in Table 3.3. There were no significant variations in the feed rations during this period. Since the retention time of the digester influent averaged 21 d, the differences in the AD and the UD manures were thus attributed to the digestion process.

Table 3.3. Feed rations compositions (%) in the dairy from which manure was sampled during the four week prior to the sampling date (24 April 2012).

	Date		
Ingredient	27 Mar. 2012	12 Apr. 2012	20 Apr. 2012
Corn silage (%)	43.6	43.5	46.8
MC Grain Mix* (%)	29.1	29.0	26.6
Rumen bypass fat (%))	0.5	0.3	0.3
Hay (%)	8.9	9.4	9.2
Haylage (Alfalfa) (%)	14.4	14.4	14.0
Haylage Sudan (%)	3.4	3.4	3.1
Total (%)	100.0	100.0	100.0

*The ingredients in the MC Grain Mix did not change.

Particle size distribution (PSD) of UD and AD manure was determined using a Marvin Mastersizer (Model: MS2000, Malvern Instruments, Westborough, MA, USA). The Mastersizer uses laser diffraction of particles in liquid suspension and places the particles in 64 different size classes based on percent volume. The particle suspensions were then placed in a stirred-tank and circulated through the cell placed in the path of the laser beam. Both UD and AD samples were run on multiple sub-samples until replicate values for fine (0.01 µm to 2.1 µm), medium (2.2 µm to 52 µm), and coarse (> 52 µm) particles categories were within 5% to10%. The samples were introduced into a sample mixing chamber until the obscuration factor was 15% to 25% range (10% to 30% is the acceptable range according to the manufacturer's instructions). The particles were then circulated through the instrument until a stable signal was reached; completing the PSD analysis. The vigor of mixing should of necessity be balanced so that dispersion occurs without undue breakages of individual particles. Both UD and AD samples were treated in a similar manner during the entire process to minimize process variability. In general, laser diffraction results are reported on a volume basis, so volume mean diameters and geometric standard deviations were reported.

Total solids TS and (VS) for both AD and UD manures were performed following standard methods (APHA, 2005). The pH of liquid manure was measured using a standard pH meter (Model 900A, Orion Research Inc., Boston, MA, USA). Concentration of TAN was determined following the procedures outlined in the standard methods for the examination of water and wastewater (APHA, 1995). Electrical conductivity (EC) was measured just before the experiments using an EC meter (Model Mettler Toledo SG7-FK2, SevenGo™ conductivity meters, Columbus, OH USA). The EC values were converted to ionic strength (mol L^{-1}) using established EC-ionic strength relationship (Jenkins, 1980). Viscosity measurements were performed using a Brookfield viscometer (Fig. 3.9a); Model DV-II+Pro Viscometer, Brookfield Engineering Laboratories Inc., MA, USA) at a manure temperature of 45°C. The most important procedures for the viscosity measurements are the selection of appropriate spindles (Fig. 3.9b) and rotational speed (rpm) during the measurements. Viscosity measurements, according to manufactures instructions, are acceptable within the torque range of 10% to 100% for any combination of spindle/speed rotation because of significant errors below the 10% torque range. For this study, the selected spindle No. 21 set at a rotational speed of 100 rpm was found adequate because it operated within the prescribed torque range at manure temperature of 45°C. Below this temperature, the percentage torque was < 10% which was unacceptable.

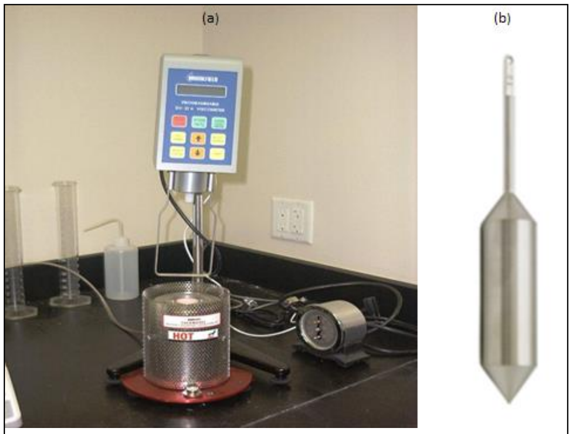

Fig. 3.9. Viscosity measurement apparatus: (a) Brookfield –II+ Pro viscometer, and (b) Spindle.

The fraction of unionized and overall mass transfer coefficients of NH$_3$ were determined in a modular laboratory-scale convective emission chamber (CEC) adapted from previous research (Arogo et al. 1999; Shaw, 1994; Zhang, 1992). The CEC was started approximately 20 min prior to each experimental run to allow it to acclimate to specified conditions. All experiments were performed at both the original manure pH and at a pH of 11.5, and at liquid temperatures of 15°C, 25°C, and 35°C. The pH of 11.5 was chosen because at pH of 11.0 and above, TAN comprises entirely of unionized NH$_3$ or NH$_4^+$ ions are fully dissociated. As shown in the data analysis section that follows, this is important for computation of both the mass transfer coefficients and the fraction of unionized ammonia at the pH of interest. For pH 11.5, a well-mixed 2.3 L manure sample at each temperature level was poured into a test pan and the pH adjusted to pH of 11.5 with NaOH solutions. Airflow speed and air temperature were held constant at 1.5 m s^{-1} and 25°C for all experimental runs. To monitor ammonia volatilization, a 2.5 ml liquid sample was randomly taken from two locations within the pan using a pipette every 0.5 h for 3 h. Simultaneous observations of airflow speed and liquid temperature were also recorded. Sampled liquids were immediately injected into 5 ml 0.2 M sulfuric acid in test-tubes of volume 15 ml to stop ammonia volatilization and capped to avoid spillage of the samples. The collected samples were stored in a refrigerator at 4°C till the analysis of TAN concentration. Liquid manure temperature, pH, and electrical conductivity were also determined at the beginning and at the end of each experiment. Each test was conducted in duplicate.

The fraction of unionized NH3 (β) and the mass transfer coefficient of NH3 (K_{oL}) were computed using approaches established in previous research (Vaddella et al., 2011; Arogo et al., 2003; Arogo et al., 1999). In order to quantify the role of PSD on ammonia volatilization from liquid manure, it is necessary to evaluate the particles size characteristics of the manure solids. The volume median diameter (VMD) and the geometric standard deviation (GSD) fully characterize the PSD were computed using standard methods (Wang et al., 2013; Karanasiou et al., 2007; Redwine et al., 2002).

Microsoft Excel was used for analysis of particle size distribution (PSD), plotting of graphs, and regressions analyses. The means of mass transfer coefficients and fraction of ammonia in TAN were analyzed using a two-way ANOVA: factor one – Manure type (UD & AD) and factor two – Temperature. ANOVA for the treatment-means were performed using SAS (SAS, 2006). Pairwise comparisons for treatments means were performed using Tukey's Studentized Test at significance level of $\alpha = 0.05$.

3.3. Objective 4: Evaluate effect of manure AD on nutrients (nitrogen and phosphorus) use for crop growth.

A three year study was conducted at a commercial dairy to evaluate the effect of type of manure and method of application for corn silage and winter wheat production. Corn silage was grown followed by a second crop of winter wheat at a commercial dairy in Monroe, WA from late spring of 2011 to the spring of 2014. The field had a long history of manure application as evidenced by the % OM and concentration of Bray P in soil. Two manure sources (AD and non-AD) and two methods of manure application (injection and broadcasting) were utilized on replicated field plots (250 ft. long and 28 ft. wide as shown in Fig. 3.4) with a 14 ft. manure injector (Fig. 3.10). Desired rates of manure applications were ensured with an in-line Siemens manure flow meter.

Fig. 3.10. Manure application equipment.

Soil samples were obtained at a one foot depth each spring and fall for analyses of nitrate-N (spring and fall), and organic matter, Bray – P, and pH (spring). Corn silage was planted in May (Fig. 3.11), harvested in October of each year and followed by winter wheat harvest the next spring. Corn silage yield samples were obtained by manual harvest of 4 random 10-ft rows for total weight. Each ten ft. row was chopped with an Ohio chopper, subsampled, and dried for DM and ground (1 mm) for subsequent chemical analyses. Plant population at harvest was estimated based on plant counts in a 10 ft. section of a row. Wheat yield was obtained by manual clipping of duplicate 2 x 2 ft. square areas randomly selected in each plot (Fig. 3.11c). Wheat forage samples were dried for DM and ground (1 mm) for subsequent chemical analyses.

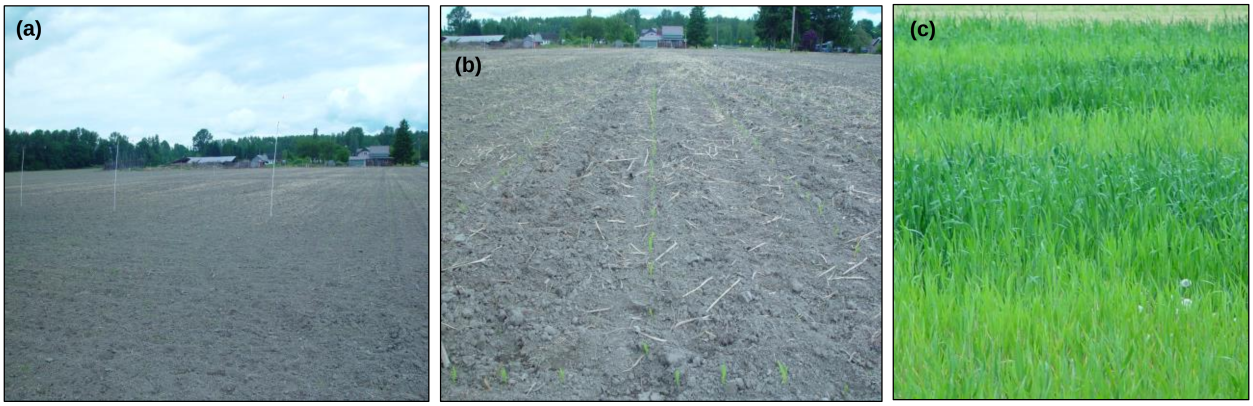

Fig 3.11. Photographic views of: (a) corn plots staked out with boundaries; (b) corn in early stage of emergence; and (c) wheat forage ready for harvest

4. **Discussion of Quality Assurance.**

1. Project site description: The site characteristics, sampling locations and rationale, and map are provided in the Review of Methods section.
2. Sampling design and procedures: Data quality was assured via: regular checks and calibration of instruments, and proper training of projects participants before during project commencement. To obtain sufficiently representative measurements data, and to fully understand the effect of season on air emissions, the respective measurements covered all four seasons during each year, where applicable. Additional details are provided within each objective in the Review of Methods section. Data completeness was achieved by assuring that raw data was properly identified, examined for inconsistency (compared to others collected simultaneously in the vicinity) and appropriately flagged (if necessary) by the data manager, and reviewed by at least one of the project PIs. Data comparability was ensured via use of common: equipment, instrumentation, metric, quality assurance methods, and protocols. This was achieved through extensive and mandatory training for all personnel and participants use of standard operating procedures (SOPs).
3. Sample handling and custody: All samples (air or liquid) were sampled in such a way as to be representative of the respective air or liquid or manure. Each sample bottle or bag were appropriately labelled (with indelible ink) and indicating legibly the: location, date, time, and name of person collecting the sample. In addition, parameters to be analyzed for and the desired conditions for sample preservation during transport and storage prior to analyzes or prior to use in further research. A standard chain of custody (where multiple personnel handled the samples) were used. All our samples were transported to the laboratory in coolers, which were cooled using ice-bags. In cases where samples had to be shipped (by air) to distant locations, liquid samples were first frozen before being packed into ice-bags-coolers. A custody seal was attached to such samples. All samples were refrigerated in the laboratory until analyzes were done.
4. Analytical method and QA/QC checks: All the studies strictly followed quality assurance procedures and experimental protocols developed in two previous national projects, the Laboratory Testing of Manure Additives sponsored by the National Pork Board in 2000 and the National Air Emission Monitoring Study supervised by U.S. EPA from 2007 to 2010. In particular the following Standard Operating Procedures (SOPs) were adhered to in this project for quality assurance and control:
    a. SOP B1 Data Acquisition and Control Hardware
    b. SOP B2 DAC Software (AirDAC) for NAEMS by Purdue
    c. SOP 1B Bag Sampling for Building Odor Emission Measurements
    d. SOP 7 Continuous Measurement of Gas Emissions
    e. SOP C1. Open path measurement of NH_3 and H_2S with the Cerex UV sentry UVDOAS.
    f. SOP G2. Compressed gas cylinders.
    g. SOP G5. Measurement of H_2S with Pulsed-Fluorescence analyzer.
    h. SOP G7. INNOVA 1412 Photoacoustic multi-gas monitor.
    i. SOP G8. Multipoint calibration of gas analyzers.
    j. SOP G9. Precision checks of gas analyzers.
    k. SOP M1. Manure sampling.

