Final Research Project Report

Process-Based Farm Emission Model for Estimating Volatile Organic Compound Emissions from California Dairies

Submitted to

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Abstract

This research addresses the critical need to quantify air emissions from dairies in California with the aim of developing a process-based farm emission model that can be used as a tool for estimating and predicting emission rates of primary air pollutants and developing effective strategies for emission mitigation. Specifically in this project, the emissions of volatile organic compounds (VOCs) from silage and dairy manure were investigated due to their importance to the air quality problems of the state. It was found that among the many VOCs emitted, alcohols (ethanol and methanol) are the predominant VOCs emitted from silage sources and volatile fatty acids (VFAs), especially acetic acid, are the major VOCs emitted from manure sources. A computer model has been developed for predicting the ethanol emission rate from silage exposed to an open air environment. The model can be used to estimate the ethanol emission rate and total emission from the silage that contain different initial ethanol concentrations and exposed to different temperatures and air velocities. Further development and testing of the emission model is needed for its application to other scenarios such as ethanol emissions during silage mixing and from deep silage layers or piles. Experimental investigations were conducted to determine the generation and emission of VFAs and alcohols from dairy manure as it undergoes microbial degradation under different conditions that are typically encountered in free stall housing and manure storages. Ethanol generation and emission from fresh manure collected in the animal housing over a 24-hour period were measured and modeled. The results from the manure storage experiments showed that the initial solids content in the manure and storage temperature were significant factors influencing the microbial activities and their products. Mathematical models and computer algorithms were developed to estimate the generation and emission rates of acetic acid and other VFAs from dairy manure storages over time under different environmental conditions. The emission model was used to predict the emission rate of acetic acid from a dairy manure lagoon for different time of the year and the strong influences of air temperature and wind velocity on the emission rate were clearly shown. The emission models developed in this project are currently being incorporated into a windows based computer modeling software for dairy emissions, which is supported by a research grant from the National Milk Producers Federation.
Executive Summary

This research addresses a critical research need for California dairies: to better quantify air emissions from various sources and develop a process-based farm emission model. The objectives of this research were to (1) develop and refine sampling and analysis methodology and experimental protocols that allow for quantification of VOCs emitted from feed silage and dairy manure sources, (2) conduct experiments to quantify the generation and emission rates of VOCs from silage and manure under different management and environmental conditions and develop mathematical relationships between the generation and emission rates of VOCs and major controlling factors, and (3) to develop process-based computer models that can be used to predict the emission rates of VOCs from different silage and manure sources.

The results of this research allowed better understanding of the major VOCs generated and emitted from silage and manure sources on dairies with respect of their emission kinetics and quantities. The emission models developed are useful for estimating the emission rate and total emissions of alcohols and VFAs from silages and manure storages on dairies. The models can be further expanded in the future to include other VOCs by the application of similar research approaches, theories, and mathematical equations and computer algorithms. The major scientific findings and deliverables of this project are summarized as follows:

- Silage and manure emit many VOCs. On mass basis, ethanol, methanol, acetic acid, acetaldehyde and acetone were the major compounds emitted from both silages and manure sources. Ethanol is the predominant compound for silages and acetic acid is for manure. In-depth investigation and emission measurement and modeling were performed for these two compounds.

- The VOC emissions from silages are mainly controlled by mass transfer processes. A computer model was developed for predicting ethanol emission from silage exposed to an open air environment. Based on the input parameters of silage exposure surface area, silage density, ethanol concentration in the silage, air velocity and temperature, the models calculate the emission rate and total emission over time. Different types of silages have different emission kinetics due to the differences in ethanol concentration and other characteristics, such as density. Corn silage was found to have a higher ethanol emission rate than alfalfa silage. More research is needed to characterize different types of silages used on dairies so that silage characteristic data can be used to further develop and calibrate the ethanol emission models for their applications to a wide range of silages. Further studies are also needed to investigate the ethanol emissions during silage mixing and from deep silage layers or piles so that the ethanol emission models could be expanded to cover those operations.

- The VOC emissions from dairy manure are controlled by both microbial generation processes and mass transfer processes. Experimental data showed that ethanol generation in fresh manure increased with the temperature and time. A model was developed to estimate ethanol emissions from dairy free stalls and was validated using the data collected from an
environmental chamber. The input parameters for the model were number of cows, average weight of a cow, manure excretion rate, air flow rate and temperature, floor surface area, and kinetic constants of ethanol generation. The model outputs were ethanol emission rate and cumulative ethanol emission. The model needs to be calibrated and validated using more experimental data, under different experimental conditions, and farm measurement data.

- Manure solid content and storage temperature were found to be significant factors affecting microbial activities and their products. Higher total solid content and temperature correlated with more production of VFAs and alcohols in the manure. The research results indicate that alcohol emissions from dairy manure can be important during the first five days after excretion from animals and become negligible after the manure goes into storages. Emissions of VFAs, especially acetic acid, are predominant for manure storages. Computer models were developed to quantify the generation and emission rates of acetic acid from manure storages that receive manure of different solids content and exposed to different environmental conditions. The models can be expanded in the future to include other VOCs generated in the manure storages. Measurement data on dairy farms for the emissions of specific compounds are needed in order to fully calibrate and validate the emission models. The measurement data should include the characteristics and environmental conditions of emission sources as well as the emission rates and cumulative emissions over time.

- Because each of the emission sources on dairies has its own characteristics and emission profile, and different sources emit different types and amounts of VOCs, it is important to characterize and understand the physical, chemical and biochemical conditions in the sources that influence the VOC generation and emissions. Due to the large number of compounds emitted, individually modeling each of the dozens of VOCs emitted from dairy sources does not appear to be practical because of the magnitude of the tasks and limited resources. Emission modeling effort should be focused on the key compounds that have significant impact on the air quality, such as ozone formation, either by emission mass quantities or reactivities. The emissions of total VOCs may be estimated from the emissions of key compounds that can be modeled and the knowledge of their relative magnitude to the total VOC emissions, which could be determined through the measurements. Process-based emission models are mostly useful for estimating the emissions of key compounds under variable conditions, understanding the changes of emissions under different conditions, and determining the conditions that are responsible for most of the emissions.

- The advantages of process-based emission models are well recognized by scientific community and livestock industry as well as research sponsors, such as US Department of Agriculture, US Environmental Protection Agency, California Air Resources Board, and National Milk Producers Federation. It will take more significant resources and time to develop a processed based VOC emission modeling package that can be used to estimate the emissions, with reasonable accuracies, from individual sources as well as the whole farm but the undertaking and results of this project are significant accomplishments toward the overall goal.
1.0 Introduction

The California dairy industry is critical for the food supply and the economy of California and the United States. In 2003, California produced 36.4 billion pounds of milk – over 20% of the national total (California Agricultural Statistics Service, 2003). The state industry’s economic impact is estimated at $35.1 billion per year (California Milk Advisory Board, 2005). But California dairies are also considered to be major contributors to air pollution, particularly in the San Joaquin Valley. Dairy operations emit particulate matter (PM) and various gases, including volatile organic compounds (VOCs), ammonia, methane and hydrogen sulfide (California Air Resources Board [CARB], 2004). Extensive efforts are under way at state, regional and local levels to estimate and reduce these emissions (San Joaquin Valley Unified Air Pollution Control District, 2005). This research addresses a critical need: to better quantify air emissions from dairies and provide a process-based farm emission model that will give the air quality regulatory agencies such as CARB, the scientific community and the dairy industry and improved ability to estimate the emission rates of primary air pollutants and develop effective mitigation strategies.