    In addition, whenever necessary, detailed performance evaluation and calibration of the instruments, used in this project, are provided in the Review of Method section of this report.
5. Overall data reduction, analysis and reporting: The raw data was pre-processed to produce data graphs and summary statistics. Results were reviewed by the respective PI for research component in question. These data pre-processing were also used to identify problems with individual devices and were the bases for calling each device check.

5. Findings:

5.1. Objective 1: Evaluate impacts of dairy manure AD on odor and gas emissions.

5.1.1. Odor Evaluation at the AD Site:

The various ways in which odor is characterized include: concentration, intensity, persistence, hedonic tone, and character descriptors. Of these; odor concentration, intensity, and persistence are the most scientific because their characterization is more objective. Odor concentration may be measured as either detection threshold (DT) or recognition threshold (RT). These terms are defined as the number of volumes of dilution odorous air requires to reach detection or recognition level. The odor detection threshold (ODT), therefore, is a dimensionless ratio. The European standard, however, states this as ODT/m^3. In this definition, ODT is thus the volume of non-odorous air required to dilute a unit volume of odorous sample air to the point where trained panelists can correctly detect a difference compared to non-odorous air.

Odor intensity describes the strength of an odor sample and is usually measured at concentration above DT. A scale of five using n-butanol, a standard reference chemical (ASTM E544-10) is usually used to perform intensity analysis. The approach is to get trained panelists sniff five different known concentrations or intensities of n-butanol in water. The panelists are then presented with diluted or full-strength odorous air samples that they rate against the n-butanol scale. Persistence indicates how easily the full-strength intensity odorous air is diluted to below the DT. The slope of the line connecting full-strength and DT on a full log-scale is the known as the persistence and values are usually negative. A more negative value indicates low persistence and vice versa. Hedonic tone is the description of pleasantness or unpleasantness of the odor. A typical hedonic tone scale ranges from -4 to +4 or -11 to +11. The more the negative number the more the unpleasantness and vice versa. Neutral odors are given zero values. Character descriptors describe the character of the odor using such terminologies as mint, citrus, earth, etc. Characters descriptors are only possible above odor DTs or above recognition levels.

The results from our study (Fig. 5.1) shows a significant increase in odor from the co-digestion material (AD influent) compared to raw manure and some slight odor increase during AD of influent mixed substrate. Solids-separation, on the other hand, had little effect on the odor concentration. The converse, however, was observed on the odor intensity and hedonic tone. These two characteristic decreased with AD of the influent as well as with solids-liquid separation. It is apparent that, importing these co-digestion substrates significantly exacerbates odor situation at the AD system as well as in subsequent handling and utilization of the ensuring AD effluents.

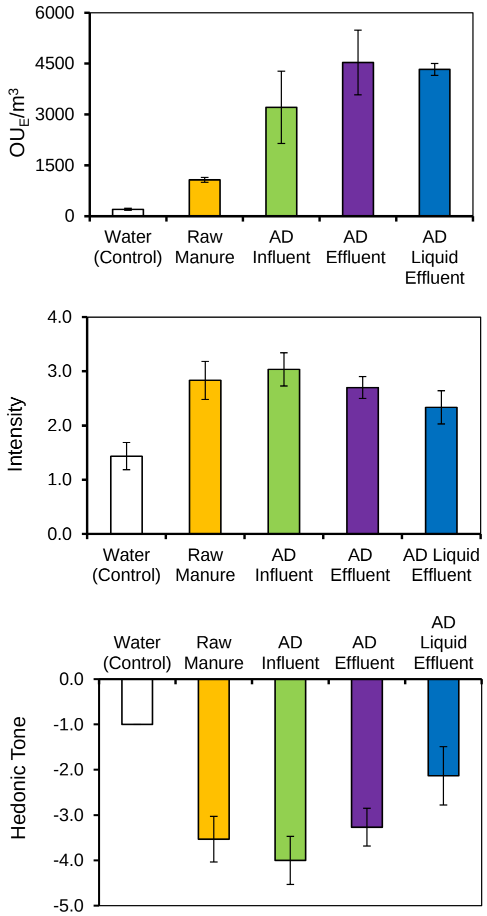

Fig. 5.1. Odor concentration, intensity, and hedonic tone for samples collected at the full-scale AD system and analyzed by a trained panelist of sniffers.

5.1.2. Odor and Gas Emissions Evaluations in the Lab-scale Studies (Purdue University):

As pointed out earlier, the AD was fed dairy manure and additional co-digestion material (such as blood, trap, and bedding). The properties of influent were, therefore, significantly influenced by both quantities and compositions of the co-digestion substrates added. Manure analysis results (Table and 5.2) showed large variations among the four samples sourced at different locations along the AD system, which were used to conduct the laboratory experiments.

Table 5.1. Results of selected parameters from regular analysis of the four manure sources in the first experiment.

Parameter	Raw Manure	Influent	Effluent	Effluent SS
pH	8.3	4.4	8.3	8.4
Total solids (TS), %	2.8	6.1	1.9	1.4
Ammoniacal nitrogen (NH_4-N), %	0.08	0.06	0.13	0.11
Organic nitrogen (N), %	0.07	0.20	0.06	0.05
Total nitrogen (TKN), %	0.15	0.26	0.19	0.16
Phosphorous (P_2O_5), %	0.08	0.10	0.07	0.05
Total sulfur (S), %	0.01	0.02	0.02	0.02

Note: Effluent SS = effluent after solid separation.

Table 5.2. Results of selected parameters from regular analysis of the four manure sources in the second experiment.

Parameter	Raw Manure	Influent	Effluent	Effluent SS
pH	7.9	7.3	7.9	8.0
Total solids, %	2.95	3.05	1.95	1.65
Ammoniacal nitrogen (N), %	0.09	0.08	0.10	0.09
Organic nitrogen (N), %	0.08	0.14	0.05	0.04
Total Kjedahl nitrogen (TKN), %	0.16	0.22	0.15	0.13
Phosphorous (P_2O_5), ppm	348	285	262	160
Total sulfur, ppm	197	200	245	145
Potassium (K2O), ppm	1063	940	636	575
Total calcium, ppm	980	754	744	459
Total magnesium, ppm	249	186	170	100
Total iron, ppm	40	52	175	99

Note: Effluent SS = effluent after solid separation.

5.1.2.1. Gas emissions

Results of gas emissions from the four different manure sources showed significant differences (Table 1.3 and 5.4). Ammonia emissions from raw dairy manure and AD influent were significantly different ($P<0.01$) in both experiments. Emissions from AD influents were higher, demonstrating the effect of co-digestion substrates. Ammonia emissions from AD effluents and AD liquid effluent (after solids separation) were also higher than that from raw manure, probably also because of the co-digestion substrates. Carbon dioxide emissions from AD influents were the highest among the four different sources. Methane emissions demonstrated variations among the four different manure sources and also between the two experiments. However, there was a general trends that emissions of CH_4 from AD effluent and AD liquid effluent were lower ($P<0.01$) than that from raw manure, showing that after the AD process, the production potential of CH_4 from manure was significantly reduced. In both studies, H_2S emissions from the AD effluents were the highest. Emissions of H_2S were significantly reduced from the two types of effluents after the AD process. The emissions of N_2O were the most irregular between the two experiments. In the first experiment, N_2O emission was the highest from the raw manure. However, in the second experiment, N_2O emission from AD effluent (before solids separation) was the highest. The reasons for these variations were still unknown but may probably be attributed to digester receiving different co-digestion material between the two sampling events.

Table 1.3. Mean ± (standard deviations) gas emissions (μg min^{-1}) from the reactors during the first experiment.

Gas	Dairy manure (R1 & 2)	AD influent (R3 & 4)	AD effluent (R5 & 6)	AD liquid effluent (R7 & 8)
Ammonia	75 ± 49	112 ± 68	158 ± 97 [a]	145 ± 92 [a]
Carbon dioxide	2782 ± 1198	6989 ± 3409	2043 ± 899 [a]	1957 ± 9[a]
Methane	196 ± 161	17 ± 29	65 ± 68	28 ± 23
Hydrogen sulfide	0.2 ± 0.3	2.7 ± 2.8	0.0 ± 0.1	0.0 ± 0.0
Nitrous oxide	3.3 ± 9.0	0.9 ± 1.9	0.4 ± 2.6 [a]	0.2 ± 0.9 [a]

[a] Treatment pairs with the same superscript were not statistically different ($P>0.05$).

Table 5.4 Mean ± (standard deviations) gas emissions (µg min^{-1}) from the reactors during the second experiment.

Gas	Dairy manure (R1 & 2)	AD influent (R3 & 4)	AD effluent (R5 & 6)	AD liquid effluent (R7 & 8)
Ammonia	129 ± 62	179 ± 88	162 ± 103	156 ± 92
Carbon dioxide	2703 ± 115	3592 ± 1540	1901 ± 1391	1720 ± 1251
Methane	226 ± 214	396 ± 376	170 ± 269	154 ± 247
Hydrogen sulfide	0.47 ± 0.80	0.61 ± 0.93	0.12 ± 0.14	0.07 ± 0.07
Nitrous oxide	1.6 ± 5.0	1.7 ± 3.6	8.2 ± 19.2	0.9 ± 4.5

5.1.2.2. Effect of ad on manure VFA concentrations

The findings of AD on VFA in this study were published in two journal articles listed in the Appendix of this report (Page et al. 2014 and 2015). In summary, six VFA, including formic acid, acetic acid, propionic acid, butyric acid, 2-methylbutyric acid, and hexanoic acid, were identified in manure samples from all reactors. Significant differences in VFA concentrations between the AD and non-AD manure were observed. Variations in VFA concentrations over the test periods in all reactors were also observed. In addition, VFA concentrations between the top and bottom manure samples were demonstrated. The VFA concentrations were significantly lower in the AD-treated manure than in the group of non-AD manure in both studies, demonstrating that AD significantly reduced VFA from the influent. The dominant VFA in raw dairy manure was acetic acid followed by propionic acid in both experiments. Acetic acid was also the dominant VFA present in AD-treated manure in both tests. This characteristic of acetic acid in dairy manure confirmed research results reported in the literature. The dominant VFA in AD influent depended on the substrates added to raw manure. Formic and butyric acids were the predominant VFA present in the AD influent manure in the first test followed by acetic acid. Acetic acid was the predominant VFA present in the AD influent in the second test followed by propionic acid. The total concentration of VFA in AD-treated manure reached concentrations above the threshold of unequivocal unacceptability of odor for VFA during the first 20-30 days of storage, but AD helped reduce the time for concentrations to reach an acceptable level. Therefore, AD of dairy manure demonstrated the potential of reducing odor emissions during subsequent manure handling (storage or application). The concentrations of the total VFA in AD-treated manure exhibited a general decreasing trend over the three months of storage. However, concentrations in non-AD treated manure were sporadic and less predictable. The VFA exhibited highly variable temporal and spatial variations in both studies. The complexity of characteristics of VFA within this study displays the difficulty in predicting concentrations and compositions of VFA in dairy manure when co-digestion is utilized.

5.1.2.3. Effect of AD on odor characteristics

5.1.2.3.1. Odor Concentration

Odor emissions from the AD influent decreased from 1181 to 345 OU_E m^{-3} in the first test (71% decrease) and from 3090 to 121 OU_E m^{-3} in the second test (82% decrease). Similar decreases were observed from all sources as the odor concentrations decreased by 56 to 86% in test 1 and by 82 to 96% in the second test. The addition of food wastes to the raw manure resulted in a more odoriferous AD influent. This was especially true in the first test when the overall geometric mean odor concentrations of the raw manure and the mixed AD influent were 556 and 1181 OU_E m^{-3}, respectively. The differences between Raw Manure and AD Influent were high initially in the second test but disappeared after four weeks. The effects of AD and SS on odor characteristics are dependent on the odor characteristics of the AD influent.