Understanding the range of emissions from the dairies and related processes is a major prerequisite for designing these emission mitigation strategies. At present, regulatory agencies such as CARB and the US Environmental Protection Agency (US EPA) estimate dairy emissions based on emission factors (NRC, 2003). Such estimates fail to take into account the great variations in emissions on actual farms due to different management strategies e.g., manure management and feeding practices. Nor do they account for emission changes due to varied environmental conditions. In 2003, the National Academy of Sciences (NRC, 2003) found that EPA’s current methodologies should be improved by using site-specific “process-based” models instead of an “emission factor” approach. For air pollutants like VOCs that impact local and regional air quality, hourly emission rates are needed to assess their impact to air quality in different parts of the state and develop effective emission mitigation strategies.

Some VOCs emitted from dairies are reactive organic gases (ROG) that could lead to the formation of ground level ozone (O$_3$) (California Air Resources Board, 2009). Ozone (O$_3$) is a persistent public health problem with serious economic consequences in the United States. Elevated ozone concentrations in the ambient air is a serious air quality problem for California, especially San Joaquin Valley and Southern California. The results of several recent studies showed that animal feed, especially silages, is the major sources of ROGs on dairies. Other sources include manure storages and land application. The ROG emission fluxes measured from silage and other animal feed (e.g. total mixed ration) were found to be higher than the comparable fluxes from animal manure (Alanis et al., 2008; Schmidt and Card, 2009). A recent study at University of California, Davis (UC Davis) (Howard et al., 2009) investigated the ozone formation potential (OFP) of seven types of animal feed and feed ingredients with the results showing that the emissions of silages (corn silage, alfalfa silage, and cereal silage) had the highest OFP and ethanol and other alcohol species accounted for more than 50% of the ozone formation for most types of feed.

It is common to estimate the average emission fluxes and emission factor (total emissions) of VOCs and other air pollutants based on the measurement data in the laboratories and/or on the
farms. However, because of the fact that the emission processes are typically dynamic and the emission rates and total emissions vary with time and other factors such as source characteristics and environmental conditions, it is critical to conduct in-depth analysis and investigations on the physical, chemical and biological processes responsible for the emissions from a particular source and quantify the kinetics of the emissions so that emission rate and total emissions can be determined more accurately. Theoretical knowledge and experimental data can be used to develop computer models for simulating the conditions that experiments could not cover and also allowing the calculation of emission rates and total emissions from a changing source (e.g. silage and manure) and variable conditions (Zhang et al., 2009). Significant effort has been made by various researchers, including those involved in this project, on the development of process-based emission models. So far, ammonia emission models are the most developed. The work in this project is one of the initial efforts in developing the VOC emission models for dairies. Silage and manure storages were studied as the emission sources. The VOC emissions from corn and alfalfa silages and dairy manure were characterized and measured, and computer models were developed for estimating and predicting ethanol emissions from silages and VFA emissions from manure storages. Ethanol is a major VOC present in silages and VFAs are the major VOCs present in fresh and stored manure.
2.0 Project Objectives

The ultimate goal of this research was to develop a process-based emission model that can be used to estimate the emission rate of volatile organic compounds (VOCs) from dairy operations. This process-based model will predict emissions from typical animal feeding and manure management practices under varying environmental conditions, thus it will also be useful in the evaluation of VOC emission mitigation techniques. The major sources for dairy VOC emissions include animals, feed, and manure which can further be broken down into collection and storage facilities, and land application (Figure 1).

In this project we proposed measurements and modeling of VOC emissions from animal feed and manure housing and storage. The following objectives were pursued.

Objective 1. Develop and refine sampling and analysis methodology and experimental protocols that will allow quantification of VOCs emitted from feed silage and manure sources on dairies.

Objective 2. Conduct experiments to quantify the generation and emission rates of VOCs from silage (fermented animal feed) and manure under different management and environmental conditions and develop mathematical relationships between the generation and emission rates of VOCs and major controlling factors.

Objective 3. Develop process-based computer models that can be used to predict the emission rates of VOCs from different silage and manure sources.
3.0 Overall Research Approach and Methods

In this project, we used a combination of experimental investigation and mathematical modeling approaches to gain scientific understanding about the VOCs and emission kinetics for animal feed and manure sources, and develop computer models to predict their emission rates. We employed state of art analytical equipment in the analysis and quantification of VOC emissions from silage and manure sources. The analytical equipment included gas chromatography (GC) combined with mass spectroscopy (MS) and flame ionization detection, proton transfer reaction mass spectroscopy (PTR-MS), and photoacoustic spectroscopy. We used different experimental devices to simulate the conditions of silage and manure in the laboratory that reflect the conditions that occur on dairy farms for the areas of animal housing, feed and manure storages on dairy farms. We studied and quantified generation and emission rates of major VOCs from these sources. These devices included emission flux chambers, a wind tunnel and environmental chambers. Originally we proposed using biobubbles to measure the emissions but the concentrations of target VOCs in the biobubbles were found below the sensitivities of our instruments for emission measurement and monitoring and we were not able to pursue experiments at that scale.

Previous research studies documented high emissions of alcohols, aldehydes, and volatile fatty acids (VFAs) from fermented feed (silage), which is a widespread and typical component of California dairy cow diets. For manure sources, some of the VOCs are present in fresh manure but most of them are produced during the manure degradation processes. Previous research on VOCs emitted from animal feeding operations was mainly concerned with those compounds associated with odors. Using GC/MS and GC/FID, the only compounds that we were able to measure with high repeatability and certainty were alcohols and VFAs. Even though we identified other compounds as well, we concentrated our effort in the quantification and modeling of the emissions of ethanol from silages because of its high emission rates. We successfully developed a computer model for predicting the ethanol emission from silages exposed to an open air environment. Using this model, ethanol emission rate and total emission can be estimated for silages at different initial ethanol concentrations and different air temperatures and velocities. Measurements of ethanol emission from silage using a laboratory-scale wind tunnel were used to assist the model development. In addition, the ethanol emission model was validated using measurement data from an environmental chamber. The model was later used to predict ethanol emission from corn silage exposed to variable environmental conditions that were measured on a dairy farm in the San Joaquin Valley, CA. The predicted ethanol emission rates were comparable with the measured emission rates in the field by other researchers. Controlled experiments were conducted to quantify the generation rates of VFAs and alcohols in dairy manure under different storage conditions. The data were used to develop mathematical correlations of VFA generation rates with storage temperature and time at different total solid content of the manure. An emission model was developed to calculate the emission rate and cumulative emission of acetic acid from manure storage lagoons under different manure and environmental conditions. The emissions models developed from this project are being incorporated into a computer modeling software for dairy emissions, which is supported by National Milk Producers Federation.
4.0 Identification of Volatile Organic Compounds Emitted from Silage and Dairy Manure

4.1 Introduction

Very little was found in the literature in respect to VOC emissions from silage sources though a number of articles report the VOCs emitted from the dairy farm and manure. In the recent past, several research efforts have been undertaken to better quantify emissions from dairies and other agricultural sources. Seventy different VOCs were identified on eight dairy farms in Sweden by Sonesson et al. (2001). Measurements to identify VOCs from livestock facilities with a focus on odorants such as amines, sulfides, phenols, and volatile fatty acids (VFAs), were conducted by McGinn et al. (2003) and Rabaud et al. (2003). Hobbs et al. (2004) measured emissions from dairy cattle manure in the UK and identified approximately 20 compounds with acetic acid and dimethyl sulfide as dominant species.

A total of 113 compounds were identified at the Washington State University Dairy Farm (Filipy et al., 2006) using GC/MS, sorbent tubes, and cryogenic trap techniques. The wide range of VOCs included alcohols (in which ethanol was dominant), aldehydes, ketones, esters, ethers, sulfides, carbonyls, aromatics, and other hydrocarbons. VOC emissions from dairy cows and their waste at various stages of lactation were recently measured at the University of California, Davis dairy using a proton-transfer-reaction mass spectrometer (PTR-MS) (Shaw et al., 2007). The measurements of alcohols, VFAs, phenols, and methane emitted from dairy cows and their manure under controlled conditions were reported by Sun et al. (2008).