The overall geo-mean odor concentrations (excluding the first sampling when only Raw Manure and AD Influent were sampled) of AD Effluent (294 OU_E m^{-3}) and SS Effluent (271 OU_E m^{-3}) were reduced by 67% and 69% compared with AD Influent (887 OU_E m^{-3}), respectively. Previous research has shown that the normal release of gases from manure is disturbed by the transfer of the material into the reactors and that the first few weeks therefore may not represent actual storage conditions as much as the last few weeks. The actual reductions as affected by AD would not be evident until after the stored manure stabilizes after the major disturbance. This was apparently the case in this test because the effects of AD were greater when the first month of data was excluded from the analysis. Based on the data from days 36 to 92, the overall geo-mean odor concentrations of AD Effluent (245 OU_E m^{-3}) and SS Effluent (237 OU_E m^{-3}) were reduced by 74% and 75% compared with AD Influent (946 OU_E m^{-3}), respectively.

During the second test, the overall geo-mean odor concentrations of AD Effluent (259 OU_E m^{-3}) and SS Effluent (205 OU_E m^{-3}) were reduced by 43% and 59% compared with AD Influent (582 OU_E m^{-3}), respectively. Excluding data from the first month, the overall geo-mean odor concentrations of AD Effluent (197 OU_E m^{-3}) and SS Effluent (142 OU_E m^{-3}) were reduced by 39% and 57% compared with AD Influent (298 OU_E m^{-3}), respectively. The effect of SS was negligible in the first test. The odor concentrations of the reactors with SS effluent were about 28% less than AD effluent.

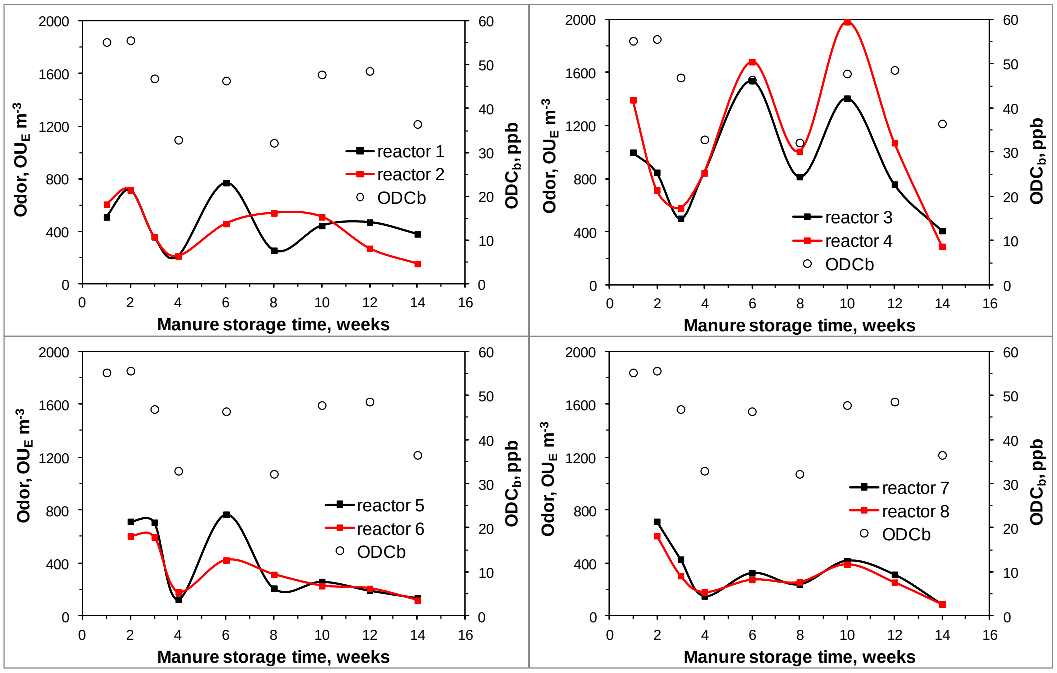

Fig. 5.2. Geometric means of odor concentrations in the exhaust air from the 8 reactors during a 3-month manure storage test.

5.1.2.3.2. Hedonic tone

The hedonic tone (HT) was assessed by each odor panelist at the dilution step at which the odor could be recognized. Since HT is related to odor concentration, this assessment removes the effect of odor concentration and simulates the odor impact downwind of the facility. The hedonic tone was assessed on a scale of -10 to 10 with -10 the most unpleasant odor ever experienced and +10 the most pleasant fragrance every experienced.

In test 1, HT at recognition was measured after the first 30 days. The overall average HT of the Raw Manure was -2.2. Adding the food wastes worsened the unpleasantness because the overall average HT decreased to -5.7 for the AD Influent. The AD treatment, however, removed this increase by lowering the overall average to -2.14. Solids separation resulted in only slightly lower numerical HT to -1.75. Similar trends occurred in the second test as the overall average HT at recognition were -1.33, -2.33, -1.33, and -1.27 for Raw Manure, AD Influent, AD Effluent, and SS Effluent. The conclusion of both tests as a whole is that all sources exhibited similar hedonic tones except the AD influent which 0.5 to 4.0 HT points higher than the other sources.

The measurements of intensity at recognition resulted in a trend that was very similar to HT at recognition. The food wastes increased the overall average intensity (after day 30) by 0.69 and 0.34 units in tests 1 and 2, respectively. The AD reduced the intensity of the influent by 0.86 and 0.32 units in tests 1 and 2, respectively. The SS had virtually no effect on intensity at recognition.

5.2. Objective 2 Findings: Evaluate impacts of dairy manure AD on NH_3 emissions.

5.2.1. Effects of AD and Solids Separation on Manure Characteristics:

The characteristics of the raw manure (RM), AD influent, AD effluent and AD liquid effluents used in the simulation studies are shown in Table 5.5. The effects of AD and solids separation on key parameters are presented in Table 5.6. The AD influent had a higher fraction of VS compared to raw manure samples most probably due to addition of co-digestion materials to the raw manure. Addition of co-digestion substrates also apparently increased the contents of TS and VFA while reducing concentrations of TAN and pH, indicating co-digestion substrates (i.e. expired carbonated beverages; fats, oils, greases (FOG)) with relatively low nutrient content but lower pH.

The AD process significantly increased TAN concentration and effluent pH while decreasing TS, VS, and VFA. The increase in TAN is attributable to organic nitrogen mineralization during the digestion process (Powers et al., 1999; Sommer et al., 2006), whereas increased pH was most likely due to higher ammonia N in the AD effluent as well as conversion of organic carbon and phosphorus to inorganic carbonate and phosphate buffer systems, leading to higher overall alkalinity and pH. Similar TAN and pH increases were observed in previous studies (Amon et al., 2006; Immovilli et al., 2008; Frear et al., 2011; Koirala et al., 2013). The higher VFA concentration of AD influent may be possibly due to the addition of co-digestion substrates (Frear et al., 2011; Page et al., 2015). The decrease in TS, VS and VFA concentrations in AD effluent is emblematic of anaerobic biodegradation of organic compounds during the AD process (Madsen et al. 2011). These results were in partial agreement with those from previous studies (Frear et al., 2011; Page et al., 2014), although the limited VS reduction (42%) and relatively high residual VFA concentration (2,468 mg L^{-1} and 55% reduction) indicate an AD performance below that expected of a co-digestion system, indicating concerns with operation or use of effective hydraulic retention time (HRT) (Frear et al., 2011).

Solids-liquid separation significantly reduced TS, VS, TAN, and VFA. The solids-liquid separation removed 64% of TS and 67% of VS from AD effluent, indicating an effective performance by the slope-screen system in removing the recalcitrant fibrous and other solids in the effluent. The concentrations of TAN and VFA were approximately 56% and 86% less in AD liquid effluent than in AD effluent. The reduced TAN and VFA concentrations in AD liquid effluents relative to AD effluents were attributed to lower levels of solids in AD liquid fraction (Zhang and Westerman, 1997) with the solids and associated water carrying a significant portion of TAN and VFA, either as part of the water or adhered to the solids.

Table 5.5. Characteristics of RM, AD influent, AD effluent and AD liquid effluent applied to simulations.

Property	RM	AD influent	AD effluent	AD liquid effluent
Total solids (mg kg^{-1})	32717	33300	21967	7917
Volatile solids (mg kg^{-1})	26567	28567	16583	5150
TAN (mg L^{-1})	978	755	1637	723
VFA (mg L^{-1})	1338	5512	2468	352
pH	7.03	5.74	7.32	6.63

Table 5.6. Effects of AD and solids-separation on TS, VS, TAN and VFA.

Property	Effect of AD			Effect of solids-separation		
	AD Influent	AD Effluent	Change (%)	AD effluent	AD liquid effluent	Change (%)
Total solids (mg kg^{-1})	33300	21967	-34*	21967	7917	-64
Volatile solids (mg kg^{-1})	28567	16583	-42	16583	5150	-69
TAN (mg L^{-1})	755	1637	117	1637	723	-56
VFA (mg L^{-1})	5512	2468	-55	2468	352	-86

*Negative signs denote reductions, while positive signs indicate increases.

5.2.2.Ammonia Emissions from Manure Storage:

The results of cumulative NH_3 loss and the dynamic NH_3 fluxes from simulated storages of RM, AD influent, AD effluent, and AD liquid effluent are presented in Fig. 5.3. The cumulative mean NH_3 emissions during the 21-d tests were: 2399 ± 101 mg from AD effluent; 962 ± 47 mg from RM; 870 ± 15 mg from AD liquid effluent; and 197 ± 16 mg from AD influent (figure 3a). Mean cumulative NH_3 emissions, within the 21 d, was significantly higher from AD effluent than from the storage of RM, AD liquid effluent, and AD influent. Emissions from RM and AD liquid effluent, however, were not significantly different. During day 1, higher NH_3 fluxes were observed from the AD effluent (3.95 g m^{-2} d^{-1}) and RM (1.65 g m^{-2} d^{-1}) storages compared to fluxes from AD liquid effluent (1.1 g m^{-2} d^{-1}) and AD influent (0.25 g m^{-2} d^{-1}). The higher fluxes from AD effluent and RM decreased at constant rates to 2.02 and 0.70 g m^{-2} d^{-1} by 21 d, while fluxes from AD liquid effluent and AD influent remained approximately constant throughout the study period (figure 5.4b).

Lab simulated manure storages of AD effluent indicated significantly higher NH_3 emissions (92% more) than from AD influent (undigested manure) during the 21-day period. Ammonia flux from the AD effluents ranged from 3.95 to 2.02 g m^{-2} d^{-1} compared to 0.25 g m^{-2} d^{-1} from AD influent. Similar NH_3 emissions were observed from field studies. Field measurements of ammonia emissions from storages of AD and non-AD manure ranged from 0.12 to 1.4 g m^{-2} d^{-1} and 0.09 to 0.79 g m^{-2} d^{-1}, respectively (Fig. 5.4). Immovilli et al*.* (2008) also showed that the anaerobically digested cattle slurry resulted in higher (0.208 g m^{-2} h^{-1}) NH_3 loss compared to undigested slurry (0.121 g m^{-2} h^{-1}) during laboratory storage tests. Post-separation storages of AD liquid effluents showed significant reductions of NH_3 emissions (64%) compared to storage of unseparated AD effluent. The reduced NH_3 loss measured from AD liquid effluents relative to AD effluents is attributable to reduced TAN removed with separated solids. This conclusion is consistent with observed ammonium-solids adsorption phenomenon (De Visscher *et al.*, 2002; Vaddella *et al.*, 2013). Removal of solids and adsorbed TAN may, therefore cause significant reductions of NH_3 emissions during storages of AD liquid effluents. These results concur with previous studies on NH_3 emissions abatement via removal of biodegradable solids and associated organic nutrients during solids-liquid separation treatment (Zhang and Westerman, 1997). Szoegi and Vannotti

(2007) showed that a 60% TS removal resulted in a reduction (73%) of NH_3 emission from swine lagoons. Based on the results reported herein and from available literature, it is evident that solids-liquid separation treatment can significantly mitigate NH_3 emissions from AD liquid effluents.