Ngwabie et al. (2008) reported chemical ionization mass spectrometry and photo-acoustic spectroscopy measurements of mixing ratios of VOCs over a two week measurement period in a large cowshed in Mariensee, Germany. Numerous VOCs were detected with alcohols (ethanol, methanol, C3–C8 alcohols) being dominant, followed by acetic acid and acetaldehyde, and included ketones, amines, sulfides, aromatic compounds, and VFAs. These results indicated that animal husbandry VOC emissions are dominated by oxygenated compounds. Alanis et al. (2008) quantified emissions of six VFAs from non-enteric sources at a small research dairy in California. Both animal feed and animal waste were found to be major sources of VFAs, with acetic acid contributing 70–90% of emissions from the sources tested.

Silage can be made from many field crops (usually from grass crops including corn) and sometimes is a mix of two crops. Typically, there are a few different silage piles located at the dairy. Except for the vertical open-face, silage piles are covered with heavy plastic sheeting and sealed along the sides to prevent exposure to air (oxygen), which leads to silage spoilage and emission of different VOCs (Figure 1). Cows are fed with a total mixed ration (TMR), which is a mixture of various components formulated to provide the optimum amount of nutrition to satisfy maintenance and lactation requirements of the cows. Silage is the largest component of the TMR. Typically, 15–30 cm (0.5-1 ft) of silage is removed from silage pile face several times daily leaving this open part exposed to ambient air. After that, various feed components are loaded into a large truck where they are mechanically mixed and delivered to the animals.
Laboratory experiments were carried out to obtain the speciation and emission profile of VOCs from representative samples of silage obtained under controlled conditions with an aim of understanding the major VOCs and their emission profile from silage sources in terms of mass quantity so that experiments could be performed to collect data for VOC emission modeling purposes. We used a combination of gas chromatography/mass spectroscopy (GC/MS) and proton transfer reaction mass spectrometer (PTR-MS) to identify and quantify VOCs. In addition to analysis of silage samples, dairy manure samples were also analyzed to characterize the VOCs and their emission profiles.

4.2 Research Methods

4.2.1 Collection of silage and manure samples

Silage samples were collected from a typical large size commercial dairy located in Yolo County, California (Figure 2). The dairy housed approximately 3000 cows using free stall, naturally ventilated barns with open walls. Silage piles were co-located with other feed storage structures forming a feeding center. All silage samples (corn and alfalfa) were collected early in the morning, immediately after a new portion of silage was removed. After collection, the samples were immediately put into plastic bags, sealed and transported to the laboratory at UC Davis. Afterwards, all the samples were put into a cold storage room at 4°C (39.2°F) for later analysis and experiments.

Figure 2. Typical silage pile at a commercial dairy

Manure samples were collected from lactating cows fed with standard ration on a research dairy farm at UC Davis. After collection, manure samples were also transported immediately to the laboratory for cold storage until use. The manure samples contained both feces and urine in equal amounts.
Two methods were used to measure the VOCs emitted from silage and manure samples. They are headspace measurement and emission flux chamber measurement. The headspace measurements were performed to qualitatively identify compounds emitted from feed samples and flux chamber measurements were for determining the emission profiles and rates from feed and manure under selected conditions.

4.2.2 Headspace measurement

In these experiments, a 1 L (0.26 gal) glass bottle (carboy) was flushed with nitrogen for 30 min, then 25 g (0.88 oz) of tested silage sample was placed inside and the carboy was immediately closed and tightly sealed with a septum. Upon reaching equilibrium under laboratory conditions (temperature of about 22°C (71.6°F)), head space sampling was performed using the solid phase microextraction (SPME) technique with direct injection onto a GC/MS system.

A number of preliminary experiments were conducted using the SPME technique in order to initially identify VOCs. With this technique detection limits could reach parts per trillion for certain compounds. This method allowed us to identify analytes in the sample matrix present in low concentrations. Initially, the full scan mode was used to search for a wide range of compounds. Later on, the much more sensitive and selective selected ion monitoring (SIM) mode was used to look for specific compounds identified with the help of SPME. Later, a direct injection method was developed for the analysis of the headspace samples. Gas chromatograph (Agilent 6890A, Palo Alto, CA) separations were performed using a 30 m × 0.25 mm × 1.4 μm ZB-624 capillary column (Phenomenex, Torrance, CA). Helium was used as a carrier gas. The GC oven temperature was programmed as follows: initial oven temperature was set to 35°C (95°F) for 5 min; then ramped by 8°C (46.4°F) min⁻¹ to 220°C (428°F) for a hold time of 5 min. The second ramp was 10°C (50°F) min⁻¹ to 240°C (464°F) with the hold time of 2 min. Injector temperature was set at 200°C (392°F). Mass spectrometry measurements were performed using an Agilent MS 5973N instrument. Electron ionization conditions were as follows: ion energy -70eV, scan range from 30 to 300 AMU and the tune reference compound was perfluorotributylamine. All the tests were run in triplicates. A number of standard mixtures consisting of six individual alcohols and five VFAs prepared for the GC/MS calibration. These mixtures were used to generate headspace concentrations similar to the ones detected for material samples in the carboy. After equilibration for 30 min, a 200 μl headspace sample was injected directly onto the column.

4.2.3 Flux chamber measurement

Flux chambers (Odotech Inc., Montreal, Canada) and gas analyzer shown in Figures 3 and 4 were used for the emission measurement. Each chamber had a volume of 60 L (2.12 ft³) and the airflow through each chamber was 10 l/min (0.35 ft³/min), providing 6 air exchanges per hour in the chamber. The chambers were housed in laboratory at a temperature of 20-23°C (68-73°F). A gas analyzer, INNOVA 1412 Photoacoustic Gas Monitor (INNOVA Gas Analyzer) (LummaSense Technologies, Ballerup, Denmark) was used to measure the ethanol concentration in the emitted gases. The details on research methods are described below. This research was carried out at UC Davis.
First we conducted eight experiments with different silage and manure samples using PTR-MS in conjunction with the INNOVA Gas Analyzer to measure VOCs. Later we conducted six additional experiments only with the INNOVA Gas Analyzer. During the investigation of ammonia interference on the methanol and ethanol measurement with the INNOVA Gas
Analyzer, we discovered that the NH$_3$ had about 20% interference on methanol and ethanol when the INNOVA did not have an ammonia filter installed while ammonia was present in the measurement air in the concentration range of 0 - 40 ppm and had almost zero interference after ammonia filter was added to the analyzer. Because of ammonia interference problems with alcohol measurements, photoacoustic data from the first experiments was not used. For latter emission experiments, we used the INNOVA with the ammonia filter installed when measuring alcohols. The PTR-MS uses chemical ionization with H$_3$O$^+$ as a reactant and proton donor. If the target VOC has a proton affinity (PA) greater than that of H$_2$O, the proton is transferred to the VOC, which is then detected by a quadropole MS. Proton transfer reactions occur on every collision of a H$_3$O$^+$ ion with a VOC molecule, whenever PA$_{VOC} >$ PA$_{H_2O}$, thus defining the reaction rate. An applied electrical field defines the ion reaction time. Therefore the PTR-MS allows quantification of unidentified or uncalibrated gases (Lindinger et al., 1998), which is an important benefit for these measurements. Many VOC types, including alcohols, aldehydes, aromatics, ketones, amines, nitrites, sulfides, and acids, have PA > PA$_{H_2O}$. Alkanes, some alkenes, and halogenated compounds are not detected. The PTR-MS also provides much more accurate measurements for polar VOC (e.g. aldehydes or ketones) than any technique requiring sample storage (e.g. canisters (Ochiai et al., 2002)). Compound detection limits are extremely low at 30-50 pptv, even in complex gas mixes. The PTR-MS was operated continuously, alternating between Single Ion Mode (SIM) and Scan Mode (SCAN). SIM monitored a small set of specified masses, and was used to obtain better precision than was possible when monitoring masses 20-140 amu in SCAN mode. Scan mode was useful for detecting all compounds in that mass range with PA > PA$_{H_2O}$. The PTR-MS routinely was switched between 3 sampling locations: inlet air to the chamber, outlet air from the chamber, and inlet air redirected through a catalytic converter to remove all VOC and create an instrument blank (Shaw et al., 2007). Gaseous calibration mixes (Apel-Reimer Environmental, Inc.) were available for a subset of the observed VOCs. Mixes were added by dynamic dilution to the blank for the last 10 minutes of each sampling hour. Uncertainties for calibrated compounds, determined as the difference between expected and measured concentrations, were Acetonitrile < 5%, Acetaldehyde 40%, Acetone 9%, MVK 10%, Methanol 15%, and Benzene 20%. Concentrations were also determined for unidentified or uncalibrated compounds, but the measurement uncertainty was larger. These were determined by propagating reaction rate and PTR-MS uncertainties and were < ± 40%. The precision for measuring calibrated compounds determined by variance of calibration standard measurements for Methanol, Acetonitrile, Acetaldehyde, Acetone, MVK, and Benzene were determine for 20-minute averages < 3% and 2-minute scans 10%. It was not possible to quantify precision of uncalibrated compounds, but it is likely to be similar to the calibrated compounds.