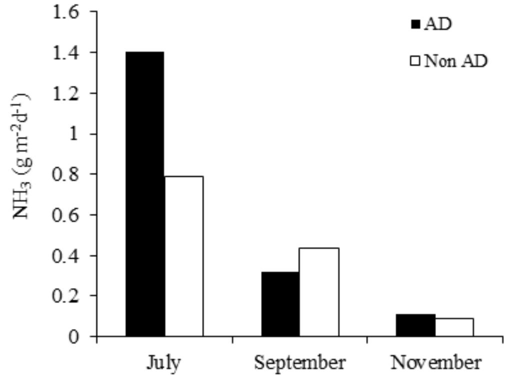

Fig. 5.3. Ammonia emissions from simulated lab-scale storages: (a) Cumulative emissions (mg d^{-1}), (b) dynamic emissions fluxes ($gm^{-2}d^{-1}$). Vertical bars represent standard deviations from means (*n*=3).

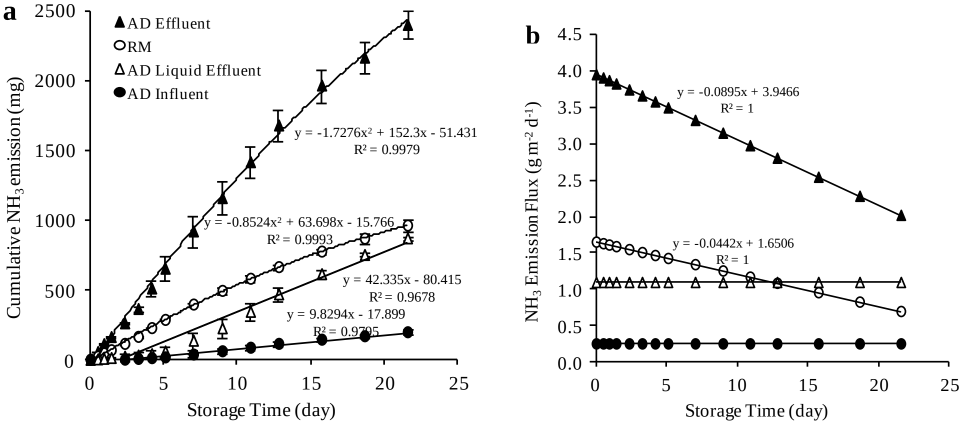

Fig. 5.4. Field emissions of NH_3 from anaerobically digested (AD) and non-anaerobically digested (non-AD) manures.

5.2.3.Changes in Manure Properties During Post-AD and Post-Solids Separation Storages:

A summary of the characteristics of the four dairy manures (RM, AD influent, AD effluent, and AD liquid effluent) after the 21 d storage period are summarized in Table 5.7; while Table 5.8 represents the respective changes of properties in question. The AD influent had the highest TS levels both at the start and end of the storage, while AD liquid effluent exhibited the lowest TS concentrations. The TS content in AD influent and AD effluent decreased by approximately 12% and 6%, respectively, during this period, while only marginal increase (approximately 1%) in TS in AD liquid effluent was observed. The changes in VS were similar to those of TS. Evaporative moisture loss from manure surfaces can explain these observed increases (Smith et al., 2007; Page et al., 2014).

Approximately 38% and 16% reduction in TAN in AD effluent and AD liquid effluent, respectively, were observed during the 21 d storage period. However, a 25% increase in TAN was recorded in the AD influent. This increase in the TAN content in AD influent was probably due to mineralization of organic nitrogen (Sommer et al. 2006). In a similar recent study, Page et al. (2014) also observed an increase in TAN in AD influent at the end of a three-month storage of dairy manure.

Volatile fatty acids concentrations in AD influent were the highest at the beginning and end of storage period. This higher VFA concentration is likely due to the higher initial biodegradable VS in the AD influent. Higher organic matter degradation usually leads to higher microbial activities resulting in more VFAs production (El-Mashad et al., 2011) and greater methane formation during anaerobic storage, thus in part explaining both the still high effluent VFA concentration and VFA reduction (21%) of AD influent post storage. The concentrations of VFAs were lowest in the AD liquid effluent in the start and end of storage study most likely due to its lower TS and VS contents. The results indicated that AD effluent reduced VFA by 40%, while solids-liquid separation resulted in a very high 116% increase in VFA during storage. An explanation for these observations is that the AD effluent, rich in anaerobic culture attached to solids and undigested VFAs (Table 5.8) leads to significant degradation of the VFA into methane during the storage. Conversely the AD liquid effluent after solids separation in reduced in anaerobic culture, particularly methanogenic populations, leading to build up of VFAs without significant and subsequent conversion and release of methane.

Table 5.7. Characteristics of RM, AD influent, AD effluent and AD liquid effluent after 21 d of storage.

Property	RM	AD influent	AD effluent	AD liquid effluent
Total solids (mg kg^{-1})	29958^{b}* (2347)**	37297^{a} (6747)	23256^{b} (1247)	7856^{c} (864)
Volatile solids (mg kg^{-1})	23741^{b} (2181)	32511^{a} (6359)	17188^{c} (1072)	4916^{d} (682)
TAN (mg L^{-1})	898^{a} (87)	946^{a} (41)	1009^{a} (65)	610^{b} (29)
VFA (mg L^{-1})	2733^{b} (165)	4358^{a} (84)	1490^{c} (118)	753^{d} (109)

*^{abcd} Values in each row within each treatment followed by the different superscripts (a, b, c, d) are significantly different ($P < 0.05$); **Values between parentheses represent standard deviation of the mean (n=3).

Table 5.8. Post-AD and post-solids Separation storage of dairy manure: manure characteristics at the beginning and at the end of the storage.

Property	AD influent			AD effluent			AD liquid effluent		
	Start	End	Change (%)	Start	End	Change (%)	Start	End	Change (%)
Total solids (mg kg^{-1})	33300	37297	12*	21967	23256	6	7917	7856	-1
Volatile solids (mg kg^{-1})	28567	32511	14	16583	17188	10	5150	4916	-5
TAN (mg L^{-1})	755	946	25	1637	1009	-38	723	610	-16
VFA (mg L^{-1})	5512	4358	-21	2468	1490	-40	352	753	114

*Negative signs denote reductions, while positive signs indicate increases.

5.2.4.Ammonia Emissions from Land Application of Manure:

The results of cumulative NH_3 loss and the dynamic NH_3 fluxes from simulated land application of non-AD and AD manures are presented in Fig 5.5. Anaerobic digestion, in general, regardless of manure application methods, was more effective in reducing NH_3 emissions in comparison to raw or undigested manure. Under surface application, AD manure produced 56% less NH_3 emission than non-AD manure, while injection of AD manure resulted in 27% less emission than injection of non-AD manure. The reduced ammonia emission is partly attributed to lower solids content in the AD manure compared to non-AD manure, which enhances applied manure infiltration into the soil. Injection of non-AD manure resulted in 42% less NH_3 emissions than the surface application of non-AD manure. The difference between injected AD manure and surface-applied AD manure, however, was not significant. The results from simulation of manure injection is consistent with the work of Huijsmans et al., (2003), which showed that manure injection reduced NH_3 loss more than manure surface broadcasting or spreading.

Ammonia flux is usually the highest immediately after manure application because of the initial higher TAN concentration. Surface application of non-AD manure exhibited the highest initial NH_3 emission flux (0.78 g m^{-2} d^{-1}), while injected AD manure had the lowest initial NH_3 emission flux of 0.17 g m^{-2} d^{-1} (only 22% the ammonia flux from surface applied non-AD manure, figure 5b). For similar application method, AD manure was more effective in reducing NH_3 emissions (i.e. retained higher manure fertilizer-value) than non-AD manure.

Ammonia fluxes from treatments receiving non-AD manure dropped fast to approximately zero within 3 d, while the fluxes from treatments receiving AD manure gradually approached zero within 5 d. These decreases were attributed to the decrease of TAN concentration in soil surface from either ammonia emission, TAN infiltration, TAN-nitrification. In this study, the lower solids content of AD manure may have improved AD manure infiltration into the soil so that its initial emission flux was less than that of non-AD manure and thus needed more time to volatilize. Ammonia fluxes from applied manure were low after the first 2 d and the cumulative NH_3 emission reached 50% of its maximum within the first 1 or 2 d explaining why most of the ammonia emissions occurred within 5 d after manure application.

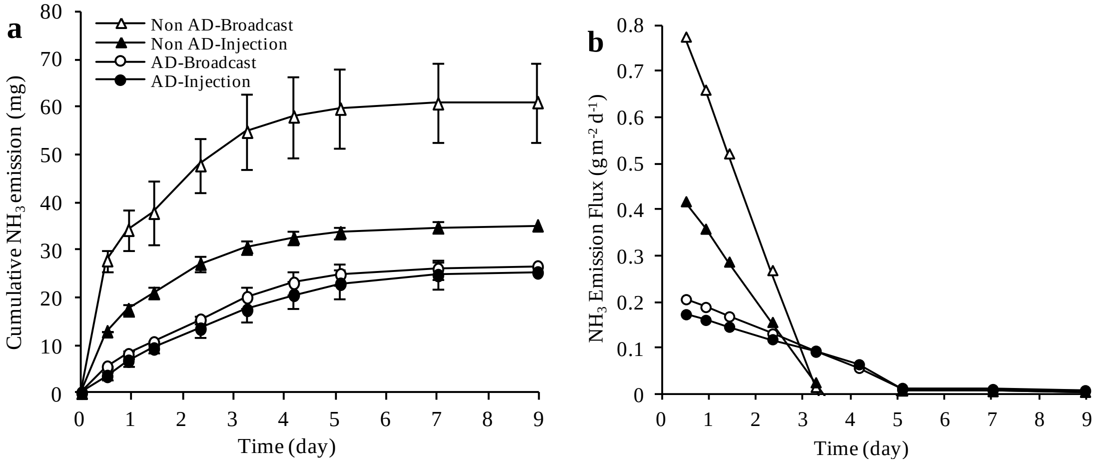

Fig. 5.5. Lab-scale calculated cumulative NH_3 emission (a) and NH_3 emission flux (b) following the land application. Vertical bars in (a) represent standard deviation of means (*n*=3).

Cumulative NH_3 emissions and fluxes during 7 d after manure application in the field plots are shown in Fig. 5.6. The results, in general, were similar to those obtained in laboratory studies. With respect to surface application, AD manure showed 49% less NH_3 loss compared to the non-AD manure. Injection of AD manure did not significantly reduce total NH_3 flux (Fig. 5.6a) over injection of non-AD manure. The initial flux from AD manure, however, was lower than from non-AD manure (Fig. 5.6b). Accordingly, application of AD manure not only resulted in significantly less NH_3 emission but also exhibited a lower flux as opposed to non-AD manure. With respect to application methods, surface application resulted in 63% and 25% more NH_3 loss than injection of non-AD manure and AD manure, respectively. These results suggested that manure injection was a more effective method for mitigation of NH_3 emission than surface application. Ammonia fluxes were generally low after 2 d, with 50% of cumulative NH_3 emission being reached within 1 d and NH_3 emission almost complete within 5 d after manure application.

The patterns of NH_3 emission were, somewhat, different from that observed in controlled laboratory studies most probably due to differences in manure characteristics, and diurnal variation in ambient temperature, wind speed and radiation factors within exposed field plots. In the field studies, for example, injecting AD manure reduced NH_3 emissions significantly compared to surface application of AD manure. The same test in the lab did not indicate similar significant advantage in mitigation NH_3 emissions. These discrepancies may be attributed to inadequate replication or simulation of manure injection in the lab studies to match field applications.

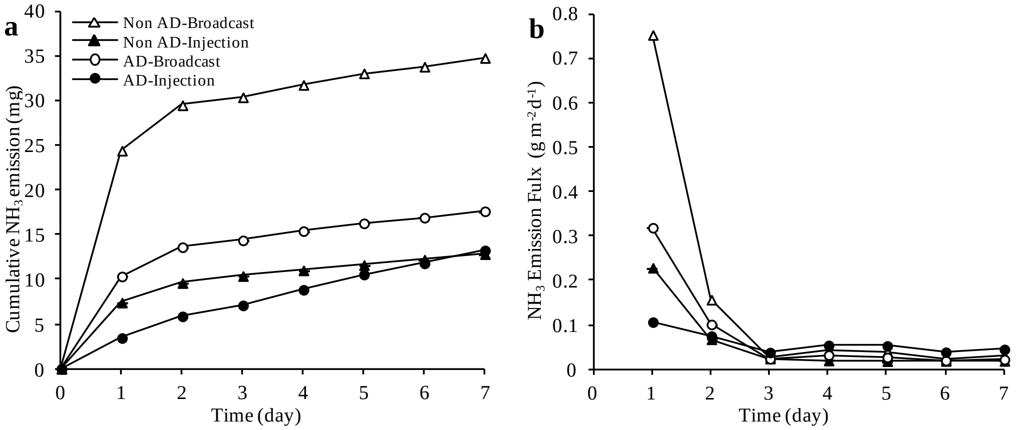

Fig. 5.6. Field-scale calculated cumulative NH_3 emission (a) and NH_3 emission flux (b) following the land application.

5.3. Objective 3 Findings: Evaluate impacts of dairy manure AD on greenhouse gases (GHG) emissions.

5.3.1. GHG Emissions from Field Plots:

Computations of emissions rates of the respective gases from land applied AD and non-AD manures are presented in the Figure 5.7. The cumulative concentrations of the respective gases within the closed chambers during the first hour were linear as the high linear regression goodness-of-fits show (R^2 ranging from 0.92 to 1.00). These results indicated constant rates of change of headspace gas concentrations within the period of measurements. Linear regressions of concentration (ppm-v) versus time data, therefore, were used to determine the rate of change of concentrations, which is basically the slope of the respective linear regression (Parkin et al., 2004).

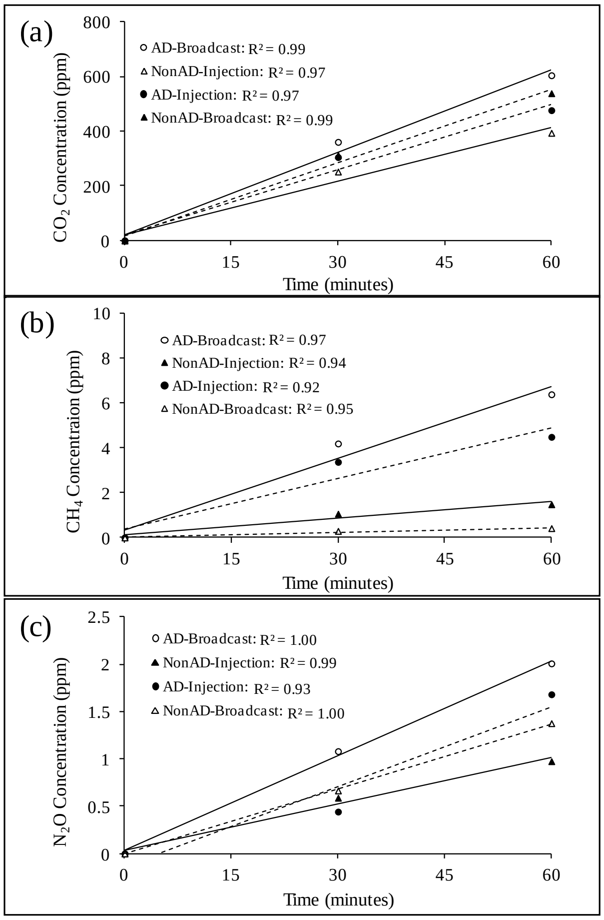

Fig. 5.7. Computations of concentrations on the land applied AD and non-AD manure: (a) carbon dioxide, CO_2; (b) methane, CH_4; (c) nitrous oxide, N_2O.

Figure 5.8 show the normalized cumulative emissions of CO_2, CH_4, and N_2O during two weeks after the AD and non-AD were broadcasted or injected in the field-plots. Emissions of CO_2 were significantly higher from field plots applied with non-AD than from field plots receiving AD manure. Compared with surface spreading, manure injection, nevertheless, did not play a significant role in the emissions of CO_2. These observations concur with those of similar studies conducted in the past. In Flessa and Beese (1999) studies, CO_2 emissions after surface spreading and slit injection of cattle slurry were not significantly different.

Emissions of CH_4 were similarly significantly higher from the non-AD manure than from the AD-manure. In contrast, injecting non-AD manure in the soil significantly increased emission of CH_4 although no significant effect on CH_4 emission was observed from injected AD-manure. Similar results were reported in previous studies on application of cattle slurry using similar application methods (Flessa and Beese, 1999). The higher emissions of CH_4 from injected manures were attributed to the enhanced anaerobic conditions under the soil cover. Generally, injecting organic materials in the soil provides better anaerobic conditions than broadcasting it on the surface. On the other hand, because significant degradation of organic matter in the AD-manure has already taken place in the AD vessel, further degradation to CH_4 and CO_2 is limited. In contrast, the non-AD manure is likely to have a higher proportion of degradable organic matter, which is readily digested in the anaerobic conditions. Manure injection thus resulted in more releases of CH_4 and CO_2 than previously digested manure.

Emission of N_2O from the non-AD injected and broadcasted manures were also slightly higher than from the injected and broadcasted AD-manure. Injection of liquid organic wastes into soil promotes conditions conducive to denitrification because it creates an anaerobic environment in the presence of inorganic N and readily digestible C (Comfort et al., 1988; 1990). The rate of N_2O formation, however, is also a function of other factors including available oxygen and the temperature (Granli and Bockman, 1994). Thompson et al. (1987) estimated that 7 to 21% of the N added from injected cattle-manure slurry was lost via denitrification to N_2O. Rice et al. (1988), however, suggested that denitrification losses account for 50% of injected N into the soil. Therefore, although slurry injection reduces NH_3 loss, it is necessary to evaluate the gain from NH_3 loss reduction against the potential increase in the greenhouse gases (N_2O and CH_4) emissions from injected manure.

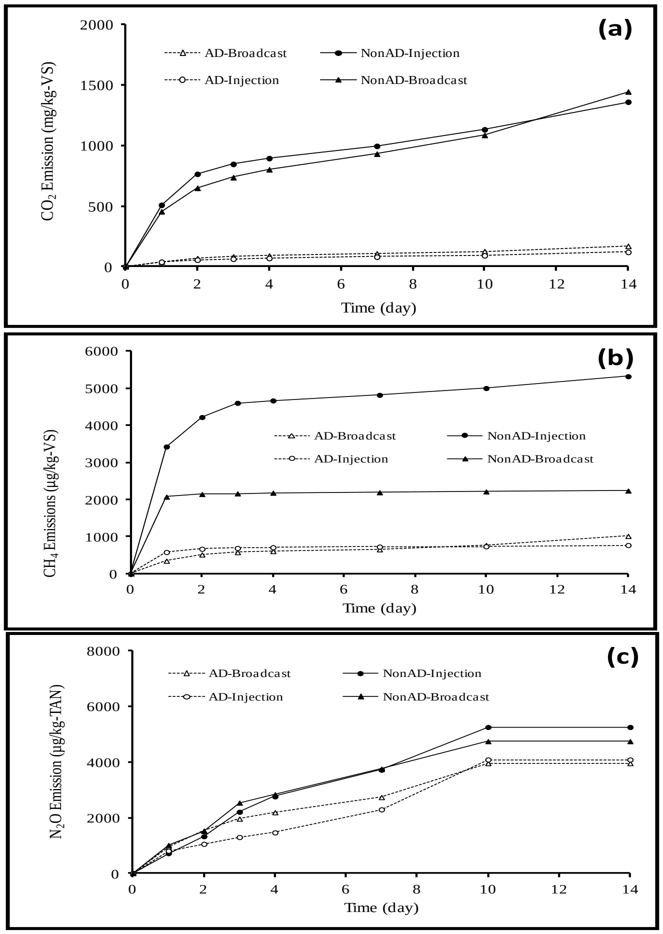

Fig. 5.8. Cumulative emissions of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) from broadcast and injected anaerobically digested (AD) and non-anaerobically digested (non-AD) manures.

5.3.2. GHG Emissions from Manure Storages:

The emissions of greenhouse gases, in all four seasonal sampling events, indicate significantly higher emissions from the non-AD manure lagoon than from the AD manure lagoon (Figure 5.9). In general, however, the emissions of CO_2 and CH_4 were highest in July (summer conditions) than in the other three sampling periods. Emissions of N_2O, on the other hand, were relatively higher in spring and fall than in winter and summer. Higher emissions of ammonia (NH_3) observed in summer (July), however, were not coupled to similar higher N_2O emissions. Emission of NH_3 is probably a direct indication of the concentration of ammoniacal nitrogen (AN) in each lagoon, since the two lagoons are in the same locality. The discrepancy between emissions of N_2O and NH_3 is attributed to the denitrification process responsible for N_2O production. The denitrification process is known to be favorable in conditions with more easily metabolizable or degradable organic C (Velthof, et al., 2003; Inubushi and Acquaye, 2004). Higher production of N_2O is thus expected from undigested (non-AD) manure, which invariably contains more easily available organic C than in digested manure. The latter phenomenon was observed in the current study. During all the four sampling events, the emission of N_2O was proportionately higher than NH_3 emissions from undigested manure lagoon than from the digested manure lagoon. The higher emissions of CH_4 and CO_2 observed from undigested manure lagoon than from the digested manure lagoon confirm higher content of easily-degradable organic C in the undigested manure compared with the digested manure.

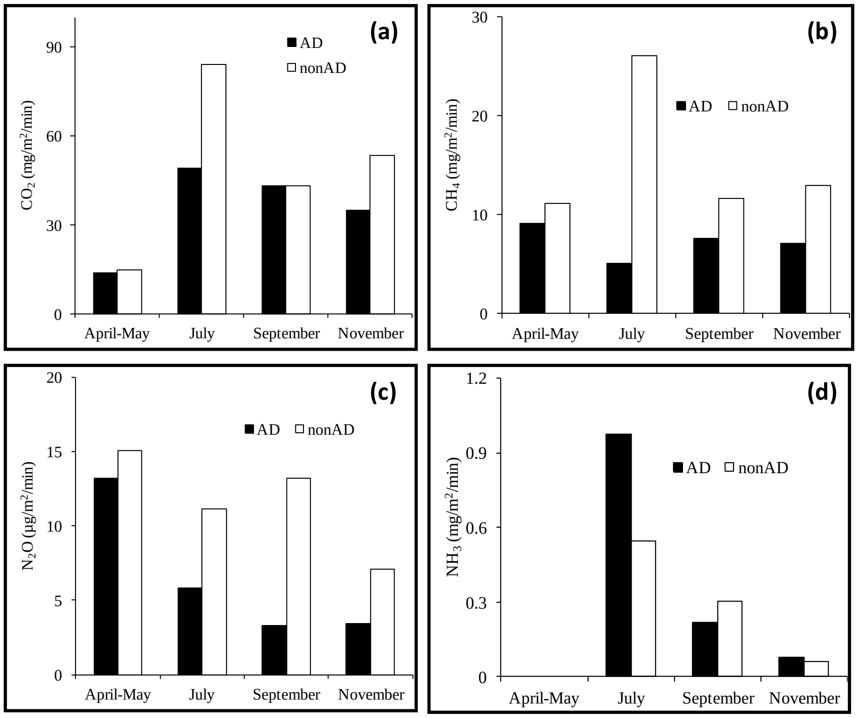

Fig. 5.9. Emissions of carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ammonia (NH_3) from anaerobically digested (AD) and non-anaerobically digested (non-AD) manures, held in anaerobic lagoons, during four sampling events in 2011.

5.3.3.Modeling NH3 Emissions:

5.3.3.1. Chemical properties of manures

Characteristics of manure before and after AD are presented in Table 5.9. The results showed significantly ($p < 0.05$) greater values of pH, TAN, IS, and viscosity in AD manure as compared to UD manure. The mineralization of organic matter during the AD process was responsible for higher TAN and IS; whereas increased ammonia nitrogen (alkaline in nature) contributed to the higher pH observed in AD manure. On the other hand, increased viscosity of the manure has been attributed to the breakdown of solid organic matter during the AD process (Goel et al., 2004). These physical-chemical changes following AD of manure affect ammonia volatilization in different ways. On one hand, increased in pH and TAN, for instance, may increase the potential of ammonia volatilization from AD compared to UD manure; whereas on the other hand, higher viscosity may impede ammonia volatilization.