Because PTR-MS could not detect ethanol, a second set of experiments was conducted for the purpose of collecting ethanol emission data from silage and manure samples. The sample size of silage tested in each flux chamber experiment was 200 g (7.05 oz) (wet weight) for silage, 400 g (14.1 oz) (wet weight) for fresh manure, and 200 g (7.05 oz) (wet weight) for dry manure. The duration of each experiment was 12 hours for silage samples and 22 hours for manure samples. A circular pan of 25 cm (0.8 ft) diameter was used to hold the testing sample in the flux chamber.
4.3 Results and Discussions

4.3.1 Silage characteristics

The average characteristics of corn and alfalfa silages are shown in Table 1 for the first and second series of experiments. The pH of both corn and alfalfa silage samples were close to 4.0. The moisture content of corn silage was about 67% and 37% in the first and second experimental series, respectively. The alfalfa silage had a moisture content of about 68% in both experimental series.

Table 1. Characteristics of silage samples used in the first series (headspace and flux chamber) and second series (flux chamber) of experiments

<table>
<thead>
<tr>
<th></th>
<th>Corn silage</th>
<th>Alfalfa silage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment series</td>
<td>First</td>
<td>Second</td>
</tr>
<tr>
<td>pH</td>
<td>First</td>
<td>Second</td>
</tr>
<tr>
<td></td>
<td>3.86</td>
<td>4.25</td>
</tr>
<tr>
<td>TS (%)</td>
<td>32.6</td>
<td>62.98</td>
</tr>
<tr>
<td>VS (%)</td>
<td>31.01</td>
<td>55.60</td>
</tr>
</tbody>
</table>

4.3.2 VOCs identified in headspace measurements of silage and dairy manure samples

Table 2 shows the VOCs detected from silage samples. The results show that alcohols (methanol and ethanol), VFAs (acetic, propionic, and butyric acids) and acetaldehyde were main VOCs from both corn and alfalfa silage.
Table 2. Volatile organic compounds identified in silage headspace experiments (concentrations in ppmV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Corn Silage</th>
<th>Alfalfa Silage</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alcohols</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>675.71</td>
<td>7.76</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>214.89</td>
<td>11.9</td>
</tr>
<tr>
<td>1-Butanol</td>
<td></td>
<td>5.56</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>70.66</td>
<td>BQL</td>
</tr>
<tr>
<td>Isopentyl alcohol</td>
<td>BQL</td>
<td></td>
</tr>
<tr>
<td>Hexanol</td>
<td>BQL</td>
<td>BQL</td>
</tr>
<tr>
<td><strong>VFAs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>130.84</td>
<td>82.1</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>BQL</td>
<td></td>
</tr>
<tr>
<td>Isobutyric acid</td>
<td>BQL</td>
<td></td>
</tr>
<tr>
<td>Butyric acid</td>
<td>BQL</td>
<td></td>
</tr>
<tr>
<td>Isovaleric acid</td>
<td>BQL</td>
<td></td>
</tr>
<tr>
<td><strong>Esters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>BQL</td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>33.77</td>
<td>BQL</td>
</tr>
<tr>
<td>Propyl acetate</td>
<td>96.12</td>
<td>2.62</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>15.9</td>
<td></td>
</tr>
<tr>
<td>Isoamyl acetate</td>
<td>7.52</td>
<td>BQL</td>
</tr>
<tr>
<td>Hexyl Acetate</td>
<td>BQL</td>
<td>BQL</td>
</tr>
<tr>
<td>Ethyl propionate</td>
<td>12.99</td>
<td>2.07</td>
</tr>
<tr>
<td>Propyl propionate</td>
<td>17.57</td>
<td>4.41</td>
</tr>
<tr>
<td>Ethyl butyrate</td>
<td>78.55</td>
<td>31.99</td>
</tr>
<tr>
<td>Propyl butyrate</td>
<td>45.85</td>
<td></td>
</tr>
<tr>
<td>Butyl butyrate</td>
<td>45.26</td>
<td></td>
</tr>
<tr>
<td>Ethyl hexanoate</td>
<td>9.43</td>
<td></td>
</tr>
<tr>
<td>Propyl hexanoate</td>
<td>BQL</td>
<td>BQL</td>
</tr>
<tr>
<td>BQL</td>
<td>Below Quantification Limit</td>
<td></td>
</tr>
</tbody>
</table>
4.3.3 VOC emission potential and profiles of silage and dairy manure samples

Many compounds were detected and measured by the PTR-MS and included methanol, formaldehyde, acetonitrile, acetic acid, acetaldehyde, acetone, methyl ethyl ketone, hexanal, dimethyl sulfoxide, phenol and aromatic compounds such as benzene, toluene, styrene, trimethylbenzene. Information across the mass spectrum to quantify unexpected major contributors to the VOC emission profile was collected as well. A number of oxidation products and monoterpene compounds were also detected. Four major compounds were detected with high certainty by PTR-MS: methanol, acetic acid, acetaldehyde, and acetone. One compound with m/z 41+ was detected in significant quantity and is believed to be propenol but more research is needed to confirm its identity. Emission rates and accumulative emissions of VOCs detected by PTR-MS for silage and manure samples in the first series of flux chamber experiments are shown in Figures 5-13. Data collected with the photoacoustic gas analyzer was not used due to interference of ammonia with the ethanol measurements. Over the experimental time (i.e., 12 hours for silage and 24 hr for manure), the total emission from corn silage was 0.48 g/m² for methanol, 7.0 g/m² for acetic acid, 0.18 g/m² for acetaldehyde, 0.06 g/m² for acetone. The total emission for alfalfa silage was 0.44 g/m² for methanol, 5.0 g/m² for acetic acid, 0.05 g/m² for acetaldehyde, 0.02 g/m² for acetone; The total emission for fresh dairy manure was 0.085 g/m² for methanol, 0.14 g/m² for acetic acid, 0.085 g/m² for acetaldehyde, 0.019 g/m² for acetone. The total emission expressed as g/m² was calculated based on the cumulative emissions of each compound during 12 hr period divided by the area occupied by the silage inside the flux chamber.
Figure 6. Methanol, acetaldehyde and acetone cumulative emissions from corn silage in a flux chamber

Figure 7. Acetic acid emission rate and cumulative emission from corn silage in a flux chamber
Figure 8. Methanol, acetaldehyde and acetone emission rate from alfalfa silage in a flux chamber