The concentration of TS in the UD manure was approximately 48% more than in the AD manure. The lesser amount of VS in the AD manure (0.84%) than in UD manure (2.05%) indicated a higher content of organic matter in UD than in AD manure. The former and latter observations were in agreement with theory and with other studies (Martin, 2004; Ortenblad, 2000). An inverse relationship between ammonia dissociation and TS concentration in liquid manure has been reported in past research (Vaddella et al., 2011; Liang et al., 2002); which suggests that the decrease in TS concentration following AD of dairy manure may exacerbate ammonia volatilization.

Table 5.9: Properties of undigested and anaerobic digested liquid manure.

Type of Manure	pH	TAN (mg L^{-1})	Viscosity (Pa s)	IS (mol L^{-1})	TS (%)	VS (%)
UD Manure	7.58±0.08*	480±2	0.058±0.005	0.228±0.001	3.27±0.07	2.05±0.10
AD Manure	8.20±0.05	512±3	0.119±0.002	0.274±0.002	1.71±0.10	0.84±0.05

*Mean ± Standard deviation (n = 3).

5.3.3.2. Particle size distribution

Particle size distribution (PSD) analysis was performed to characterize solids in the AD and UD manures. Key PSD statistics and PSD plots of respective manure solids are presented in Table 5.10 and fig. 5.10, respectively. Mastersizer model MS2000, with a range of 0.01 µm to 2000 µm, was used for our PSD analysis. Figure 5.10 was scaled from 0.1 µm to 1000 µm in the x-axis because that was the predominant range of PSD in our analysis. The volume median diameters (VMD) of AD and UD manures solids were not significantly different (p = 0.65). The respective geometric standard deviations (σ_g), however, were significantly different (p = 0.001) between solids of AD and UD manures. These results suggest that UD solid particles were only slightly larger but more widely distributed than that of the solids of AD manures. The PSD of solid particles for AD and UD manure were heavily right-skewed (Fig. 5.10), indicating higher concentrations of coarse particles. In general, organic matters are degraded during the AD process, which may explain the slightly lesser VMD and narrower distribution of solids from AD manure compared to UD manure solids. The PSD of manure solids is an indicator of their relative potential to adsorb TAN. Fine particles, in general, have a higher potential for TAN adsorption than coarse particles. The adsorption of TAN on manure solids effectively reduces ammonia volatilization. The manure solids particle size and PSD analyses, before and after the anaerobic digestion process, did not indicate a significant change in the TAN adsorption potential on manure solids for this phenomenon to play a significant role in the ammonia volatilization process.

Table 5.10. Particle Size Statistics for Anaerobically Digested and Undigested manure.

Manure Type	Volume median diameter, VMD (µm)	Geometric Standard deviation, GSD (dimensionless)
AD Manure	45.15^a	7.18^a
UD Manure	46.76^a	9.18^b

*Means with the same letter (a, b, or c) in the same column were not significantly different at α =0.05.

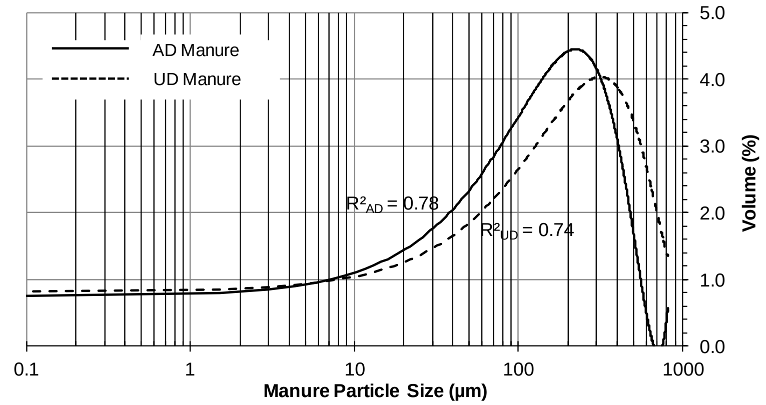

Fig. 5.10: Comparative particle size distribution for anaerobically digested and undigested manures (R^2 = 0.78 and 0.74 respectively).

5.3.3.3. Anaerobic digestion and the overall mass transfer (K_{oL})

The overall mass transfer coefficients (K_{oL}), determined at the three liquid temperatures, as well as the relationships between K_{oL} and liquid temperature are presented in Table 5.11 and fig. 5.11, for both UD and AD dairy manures. A two-way analysis of variance (ANOVA) showed significantly ($p < 0.001$) greater K_{oL} for the UD manure than for the AD manure (table 4); indicating higher potential for ammonia volatilization from UD compared to AD manure. The ANOVA also indicated significant differences ($p < 0.001$) in the K_{oL} at different temperatures. The K_{oL} for both AD and UD manure decreased with temperature (R^2 = 0.57 and 0.98, respectively). In contrast, previous research reported increases in K_{oL} with increasing manure temperature (Vaddella, 2012; Montes et al., 2009; Arogo et al, 2003). For given environmental conditions and fixed manure temperature, the manure properties which may influence K_{oL} are the viscosity of manure, TS concentration, and concentration of $NH_{3(L)}$ in the manure. Compared to UD manure; higher viscosity of AD manure implied decreased K_{oL}; while increased concentration of $NH_{3(L)}$ and lower TS concentration increased the K_{oL}. Overall, therefore, the net effect of lower TS concentration and higher $NH_{3(L)}$ concentration on K_{oL} was evidently significantly lower than the effect of increased viscosity. The results, however, also showed significant interaction between temperature and manure on the K_{oL} ($p = 0.002$). Pairwise comparisons of the cell means indicated that the K_{oL} values ware significantly different at all three temperatures (15°C, 25°C, and 35°C) for the UD manure. On the other hand, although the K_{oL} values were not significantly different between 15°C and 25°C, both K_{oL} values were significantly higher than at 35°C for the AD manure. The rate of change of K_{oL} with temperature was higher in the UD manure than in the AD manure. These results suggested that low temperature had more influence on K_{oL} in both AD and UD manure and, more specifically, the K_{oL} for the UD manure was more sensitive to temperature than for the AD manure.

Table 5.11. Overall mass transfer coefficients (K_{oL}) for undigested (UD) and anaerobically digested (AD) dairy manure.

	K_{oL} ($\times 10^{-6}$ m s^{-1})	
Temperature (°C)	UD Manure	AD Manure
15	2.96^{aA}	1.98^{aB}
25	2.40^{bA}	2.13^{aA}
35	2.06^{cA}	1.38^{bB}

*Means with the same lower case letter in the same column or with the same letter in the same row were not significantly different at $\alpha = 0.05$.

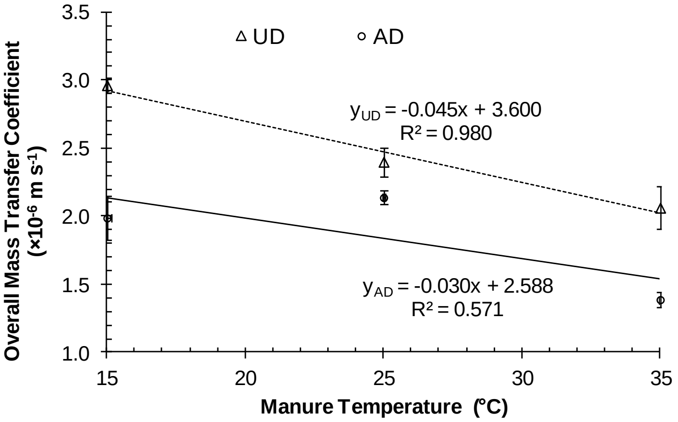

Fig. 5.11. Relationships between the overall mass transfer coefficients (K_{oL}) and temperature for AD and non-AD manures (Error bars show the respective standard deviations from means).

5.3.3.4. Anaerobic digestion and ammonium ion dissociation

The fraction of NH_3 ion dissociation (β) is a direct measure of NH_4^+ dissociation in solution or in the liquid manure. The values of β used in most ammonia volatilization models are estimated from ammonium dissociation in pure water and incorporating the effects of the ions and solids present in the manure (Montes et al., 2009). Past studies indicated that increases in temperature and pH of the liquid manure increases the ammonium dissociation and thus β (Vaddella et al., 2011, Arogo et al., 2003). The fraction of NH_3 of TAN (β) as functions of temperature and manure type (AD and UD) are shown and figure 5.12, while ANOVA results are presented in Table 5.12. The proportion of NH_3 in TAN increased with temperature for both manure types, UD and AD (R^2 = 0.98 and 0.94 respectively). The proportion of NH_3 in TAN was not only significantly greater ($p < 0.001$) in AD than in UD liquid dairy manure, but also increased significantly ($p < 0.001$) with manure temperatures. The larger the β is, the greater the potential of ammonia volatilization from the manure. These results, therefore, suggest increased ammonia emission from AD compared to UD liquid dairy manure, which is also exacerbated by increasing temperatures. The observed larger β values for AD manure suggested that the decrease in β as a result of increased IS after AD was more than counteracted by the increase in β resulting from increases in the higher pH and the lower TS concentration of digested manure (Table 5.12). TAN is the sum of ionized NH_4^+ and unionized $NH_{3(L)}$; the proportions of each depends on pH and temperature of manure solution. Specifically, the NH_3 fraction of TAN (β) in solution increases with pH of the liquid manure. A two-way ANOVA indicated significant interaction between temperature and manure type on β was observed ($p = 0.005$); which is also evident in figure 4. The linear regressions presented in figure 5.12 suggest that β was more sensitive to temperature in the AD manure than in the UD manure.

Table 5.12. Fraction of NH_3 (β) with respect to total ammoniacal nitrogen for undigested (UD) and anaerobically digested (AD) manure.

	β	
Temperature (°C)	UD Manure	AD Manure
15	0.070^{aA}	0.113^{aB}
25	0.092^{bA}	0.140^{bB}
35	0.132^{cA}	0.201^{cB}

*Means with the same lower case letter in the same column or upper case letter in the same row were not significantly different at α = 0.05.

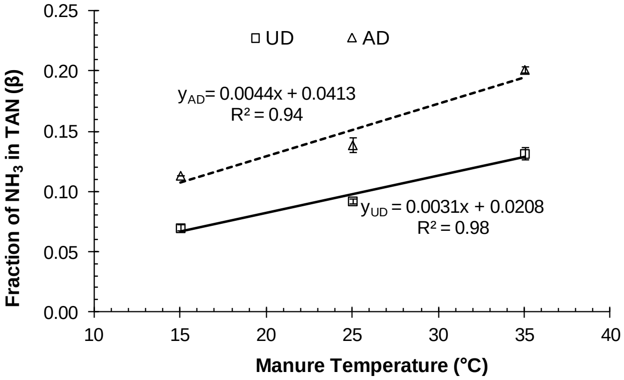

Fig. 5.12. Relationships between fraction of NH_3 (β) in TAN and manure temperature for anaerobically digested (AD) and undigested (UD) manures.

5.3.3.5. Relative contributions

The respective relative net contributions of each key parameter to the ammonia volatilization process, at manure temperature of 15°C, are summarized in Table 5.13. The relative contributions were computed as the ratio of the respective value for the AD manure to that of the UD manure; at similar conditions. These results indicate that the largest change in the process was attributed to the increase in the proportion of the unionized NH_3 of TAN (β) that occurred with AD; which would potentially increase ammonia volatilization by approximately 61%. As discussed earlier, the significant increase in pH from 7.6 to 8.2 was probably predominantly responsible for the higher dissociation of NH_4^+ to $NH_{3(L)}$. Increases were observed in concentration of TAN after AD of manure, which in general also implied increased potential of ammonia volatilization. The contribution of the increases in TAN concentration to the potential increase in ammonia volatilization was approximately 7%. The AD of manure resulted in a 33% decrease in the overall mass transfer of ammonia (K_{oL}). The decrease in K_{oL} was attributed to the increased viscosity after AD of manure. The effective relative increase in initial ammonia flux (i.e. flux at the beginning of storage) from the AD compared to the UD manure from the observed changes in K_{oL}, β, and TAN was ~16% at 15°C; according to the ammonia flux model (equation 4).

Table 5.13. Changes in the key manure parameters after anaerobic digestion of dairy manure at manure temperature of 15°C.