Figure 9. Methanol, acetaldehyde and acetone cumulative emission from alfalfa silage in a flux chamber
Figure 10. Acetic acid emission rate and cumulative emission from alfalfa silage in a flux chamber

Figure 11. Methanol, acetaldehyde and acetone emission rates from fresh dairy manure as measured in a flux chamber
Figure 12. Methanol, acetaldehyde, and acetone cumulative emission from fresh dairy manure as measured in a flux chamber

Figure 13. Acetic acid emission rate and cumulative emission from fresh dairy manure as measured in a flux chamber
The emission measurement results of the second batch of experiments are shown in Figures 14 to 20, for which the photoacoustic analyzer was used to measure ethanol and methanol emissions of silage (corn and alfalfa) and manure (fresh dairy manure and one day dried manure) samples to determine the magnitude of ethanol and methanol emissions. Over 12 hours, the total emission from corn silage sample was 6.5 g/m² for ethanol and 0.16 g/m² for methanol and the total emission from alfalfa silage sample was 6.0 g/m² for ethanol and 1.5 g/m² for methanol. Over 24 hours, the total ethanol emission from fresh dairy manure was 0.8 g/m². The total emission from one-day dried manure was 1.5 g/m² for ethanol and 0.08 g/m² for methanol. It appears that ethanol is a significant compound for both silage types and in contrast, methanol is less significant but its emission from alfalfa silage was more than the emission from corn silage. Ethanol and methanol emissions from dairy manure were less than from silage.

![Figure 14. Ethanol emission rate and cumulative emission from corn silage as measured in a flux chamber](image-url)
Figure 15. Methanol emission rate and cumulative emission from corn silage as measured in a flux chamber.

Figure 16. Ethanol emission rate and cumulative emission from alfalfa silage as measured in a flux chamber.
Figure 17. Methanol emission rate and cumulative emission from alfalfa silage as measured in a flux chamber

Figure 18. Ethanol emission rate and cumulative emission from fresh dairy manure as measured in a flux chamber
Figure 19. Ethanol emission rate and cumulative emission from manure dried for one day as measured in a flux chamber

Figure 20. Methanol emission rate and cumulative emission from manure dried for one day as measured in a flux chamber
4.4 Conclusions and Recommendation for Future Research

With a combination of analytical techniques and instruments, including GC/MS, PTR-MS and an INNOVA Photoacoustic Gas Analyzer, we were able to identify 15-20 VOCs emitted from corn and alfalfa silage. We found that alcohols and VFAs were the compounds emitted in the largest quantities. The emission rates of these compounds change with time under the same environmental conditions due to the change concentrations in the source, and emissions are also substantially influenced by air velocity and temperature. The emission profiles of these VOCs are different for silage and manure samples. The most important silage VOCs are thought to be produced during the main fermentation stage of silage production, and therefore, generation of additional VOCs after this time is not significant. On the other hand, the emissions of fresh manure samples are very complex and some of the compounds are produced by microbial activities at the same time of emission. Once exposed to the air, microbial activity continued in the manure generating new compounds, including alcohols and VFAs. The emission rate also varies with time depending on the changes of the VOC concentrations in the manure. More research is needed to characterize the microbial activities responsible for the VOC generation in order to determine the generation and emission rates from manure under different conditions.
5.0 Measurement and Modeling of Ethanol Emissions from Silage

5.1 Introduction

Sources of VOCs on dairy farms include manure, feed, and cattle themselves. Many VOCs have been identified on dairy farms, including alcohols, organic acids, aldehydes, ketones, and esters (Sunesson et al., 2001; Rabaud et al., 2003; Hobbs et al., 2004; Schmidt, 2006; Filipy et al., 2006; Shaw et al., 2007; Alanis et al., 2008; Ngwabie et al., 2008; Sun et al., 2008). Studies that have measured VOC emissions from isolated sources on dairy farms have shown that VOC fluxes from animal feed, including silage and total mixed ration (TMR), are much greater than from other sources (Schmidt, 2006; Shaw et al., 2007; Sun et al., 2008; Montes et al., 2009). Although few studies have measured VOC emissions from silage, those found in the literature have shown that emissions of ethanol are much greater than those of other compounds (Schmidt, 2006; Krauter et al., 2009; Mitloehner, 2009). Schmidt and Card (2009) reported that emission of ethanol was greater than emission of other VOCs from silages. Krauter et al. (2009) indicated that ethanol accounts for about 75% of total reactive organic gases emitted from silage sources and methanol accounts for 8-10%. Ethanol can be an important contributor to the ozone formation potential of silage emissions. In this work, we focused our measurement and modeling effort on ethanol emissions because of its high emission rates from dairies.

Ethanol is one of the microbial products produced during the main fermentation stage of silage production, which normally stabilizes within one week (Pahlow et al., 2003). Little microbial activity occurs after this stage due to low pH and a lack of oxygen. The concentrations of alcohols and VFAs in the silage vary with the characteristics of the forage that was used in making the silage, the environmental conditions and the conditions in which the fermentation process occurred (Pahlow et al., 2003). Ethanol concentrations in the range of 0.1% to 4% (dry matter basis) have been reported in different types of silage (Driehuis and van Wikselaar, 2000; Keady et al., 2000; Kim and Adesogan, 2006).

The objectives of this research were to study ethanol emission from silage exposed to an open air environment; and to develop a mathematical model for calculating the ethanol emission from silage subject to different environmental conditions (temperature and air velocity). The model can be used to predict the ethanol emission rate under variable environmental conditions.

5.2 Ethanol Emission Model

An emission model was developed to predict the ethanol emission from silages exposed to air where temperature and air velocity may change. The emission model was used to predict ethanol emission from corn silage under different conditions. Model simulations were run using Matlab software (The Math Works Inc., Natick, MA, USA).

The model is applicable to thin layers (e.g. 3 cm (1.2 inch)) of silage exposed to open air. It assumes that the flux of ethanol is proportional to its concentration in the silage (i.e. it is a first-order model) as shown in Figure 21. In reality, as ethanol is depleted from the surface of silage, resistance to emissions increases, as internal resistance becomes more important. The relative
importance of internal (silage phases) vs. external (air phase) resistance depends on the relative magnitude of mass transfer coefficients and the depth of a silage layer (Hafner et al., 2009). As is shown below, our first-order approach provides a reasonable approximation for the thin layers of silage used in this work. However, it should be recognized that mass transfer coefficients presented below are effective values that incorporate other parameters, including the effect of ethanol partitioning and the effect of internal resistance. Therefore, model results are valid only at conditions similar to those used to develop the model, as described below.

![Figure 21. Schematic of a first order mass transfer model for ethanol emissions from thin silage layers](image)

A mass balance of ethanol in the silage exposed to the air is governed by the following equation:

\[
\frac{dC_s}{dt} = -K_L \cdot A \left( C_s - \frac{C_{amb} \cdot M_c \cdot \rho_{silage}}{H_{cc} \cdot \rho_{water}} \right)
\]  

(1)

Where:

- \( V \) = volume of the silage layer (m³ or ft³)
- \( K_L \) = average effective mass transfer coefficient (m/s or ft/s)
- \( A \) = exposed surface area of the silage layer (m² or ft²)
- \( C_s \) = ethanol concentration in silage (kg/m³ or lb/ft³)
- \( C_{amb} \) = ethanol concentration in ambient air (kg/m³ or lb/ft³)
- \( H_{cc} \) = dimensionless Henry’s law constant
- \( M_c \) = moisture content of silage (kg/kg or lb/lb)
- \( \rho_{silage} \) = density of silage (kg/m³ or lb/ft³)
- \( \rho_{water} \) = density of water (kg/m³ or lb/ft³)
- \( t \) = time the silage has been exposed to moving air, s

Assuming \( C_{amb} \approx 0 \), the mass balance equation becomes:

\[
\frac{dC_s}{dt} = -K_L \cdot A \cdot C_s
\]  

(2)

After integration, the following equation is obtained and can be used to calculate the ethanol concentration (\( C_s \)) in the silage as a function of initial ethanol concentration (\( C_{s0} \)) and time.

\[
C_s = C_{s0} e^{-\frac{K_L A}{V} t}
\]  

(3)
The effective mass transfer coefficient ($K_L$) is influenced by air velocity and temperature and can be determined experimentally. In this research, the ethanol concentration in silage over time was determined from emission experiments conducted in a wind tunnel and the value of $K_L$ was estimated using the nlinfit routine in Matlab (The Math Works Inc., Natick, MA, USA).

### 5.2.1 Ethanol emission rate estimation

Ethanol emission rate under different weather conditions was estimated as follows (Guo, 2002; Parker et al., 2008):

$$ F = K_L \left( C_s - \frac{C_{amb} \cdot M_c \cdot \rho_{silage}}{H_{cc} \cdot \rho_{water}} \right) $$

where

- $F$ = ethanol emission rate (kg/m$^2$-s) or (lb/ft$^2$-s)
- $K_L$ = overall solute transfer coefficient (m/s) or (ft/s)
- $C_s$ = VOC concentration in silage (kg/m$^3$) or (lb/ft$^3$)
- $C_{amb}$ = VOC concentration in air (kg/m$^3$) or (lb/ft$^3$)
- $H_{cc}$ = dimensionless Henry’s constant
- $M_c$ = moisture content of silage, kg/kg (lb/lb)
- $\rho_{silage}$ = density of silage, kg/m$^3$ or (lb/ft$^3$)
- $\rho_{water}$ = density of water, kg/m$^3$ or (lb/ft$^3$)

$C_{amb}$ was assumed to equal zero in the open air environment, so the above equation simplifies to:

$$ F = K_L C_s $$

The above equation can be used to predict the emission rate from the source exposed to open air.

### 5.2.2 Henry's law constants

Warneck (2006) presented two empirical models for calculating the Henry's constants of ethanol and methanol. Henry's law constant for ethanol was also calculated using Van’t Hoff equation (Sanders, 1999). The calculated Henry law constants from these two references were converted to dimensionless Henry constant using the universal gas equation (Sanders, 1999).

Figure 22 shows the calculated Henry's constant of ethanol from both Sanders (1999) and Warneck (2006); there is a good agreement between of both methods.
5.3 Determination of Ethanol Mass Transfer Coefficient

Well-controlled experiments were used to determine the effective mass transfer coefficient using corn as a model substrate in a wind tunnel. A multiple regression was conducted using Matlab (The Math Works Inc., Natick, MA, USA) to determine the relationship between mass transfer coefficients of ethanol and both temperature and air velocity. Emission measurements were made at the USDA-ARS Pasture Systems and Watershed Management Research Unit in University Park, PA while determination of silage composition and modeling were performed at UC Davis. For alfalfa silage, mass transfer coefficient was estimated using the data collected from the environmental chamber using lsqnonlin routine in Matlab (The Math Works Inc., Natick, MA, USA) as described by Sleutels (2002).

5.4 Experimental Design, Measurement and Data Analysis

A series of trials were conducted to quantify the effects of temperature and air velocity on ethanol emissions from corn silage and on the emissions of ethanol and methanol from alfalfa silage. A 3 x 3 factorial design with two replicates was used. Temperature levels were 15 (59°F), 25 (77°F) and 35°C (95°F) and air velocity levels were 0.2, 1.5 and 2.5 m/s (0.7, 4.9 and 8.2 ft/s). Relative humidity was 70% for all trials. Ethanol and methanol emissions were measured using the wind tunnel system shown in Figure 23. A corn silage sample was placed in a tray (11 cm (4.3 inch) wide, 26 cm (10.2 inch) long and 3 cm (1.18 inch) deep) inside the wind tunnel, and
emissions were measured under controlled air velocity and temperature. The wind tunnel system was housed in a Conviron PGR15 controlled environment chamber (Controlled environments Ltd, Winnipeg, Canada) to achieve temperature and humidity control.

Air was pulled through the wind tunnel using a 12 V DC blower (0.23 m³/min (487 ft³/min) BFB0712H, Delta Products Corporation, Freemont, CA) or a 100 V AC 2.5 HP shop vacuum (Shop-Vac Corporation, Williamsport, PA). The blower drew air from the interior of the growth chamber into the wind tunnel and over the silage sample. Air flow rate was determined by measuring the pressure drop across a calibrated orifice (Oripac 5300, Lamda Square, Babylon, NY) located downstream from the silage sample using a micromanometer (TSI 8705 micro-manometer, ±1 Pa, TSI Incorporated, Shoreview, MN). Air velocity over the silage was calculated from the air flow rate and the cross sectional area of the wind tunnel above the sample. The height of the wind tunnel above the sample was set to either 3.1 cm (1.2 inch) or 1.0 cm (0.4 inch). The smaller height was used at higher velocities to minimize dilution of volatilized ethanol and resulting low concentrations.

Ethanol and methanol concentrations in the air downstream of the silage were measured using a photoacoustic gas analyzer, Photoacoustic Field Gas-analyzer-INNOVA (Model 1412, LummaSense Technologies, Ballerup, Denmark). The gas analyzer drew air samples from the air stream inside the wind tunnel 0.5 m (1.64 ft) downstream of the calibrated orifice through a Teflon sampling tube.

Figure 23. Wind tunnel system used for ethanol emission experiments

Corn silage sample was collected from a bunker silo (Figure 24). Approximately 12 kg (26.46 lb) of silage were collected from the silo face, after removing and discarding the outer 10 cm (0.33ft) of silage. Silage was placed in two plastic bags inside a large plastic tote and immediately transported to the laboratory. Once in the laboratory, the bags with silage were placed inside a walk-in cold room (~2°C (~35.6°F)) and flattened to facilitate cooling. After 3 hr of cooling, the contents of the silage bags were thoroughly mixed in large plastic container. From the mixed material 200 ± 0.5 g (7.05 ± 0.02 oz) subsamples were weighed, placed in individual
1 gallon Ziploc bags, and flattened into thin layers inside a plastic tote for storage. Mixing and sampling were done inside the cold room to minimize volatilization of ethanol. The subsamples were stored in the cold room at ~2°C (35.6°F) for the duration of the experiments.

Figure 24. Corn silage bunker where corn silage was taken for wind tunnel experiments

For each ethanol measurement trial, a Ziploc bag containing a silage subsample was selected at random and placed inside the controlled environment chamber at the prescribed temperature to equilibrate for 30 minutes (for 15°C (59°F) trials) or 1 hour (for 25°C (77°F) or 35°C (95°F) trials). The initial temperature of sample was measured with an infrared thermometer. Starting temperatures were within 1.5°C (34.7°F) of the desired temperature.

To measure ethanol emissions, the sample was removed from the Ziploc bag and evenly distributed within the 3 cm (1.2 inch) deep tray. Immediately, the top of the wind tunnel system was attached to the top of the tray and the air flow and measurement of ethanol concentrations was started. Wind tunnel air stream ethanol concentration was measured every 2 minutes, while pressure was measured every 15 seconds and average values were automatically recorded every 5 min. Trials were ended after two hours, when the wind tunnel was dismantled and the silage sample was returned to the Ziploc bag, weighed and immediately frozen at -23°C (-9.4°F).

At three times during the measurement trials, Ziploc bags with silage subsamples were randomly selected from the container in the cold room and frozen at -23°C (-9.4°F). These samples were used to estimate the initial concentration of ethanol in the silage samples and to determine if changes in the concentrations of constituents occurred during storage.