	Parameter			
	K_{oL} (m s^{-1})	β	TAN (mg L^{-1})	$Q_{Initial}$ (g m^{-2} s^{-1})
Undigested Manure (UD)	2.98±0.01	0.070±0.002	480±2	99.33±0.39
Digested Manure (AD)	1.99±0.01	0.113±0.000	512±3	115.69±0.64
AD:UD Ratio	0.667	1.614	1.067	1.164

5.4. Objective 4 Findings: Effect of manure AD on nutrients (nitrogen and phosphorus) use for crop growth.

The average composition of manure applied during the three year study is shown in Table 5.14. While variation existed form year-year, the average composition of NH4-N, total-N, were similar, with greater average total-P observed for Non-AD manure, and greater solids observed for AD manure.

Table 5.14. Average composition of manure applied during the three study, lbs. per 1000 gallons or %.

Manure type	n =	NH4-N,	Total-N	Total-P	Solids - %
Anaerobically Digested (AD)	10	4.75	8.1	1.8	1.2
Non – AD	12	4.85	9.0	3.3	0.84

The average composition of soil for spring and fall sampling times is shown in Table 5.15. No effects were observed in spring soils test due to type of manure or method of application. The fall soil NO3-N concentration was significantly lower for the NON-AD manure as would be expected as this method of manure application would result in more volatile loss of NH3 at the time of application.

Table 5.15. Average composition of soil in spring during the three year study.

Plot	Spring NO_3-N ppm	Spring Bray-P ppm	Spring OM %	Spring pH	Fall NO-3N ppm
AD-Broadcast	3.6	407	6.2	5.4	51^{b}
AD-Injected	3.6	436	6.1	5.4	52^{b}
Non-AD Broadcast	4.1	435	6.2	5.6	36^{a}
NON-AD Injected	3.5	430	5.9	5.6	59^{b}

^{a,b} Means with unlike superscripts differ, $P < 0.05$

The average yield of forage crops, manure and nutrient application, crop uptake and nutrient use by crops is shown in Table 5.16. A summary of the significance of manure type and application method on factors listed in Table 5.16 are shown in Table 5.17. There was no effect of manure type or application method on the amount of N or P uptake by corn, wheat, or total crop uptake of N and P. A significant interaction was observed for manure type x application method for Corn P uptake. This can be explained by the increased DM yield of corn for the plot treated with AD manure and broadcast application. The N use % and P use % were greater for the plots treated with AD manure and can be explained by the lower amounts of N and P that were applied with AD manure.

Table 5.16. Average yield of forage crops, manure and nutrient application, crop uptake and nutrient use by crops

Item	AD Broadcast	AD Injected	Non-AD Broadcast	Non-AD Injected
Gallons of manure applied	36636	37556	46536	50519
Plant Population, plants/acre	38013	34222	35000	36652
CS yield, tons DM/acre	4.0	3.6	3.8	3.8
Wheat yield, tons DM/acre	1.48	1.32	1.27	1.41
N applied, lbs.	334	341	421	423
P applied, lbs.	74	77	143	143
Corn N uptake, lbs.	115	100	102	106
Corn P uptake, lbs.	16.7	14.7	15.7	15.5
Wheat N uptake, lbs.	60	58	56	52
Wheat P uptake, lbs.	11.1	10.4	10.2	9.8
Total N uptake, lbs.	175	158	159	158
Total, P uptake, lbs.	27.8	25.1	25.9	25.3
N Use, %	71	65	51	48
P Use, %	161	154	26	26

Table 5.17. Summary of effect of factors on items in Table 3, P <0.05

Item	Manure (M)	Application Method (AP)	M x AP
Gallons of manure applied	0.01	NS*	NS
Plant Population, plants/acre	NS	NS	0.02
CS yield, tons DM/acre	NS	NS	NS
Wheat yield, tons DM/acre	NS	NS	NS
N applied, lbs.	0.01	NS	NS
P applied, lbs.	0.01	NS	NS
Corn N uptake, lbs.	NS	NS	0.06
Corn P uptake, lbs.	NS	NS	NS
Wheat N uptake, lbs.	NS	NS	NS
Wheat P uptake, lbs.	NS	NS	NS
Total N uptake, lbs.	NS	NS	NS
Total, P uptake, lbs.	NS	NS	NS
N Use, %	0.01	NS	NS
P Use, %	0.01	NS	NS

*NS = not significant.

In general, AD and Non-AD manure were shown to be equivalent for production of forage yield and nutrient uptake in a double crop system of corn silage-wheat forage. The fall soil NO3-N concentration was significantly lower for the NON-AD manure as would be expected as this method of manure application would result in more volatile loss of NH_3 at the time of application.

5.5. Bibliography & Reference Cited

APHA. 2005. Standard methods for the examination of water and wastewater. 21th ed. Washington: APHA.

APHA. 1995. Standard methods for the examination of water and wastewater. American Public Health Association, American Water Works association, Water Environment Federation, Washington.

Amon, B., Kryvoruchko, V. Amon, T, S. Zechmeister-Boltenstern. 2006. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. Agr. Ecosyst. Environ. 112, 153–162.

Arogo, J., P. Westerman, Z. Liang. 2003. Comparing ammonium dissociation constant in swine anaerobic lagoon liquid and deionized water. Trans. ASAE 46(5), 1415-1419.

Arogo, J., R.H. Zhang, G.L. Riskoswiski, L.L. Christensen, D.L. Day. 1999. Mass transfer coefficient of ammonia in liquid swine manure and aqueous solutions. J. of Agric. Eng. Res. 73, 77-86.

ASTM. 1992. American Society for Testing and Materials (ASTM), 1992. Atlas of Odor Character Profiles. DS 61, ASTM, Philadelphia.

ASTM. 1991. American Society for Testing and Materials (ASTM), 1991. Standard practice for determination of odor and taste thresholds by a forced-choice ascending concentration series method of limits. E679-91, ASTM, Philadelphia.

Comfort, S.D., K.A. Kelling, D.R. Keeney, J.C. Converse. 1990. Nitrous oxide production from injected liquid dairy manure. Soil Science Society of America Journal, 54(2), 421-427.

Comfort, S.D., K.A. Kelling, D.R. Keeney, J.C. Converse. 1988. The fate of nitrogen from injected liquid manure in a silt loam soil. Journal of environmental quality, 17(2), 317-322.

El-Mashad, H.M., R. Zhang, V. Arteaga, T. Rumsey, F.M. Mitloehner. 2011. Volatile fatty acids and alcohols production during anaerobic storage of dairy manure. Trans. ASABE 54, 599–607.

Flessa, H., F. Beese. 2000. Laboratory estimates of trace gas emissions following surface application and injection of cattle slurry. J. Environ. Qual. 29, 262–268.

Frear, C., W. Liao, T. Ewing, S.L. Chen. 2011. Evaluation of co-digestion at a commercial dairy anaerobic digester. Clean-Soil Air Water 39, 697–704.

Goel, R., K. Komatsu, H. Yasui, H. Harada. 2004. Process performance and change in sludge characteristics during anaerobic digestion of sewage sludge with ozonation. Water Sci. Technol. 49(10), 105-13.

Granli, T., O.C. Bockman. 1994. Processes that from N2O in soils, nitrogen oxide from agriculture. Norwegian J. Agric. Sci, 12, 18-22.

Huijsmans, J.F.M., J.M.G. Hol, G.D. Vermeulen. 2003. Effect of application method, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to arable land. Atmos. Environ. 37, 3669–3680.

Immovilli, A., C. Fabbri, L. Valli. 2008. Odour and ammonia emissions from cattle slurry treated with anaerobic digestion. Chem. Eng. Trans. 15, 247–254.

Inubushi, K., S. Acquaye. 2004. Role of microbial biomass in biogeochemical processes in paddy soil environments. Soil Science and Plant Nutrition, 50(6), 793-805.

Karanasiou, A.A., I.E. Sitaras, P.A. Siskos, K. Eleftheriadis. 2007. Size distribution and sources of trace metals and n-alkanes in the Athens urban aerosol during summer. Atmos. Environ. 41, 2368-2381.

Koirala, K., P.M. Ndegwa, H.S. Joo, C. Frear, C.O. Stockle, J.H. Harrison. 2013. Impact of anaerobic digestion of liquid dairy manure on ammonia volatilization process. Trans. ASABE 56, 1959–1966

Liang, Z. S., P. W. Westerman, J. Arogo 2002. Modeling ammonia emission from swine anaerobic lagoons. Trans. ASAE 45(3), 787-798.

Madsen, M., J.B. Holm-Nielsen, K.H. Esbensen. 2011. Monitoring of anaerobic digestion processes: A review perspective. Renew. Sustain. Energy Rev. 15, 3141–3155.

Martin, J. H. 2004. A comparison of dairy cattle manure management with and without anaerobic digestion and biogas utilization. A final report submitted by Eastern Research Group Inc. to AgSTAR Program , USEPA, Washington DC, USA.

Montes, F., A. Rotz, H. Chaoui. 2009. Process modeling of ammonia volatilization from ammonium solution and manure surfaces: A review with recommended models. Trans. ASABE 52(5):1707-1719.

Ortenblad, H. 2000. The use of digested slurry within agriculture, In: AD-Nett (ed.): AD: Making energy and solving modern waste problems, Ortenblad H., Herning municipal utilities, Denmark, pp.53–65.

Page, L.H., J.Q. Ni, H. Zhang, A.J. Heber, N.S. Mosier, X. Liu, H.S. Joo, P.M. Ndegwa, J.H. Harrison. 2015. Reduction of volatile fatty acids and odor offensiveness by anaerobic digestion and solid separation of dairy manure during manure storage. J. Environ. Manage. 152, 91–98.

Parkin, T., A. Mosier, J. Smith, R. Venterea, J. Johnson, D. Reicosky, G. Doyle, G. McCarty, J. Baker. 2003. USDA-ARS GRACEnet Chamber-based Trace Gas Flux Measurement Protocol. USDA-ARS, Washington DC.

Powers, W.J., H.H. Van Horn, A. C. Wilkie, C.J. Wilcox, R.A. Nordstedt. 1999. Effects of anaerobic digestion and additives to effluent or cattle feed on odor and odorant concentrations. J. Animal Sci. 77, 1412–1421.

Rice, C. W., J.M. Tiedje, P.E. Sierzega, L.W. Jacobs. 1988. Stimulated denitrification in the microenvironment of a biodegradable organic waste injected into soil. Soil Science Society of America Journal, 52(1), 102-108.

Redwine, J.S., R.E. Lacey, S. Mukhtar, J.B Carey. 2002. Concentration and emissions of ammonia and particulate matter in tunnel–ventilated broiler Houses under summer conditions in Texas. Trans. ASAE 45(4), 1101-1109.

SAS, 2006. SAS User’s Guide: Statistics. Version. 9.1.3. Cary, N.C.: SAS Institute.

Shaw, B. W. 1994. Use of a convective emission chamber to study particle re-suspension. Unpublished PhD diss. Urbana, I.L.: University of Illinois, Department of Agricultural and Biological Engineering.

Sommer, S.G., G.Q. Zhang, A. Bannink, D. Chadwick, T. Misselbrook, R. Harrison, N.J. Hutchings, H. Menzi, G.J. Monteny, J.Q. Ni, O. Oenema, and J. Webb. 2006. Algorithms determining ammonia emission from buildings housing cattle and pigs and from manure stores. Advances in Agron. 89, 261–335.

Szoegi, A.A., and M.B. Vanotti, 2007. Abatement of ammonia emissions from swine lagoons using polymer-enhanced solid-liquid separation. Appl. Eng. in Agric. 23, 837–845.

Vaddella, V.K., P.M. Ndegwa, J.L. Ullman, A. Jiang. 2012. Mass transfer coefficients of ammonia for liquid dairy manure. Atmos. Environ. 66, 107-113.

Vaddella V.K., P. M. Ndegwa, A. Jiang. 2011. An empirical model of ammonium ion dissociation in liquid dairy manure. Trans. ASABE 54(3), 1119-1126.

Velthof, G. L., Kuikman, P. J., & Oenema, O. 2003. Nitrous oxide emission from animal manures applied to soil under controlled conditions. Biology and Fertility of Soils, 37(4), 221-230.

Wang, L., Z. Cao, Q. Li, Z. Liu, D.B. Beasley. 2013. Concentration and particle size distribution of particulate matter inside tunnel-ventilated high-rise layer operation houses. Atmos. Environ. 66, 8-16.

Zhang, R.H., P.W. Westerman. 1997. Solid-liquid separation of animal manure for odor control and nutrient management. Applied Eng. in Agric. 13, 657–664.