Ethanol, methanol and VFAs concentrations in silage were measured using a gas chromatograph equipped with a flame ionization detector. A DB-wax capillary column (Agilent Technologies, USA) with a length of 30 m and an inside diameter of 530 µm was used. Helium was used as a carrier gas at a flow rate 5 ml/min. The initial oven temperature was 40°C (104°F) for 1 min, then ramp at 5/min to 60°C (140°F) hold for 1 min then ramp at 25°C/min (77°F/min) to a final temperature of 160°C (320°F). The inlet temperature and detector temperature were 170°C (338°F) and 270°C (518°F), respectively. Total solids (TS) and Volatile Solids (VS) were also measured using the standard methods (APHA, 1998). The TS was measured by drying the sample at 100°C (212°F) for 24 hours. The VS were measured by combusting the dried sample at 550°C (1022°F).
5.5 Emission Model Validation

The developed emission flux model was validated using the data collected from experiments conducted in a controlled environment chamber (4.4 m × 2.8 m × 10.5 m) (14.4 ft × 9.2 ft × 33.5 ft) (Figure 25) at UC Davis. In these experiments, 100 kg (220.5 lb) of corn or alfalfa silage were evenly distributed on a square - 6 mm (0.2 inch) -thick plastic sheet with an area of 12.87 m² that was located in the middle of the chamber. The thickness of silage on the floor was about 4 cm. Composite samples of silage were collected over time, after manually mixing silage on the floor, and analyzed for ethanol, methanol and VFAs as described above. Temperature inside the chamber was measured every minute using a HOBO sensor (Onset Computer, Bourne, MA). Air was blown inside the chamber at a rate of 2107 m³/hr. Ethanol concentration in the inflow and outflow was measured using the INNOVA Gas analyzer (Model 1412, LummaSense Technologies, Ballerup, Denmark). Air velocity over the chamber floor (i.e., silage surface) was measured in different locations using a hot wire anemometer. An average measured air velocity of 0.24 m/s (0.8 ft/s) was used in the simulation. The estimated mass transfer coefficients of ethanol and methanol were used in these simulations.

Figure 25. Corn silage emission measurements in an environmental chamber

5.6 Emission Model Application

The validated model was used to estimate emissions from corn silage on a farm located in the San Joaquin Valley, CA. Temperature and wind velocity for a typical July day were used as inputs for the simulation. Wind speed on the farm was measured using a sonic anemometer located at a height (h₁) of 4.25 m (14 ft). To calculate the velocity above the silage, the following equation was used (Parker et al., 2008):
\[ V_{\text{silage}} = V_{\text{measured}} \left( \frac{\ln \left( \frac{h_2}{h_0} \right)}{\ln \left( \frac{h_1}{h_0} \right)} \right) \]  

(6)

Where

- \( V_{\text{silage}} \) = wind velocity over the silage surface (m/s or ft/s)
- \( V_{\text{measured}} \) = measured wind velocity at height \( h_1 \) (m/s or ft/s)
- \( h_2 \) = height of silage above the floor, that was assumed to be 0.2 m (0.7 ft)
- \( h_0 \) = roughness length that was calculated as 10% of \( h_2 \). Smith et al. (1988) used the same percentage of the height of swath during field drying of grass in windrows.

### 5.7 Results and Discussion

#### 5.7.1 Silage characteristics

Characteristics of corn silage used in the experiments for determining the mass transfer coefficient are shown in Table 3. As can be seen ethanol and acetic acid represent the major compounds analyzed in corn silage. Bulk density of 297 kg/m\(^3\) (18.5 lb/ft\(^3\)) was calculated for corn silage. These calculations were done based on the mass of silage used in the wind tunnel and the volume occupied by the sample.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Corn silage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol (mg/kg)</td>
<td>87.66 (6.66)</td>
</tr>
<tr>
<td>Ethanol (mg/kg)</td>
<td>3720.47 (235.81)</td>
</tr>
<tr>
<td>Acetic acid (mg/kg)</td>
<td>2594.47 (248.83)</td>
</tr>
<tr>
<td>Propionic acid (mg/kg)</td>
<td>78.79 (55.71)</td>
</tr>
<tr>
<td>Iso-Butyric acid (mg/kg)</td>
<td>42.46 (49.38)</td>
</tr>
<tr>
<td>Butyric acid (mg/kg)</td>
<td>64.69 (67.59)</td>
</tr>
<tr>
<td>Valeric acid (mg/kg)</td>
<td>64.66 (93.33)</td>
</tr>
<tr>
<td>Total VFA (mg/kg)</td>
<td>2845.07 (349.54)</td>
</tr>
<tr>
<td>pH</td>
<td>3.35 (0.01)</td>
</tr>
<tr>
<td>TS (%wet base)</td>
<td>34.54 (1.81)</td>
</tr>
<tr>
<td>VS/TS, %</td>
<td>96.92 (40)</td>
</tr>
<tr>
<td>Bulk density (kg/m(^3))</td>
<td>297</td>
</tr>
</tbody>
</table>

#### 5.7.2 Estimation of mass transfer coefficients

Measured and calculated ethanol concentrations in corn silage of experiments conducted at 15 °C (59°F) and 0.2 m/s (0.7 ft/s) and 35°C (95°F) and 2.5 m/s (8.2 ft/s) are shown in Figures 26 and 27, respectively. As can be seen decreases in both temperature and air velocity increased ethanol emissions. The average estimated mass transfer coefficients \( (K_L) \) for corn silage under different experimental conditions are shown in Table 4. These averages are based on duplicate measurements.
Figure 26. Measured and predicted ethanol concentration in corn silage for an experiment conducted at a temperature of 15°C (59°F) and air velocity of 0.2 m/s (0.7 ft/s)

\[ K_L = 6.02 \times 10^{-7} \text{ m/s} \]

\[ R^2 = 0.984 \]

Figure 27. Measured and predicted ethanol concentration in corn silage for an experiment conducted at a temperature of 35°C (95°F) and air velocity of 2.5 m/s (8.2 ft/s)

\[ K_L = 1.91 \times 10^{-5} \text{ m/s} \]

\[ R^2 = 0.9905 \]
Table 4. Mass transfer coefficient of ethanol for corn silage exposed to ambient air
(Standard deviation is given in parentheses)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Air velocity (m/s)</th>
<th>Average mass transfer coefficient (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.197</td>
<td>$6.02 \times 10^{-7}$ (0.00)</td>
</tr>
<tr>
<td>15</td>
<td>1.246</td>
<td>$2.63 \times 10^{-6}$ (7.7 $\times 10^{-7}$)</td>
</tr>
<tr>
<td>15</td>
<td>2.484</td>
<td>$3.33 \times 10^{-6}$ (6.21 $\times 10^{-8}$)</td>
</tr>
<tr>
<td>25</td>
<td>0.203</td>
<td>$1.10 \times 10^{-6}$ (2.95 $\times 10^{-8}$)</td>
</tr>
<tr>
<td>25</td>
<td>1.277</td>
<td>$4.55 \times 10^{-6}$ (1.26 $\times 10^{-7}$)</td>
</tr>
<tr>
<td>25</td>
<td>2.543</td>
<td>$8.20 \times 10^{-6}$ (2.02 $\times 10^{-8}$)</td>
</tr>
<tr>
<td>35</td>
<td>0.202</td>
<td>$1.87 \times 10^{-6}$ (7.57 $\times 10^{-8}$)</td>
</tr>
<tr>
<td>35</td>
<td>1.253</td>
<td>$9.06 \times 10^{-6}$ (2.01 $\times 10^{-8}$)</td>
</tr>
<tr>
<td>35</td>
<td>2.568</td>
<td>$1.87 \times 10^{-5}$ (5.975 $\times 10^{-7}$)</td>
</tr>
</tbody>
</table>

5.7.3 Statistical analysis results

The following equation obtained from multiple regressions could be used for estimating mass transfer coefficient for ethanol from corn silage under different temperatures (15 (59°F) -35°C (95°F)) and air velocities (0.2- 2.6 m/s (0.7 – 8.5 ft/s)):

$$K_{L,\text{Ethanol}} = 10^{-5} (0.0946 + 0.0017T - 0.3686V + 0.0298TV) \quad (R^2=0.952) \quad (7)$$

Where

$T$ = air temperature, °C
$V$ = air velocity, m/s

The relation between the mass transfer coefficient of ethanol for corn silage and air velocity and temperature is shown in Figure 28.
Figure 28. Relationship between average mass transfer coefficients of ethanol for corn silage and temperature and air velocity

5.7.4 Results of emission model validation in the environmental chamber
The characteristics of corn silage used in model validation are shown in Table 5. As can be seen there is a difference in the composition of different silages used in different experiments (wind tunnel and environmental chamber) due to the variations in the silage samples.