Zhang, R. 1992. Degradation of swine manure and a computer model for predicting the desorption rate of ammonia from an under-floor pit. Ph.D. Thesis. Urbana-Champaign: University of Illinois.

6. Conclusions and recommendations.

6.1. Odor and Odor Potential.

6.1.1. Odor at the AD site:

- The results from our study shows a significant increase in odor from the co-digestion material and some slight odor increase during AD of influent mixed substrate. Solids-separation, on the other hand, had little effect on the odor concentration. The converse, however, was observed on the odor intensity and hedonic tone. These two characteristic decreased with AD of the influent as well as with solids-liquid separation.

6.1.2. Odor Characteristics at Different Locations of AD:

- Formic acid was dominant in the influent manure source.
- Acetic acid was dominant in raw, effluent, and effluent SS. Acetic acid accounted for between 60% and 75% of the total VFA in these three manure sources, but was only 21% of the total VFA in the influent manure reactors.
- Propionic acid accounted for 24% of the total VFA in raw manure and with lower concentrations in other manure sources.
- Butyric acid was the second most dominant VFA and accounted for 23% of the total VFA in influent manure, but was only <6% in other manure sources. Concentrations of butyric acid and formic acid were highly correlated (correlation coefficients <-0.969) in the influent reactors, suggesting possible conversion of one to the other or concomitant competition.
- Concentrations of 2-methylbutyric acid was the lowest among the five VFA in the non-AD manure, but was similar to propionic and butyric acids in AD-treated manure.
- In general, the pre-consumer wastes mixed with dairy manure not only increased the total VFA by more than 600% of the total VFA, compared with the raw dairy manure, but also changed in the proportions of different VFA.

6.1.3. Odor Evaluation During Storage of AD Samples:

- Concentrations of VFAs in non-AD manure decreased with time during the 90 d storage demonstrating that AD significantly reduces potential for odor from post-storage of AD effluents.
- Co-digestion substrates had considerable effects on the variations in VFA compositions and concentrations in the digester influent.
- The dominant VFA in all four manure sources was acetic acid followed by propionic acid during this study, although large quantities of formic acid was found in the previous study.
- Anaerobic digestion significantly reduced VFA in dairy manure and co-digestion substrates.
- Solid-liquid separation reduced TS but did not reduce VFA concentrations in the effluent.
- Anaerobic digestion of dairy manure and co-digestion substrate had an evident potential of reducing dairy manure odor offensiveness.
- The addition of food wastes to the raw manure resulted in a more odoriferous AD influent. The overall geometric mean odor concentrations of the raw manure and the mixed AD influent were 556 and 1181 OUE m^{-3}, respectively, during the first test.
- During storage, the overall geo-mean odor concentrations of AD Effluent (245 OUE m^{-3}) and SS Effluent (237 OUE m^{-3}) were reduced by 74% and 75% compared with AD Influent (946 OUE m^{-3}), respectively. The odor concentrations of AD Effluent (197 OUE m^{-3}) and SS Effluent (142 OUE m^{-3}) were reduced by 39% and 57% compared with AD Influent (298 OUE m^{-3}), respectively.
- The effect of solids separation on odor concentration or odor intensity were negligible.
- Manure from all sources exhibited similar hedonic tones except the AD influent which was 0.5 to 4.0 HT points higher than the other sources.

6.2. Emissions of NH_3, H_2S and GHG.

6.2.1. During Storage:

- Anaerobic digestion of dairy manure increased TAN in the effluent resulting in exacerbated NH_3 emissions from subsequent laboratory storage of AD effluents. Additional NH3 emissions mitigation measures may thus be required to curb emissions from AD effluents as opposed to storage of raw manure.
- Anaerobic digestion reduced emissions of methane and carbon dioxide from post-storage of AD effluents. The effect on emissions nitrous oxide were mixed and inconclusive. In general, AD of dairy manure significantly mitigated GHG emissions from dairy manure.
- Anaerobic digestion of dairy manure also significantly increased emissions of hydrogen sulfide during post-storage of AD effluent.
- Solids-liquid separation prior to AD effluent storage was effective at further reducing emissions of NH2 and GHG from the liquid stream of AD effluent. This practice, therefore, should be encouraged at dairy CAFO with AD systems.

6.2.2. Following Land Application:

- Regardless of manure application methods, NH_3 emissions were lower when soils received AD manure, revealing an environmental benefit of the AD process. There were no significant differences in NH_3 emissions between the two application methods from soil receiving AD manure in controlled lab-scale tests. However, manure injection was more effective in reducing NH_3 emissions than surface application for soil receiving non-AD manure in the field study.
- Coupling AD of dairy manure and manure injection into the soil to support crop production, therefore, is recommended as an improved management of this resource.

6.3. Modeling NH_3 Emissions.

- Pertinent physical and chemical characteristics of UD and AD manure, which may influence ammonia volatilization process including: PSD, TS, VS, viscosity, pH, TAN and IS, were determined. The pH, TAN concentration, viscosity, and IS were greater in AD manure than in UD manure. Concentrations of TS and VS were 48% and 59% greater in UD than AD manure, respectively.
- Overall, the characteristics of the AD and UD manures, key to NH_3 volatilization process, were significantly different. The GSD were significantly greater for the UD than AD solids but the VMD were not significantly different, indicating that PSD did not significantly alter the process.
- The NH_3 fraction of the TAN (β) was significantly greater for AD than for UD manure. The mass transfer coefficient (K_{oL}), however, was less for the AD manure than for the UD manure. The K_{oL} decreased with increase of temperature.
- The net effect of higher pH and lower TS concentration on β, from anaerobic digestion, were significantly more than the counterbalancing effect of increased IS. However, the effect of increased viscosity on K_{oL} following AD of manure was more than counteracted by the effects of lower TS concentration, increased β, and higher TAN concentration.
- At manure temperature of 15°C, potential increases in the initial ammonia volatilization of approximately 7% and 61% were observed from increases in TAN concentration, and β respectively, upon AD of dairy manure.

6.4. Utilization of AD nutrients in Crop Production.

- AD and Non-AD manure were shown to be equivalent for production of forage yield and nutrient uptake in a double crop system of corn silage-wheat forage.
- The fall soil NO_3^--N concentration was significantly lower for the non-AD manure as would be expected as this method of manure application would result in more volatile loss of NH_3 at the time of application.

7. Appendices.

7.1. Publications from this Project

7.1.1. Refereed Publications:

- Zhang, H. J.-Q. Ni, L.H. Page, A.J. Heber, R.H. Grant, P.M. Ndegwa, H.-S Joo, J.H. Harrison. 2015. Release of greenhouse gases, ammonia, and hydrogen sulfide from liquid dairy manure. Submitted.
- Neerackal, G.M., P.M. Ndegwa, H.S. Joo, X. Wang, J.H. Harrison, A.J. Heber, J.-Q. Ni, C. Frear. 2015. Effects of anaerobic digestion and solids separation on emissions from stored and land applied dairy manure. Submitted.
- Page, L.H., J.-Q. Ni, H. Zhang, A.J. Heber, N.S. Mosier, X. Liu, H.-S. Joo, P.M. Ndegwa, J.H. Harrison. 2015. Reduction of volatile fatty acids and odor offensiveness by anaerobic digestion and solid separation of dairy manure during manure storage. J. Environmental Management. 152, 91-98.
- Koirala, K., P.M. Ndegwa, H.S. Joo, C. Frear, C.O. Stockle, J.H. Harrison. 2014. Effects of suspended solids characteristics and concentration on ammonia emission process from liquid dairy manure. Trans. ASABE 57(2): 661-668.
- Sun, F., J.H. Harrison, P.M. Ndegwa, K. Johnson. 2014. Effect of manure treatment on ammonia emissions during storage under ambient environment. Water, Air, & Soil Pollution Water, Air, & Soil Pollution 225(9).
- Sun, F., J.H. Harrison, P.M. Ndegwa, K. Johnson. 2014. Effect of manure treatment on ammonia and greenhouse gases emissions following surface application. Water, Air, & Soil Pollution 225: 1923.
- Page, L.H., J.-Q. Ni, A.J. Heber, N.S. Mosier, X. Liu, H.-S. Joo, P.M. Ndegwa, J.H. Harrison. 2014. Characteristics of volatile fatty acids in stored dairy manure before and after anaerobic digestion. Biosystems Engineering 118: 16-28.
- Koirala, K., P.M. Ndegwa, H.S. Joo, C. Frear, C.O. Stockle, J.H. Harrison. 2013. Impact of anaerobic digestion of liquid dairy manure on ammonia volatilization process. Trans. ASABE 56(5): 1959-1966.

7.1.2. Conferences Publications & Presentations:

- Joo, H.J., P.M. Ndegwa, J. Harrison, E. Whitefield, A.J. Heber, J.Q. Ni. Emissions of ammonia and greenhouse gases (GHG) from anaerobically digested and undigested dairy manure systems. Paper number 1337962, ASABE Annual International Meeting. Dallas, TX, Jul 29 – Aug 1.
- Page, L., J.Q. Ni, A.J. Heber, N.S. Mosier, X. Liu, H.S. Joo, H.S., P.M. Ndegwa. 2012. Effect of Anaerobic Digestion on Volatile Fatty Acids in Dairy Manure. Paper number 1110972, ASABE Annual International Meeting. Dallas, TX, Jul 29 – Aug 1.
- G.M. Neerackal, H.S. Joo, X. Wang, P.M. Ndegwa, J.H. Harrison, A.J. Heber, J.-Q Ni. Anaerobic Digestion and Solids Separation Impacts on Ammonia Emissions from Dairy Manure Storages, In *2013 ASABE Annual International Meeting*. July 21-24, 2013 - Kansas City, Missouri.
- X. Wang, H.S. Joo, G.M. Neerackal, P.M. Ndegwa, J.H. Harrison, A.J. Heber, J.-Q. Ni. Effect of Anaerobic Digestion and Application Method on Ammonia Emission from Land Receiving Dairy Manure. In *2013 ASABE Annual International Meeting*. July 21-24, 2013 - Kansas City, Missouri.
- Koirala K., H. Joo, P. Ndegwa, C. Frear, C. Stockle, J. Harrison. Influence of Anaerobic Digestion of Dairy Manure on Ammonia Volatilization Mechanism. To be presented at 2013 ASABE Conference; July 21-24; Kansas City, Missouri.

- Zhang, H., J.-Q. Ni, L.H. Page, A.J. Heber, H.-S. Joo, and P.M. Ndegwa. 2012. Release mechanisms of greenhouse gases, ammonia, and hydrogen sulfide from liquid dairy manure. In *ASABE Annual International Meeting*. Dallas, Texas, July 29 – August 1. ASABE Paper No. 1337674: St. Joseph, Mich.: ASABE.
- Sun, F., Harrison, J.H., Ndegwa, P.M., & Joo, H. (2012). Effect of manure source on ammonia emission on first day of application. *Proceedings of American Dairy Science Association* Annual Meeting of American Dairy Science Association, Phoenix, AZ.

7.1.3. Extension Publications:

- Joo H., P. Ndegwa, J. Harrison, E. Whitefield, A. Heber, J. Ni. 2013. Potential air quality impacts of anaerobic digestion of dairy manure. From Waste to Worth: "Spreading" Science and Solutions. From Waste to Worth: "Spreading" Science and Solutions; April 1-5, 2013; Denver, Colorado.
- Sun, F. J. H. Harrison, P. Ndegwa, H. S. Joo, E. Whitefield, K. Johnson. 2013. Ammonia emissions from eight types of dairy manure during storage. From Waste to Worth: "Spreading" Science and Solutions; April 1-5, 2013; Denver, Colorado.
- Ndegwa, P.M., Joo, H.S., Harrison, J.H., Whitefield, E.M., Heber, A.J., & Ni, J.-. (2011). Impact of Anaerobic Digestion on Air Quality. PowerPoint Presentation (Field day; Monroe, Washington).

7.1.4. Dissertations or Theses

- Koirala, K. 2013. Characterization of ammonia volatilization from liquid dairy manure (Doctoral dissertation, WASHINGTON STATE UNIVERSITY).
- Page, L. 2013. Effect of anaerobic dairy manure co-digestion and effluent solid separation on volatile fatty acids during manure storage (MS thesis, PURDUE UNIVERSITY).