Table 5. Characteristics of corn silage used in environmental chamber (Standard deviations are given in parentheses)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Corn silage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol (mg/kg wet)</td>
<td>180.2(20.1)</td>
</tr>
<tr>
<td>Ethanol (mg/kg wet)</td>
<td>2935.6 (9.0)</td>
</tr>
<tr>
<td>Acetic acid (mg/kg wet)</td>
<td>4696.1(482.3)</td>
</tr>
<tr>
<td>Propionic acid (mg/kg wet)</td>
<td>221.1 (107.5)</td>
</tr>
<tr>
<td>Iso-Butyric acid (mg/kg wet)</td>
<td>138.6 (90.5)</td>
</tr>
<tr>
<td>Butyric acid (mg/kg wet)</td>
<td>38.6 (27.1)</td>
</tr>
<tr>
<td>Valeric acid (mg/kg wet)</td>
<td>0.00 (0.0)</td>
</tr>
<tr>
<td>Total VFA (mg/kg wet)</td>
<td>5094.4 (707.4)</td>
</tr>
<tr>
<td>pH (-)</td>
<td>3.87 (0.01)</td>
</tr>
<tr>
<td>TS (% wet base)</td>
<td>55.1 (0.1)</td>
</tr>
<tr>
<td>VS/TS, %</td>
<td>95.1 (2.4)</td>
</tr>
</tbody>
</table>
**Ethanol emissions from corn silage**

The measured and the predicted ethanol emission flux are shown in Figure 29. The ethanol mass transfer coefficient estimated from wind tunnel experiments (equation 7) was used in performing these simulations. Measured and predicted ethanol concentrations in corn silage are shown in Figure 30. A reasonable agreement between measured and predicted values was observed.

![Figure 29. Measured and predicted ethanol emission rate from corn silage in the environmental chamber](image)

![Figure 30. Measured and predicted ethanol concentration in corn silage in the environmental chamber](image)

Measured and estimated cumulative ethanol emission from corn silage is shown in Figure 31. As can be depicted from this figure, there is a good agreement between measured and estimated value. After exposing the silage to air inside the environmental chamber for 1 day, the cumulative measured ethanol emission accounted for 20.04 g/m² (2.4 g/kg of silage).
Ethanol emissions from alfalfa silage

The calculated and measured values for ethanol emission rate, ethanol concentration in alfalfa silage, and cumulative ethanol emission are shown in Figures 32, 33 and 34. A good agreement between measured and predicted values is evident. The estimated value of average mass transfer coefficient ($K_L$) was $1.04 \times 10^{-6}$ m/s ($3.4 \times 10^{-6}$ ft/s). This value is lower than the average $K_L$ value estimated for corn silage under similar conditions in the environmental chamber. As mentioned above, this might be due to the differences between the two silages in particle size and bulk density. The alfalfa silage had higher moisture content than the corn silage (Table 6). These might cause some resistance for ethanol transfer from alfalfa as compared with corn silage. More research is needed to determine the effect of particle size and bulk density of different silages on mass transfer coefficient. It is predicted that the ethanol emission rate from alfalfa silage is lower than from corn silage, based on the observations of lower ethanol concentrations in alfalfa and/or lower mass transfer coefficient than in corn silage.
Figure 32. Measured and predicted ethanol emission rate from alfalfa silage placed in the environmental chamber

Figure 33. Measured and predicted alfalfa silage ethanol concentration placed in the environmental chamber
The calculated and measured methanol emission rate, methanol concentration in alfalfa silage, and cumulative methanol emission are shown in Figures 35, 36 and 37. The estimated mass transfer coefficient of methanol inside the environmental chamber was $1.15 \times 10^{-6}$ m/s ($3.8 \times 10^{-6}$ ft/s). This value is higher than that was estimated for ethanol. This may be due to the smaller molecular weight of methanol as compared with ethanol.
5.7.5 Prediction of ethanol emission rate from corn silage

The model was applied to predict ethanol emission from corn silage under different temperatures (15°C (59°F) and 35°C (95°F)) and air velocities (0.2, 1.25 and 2.5 m/s) (0.7, 4.1 and 8.2 ft/s). Simulations were also performed for two initial ethanol concentrations in silage. The simulated results obtained at 35°C (95°F) (Figures 38 to 39) show that at air velocities of 1.25 and 2.5 m/s
(4.1 and 8.2 ft/s) ethanol emission occurs within the first five hours after exposing silage to air and the emission rate decreases to less than 1% of the initial ethanol concentration in silage afterwards. At an air velocity of 0.2 m/s (0.7 ft/s), the emission occurs within 21 hours with initial ethanol concentration of 0.55 and 1.1 kg/m$^3$ (0.034 and 0.07 lb/ft$^3$). Ethanol emission is lower at lower air temperature (15$^\circ$C (59$^\circ$F)) as shown in Figures 42 to 45.

Figure 38. Predicted ethanol emission rate at 35$^\circ$C (95$^\circ$F) . Initial silage ethanol concentration was 1.1 kg/m$^3$ (0.07 lb/ft$^3$).

Figure 39. Predicted ethanol concentration in silage. Initial silage ethanol concentration was 1.1 kg/m$^3$ (0.07 lb/ft$^3$) at 35$^\circ$C (95$^\circ$F)
Figure 40. Predicted ethanol emission rate at 35°C (95°F). Initial silage ethanol concentration was 0.55 kg/m³ (0.035 lb/ft³).

Figure 41. Predicted ethanol concentration in silage at 35°C (95°F). Initial ethanol concentration was 0.55 kg/m³ (0.035 lb/ft³).
Figure 42. Predicted ethanol emission rate at 15°C (59°F). Initial silage ethanol concentration was 1.1 kg/m³ (0.07 lb/ft³).

Figure 43. Predicted ethanol concentration in silage at 15°C (59°F). Initial silage ethanol concentration was 1.1 kg/m³ (0.07 lb/ft³).
Figure 44. Predicted ethanol emission rate at 15°C (59°F). Initial silage ethanol concentration was 0.55 kg/m³ (0.035 lb/ft³).

Figure 45. Predicted ethanol concentration in silage at 15°C (59°F). Initial silage ethanol concentration was 0.55 kg/m³ (0.035 lb/ft³).

5.7.6 Prediction of ethanol emissions under farm conditions

The ethanol emission model was applied to predict the emission rate under specific farm conditions. Wind velocity and temperature were measured on the farm (Figure 46). These simulations start (time=0) at 5:00 AM, when the first feeding starts. Simulations were performed
for two initial ethanol concentrations 1.1 and 0.55 kg/m$^3$ (0.07 and 0.035 lb/ft$^3$). The first initial concentration could be for the fresh corn silage that would be taken directly from silage pile, while the second initial condition could be for silage that would have been left outside for about 2 hours and 50% of ethanol was lost. The simulation results are shown in Figures 47 to 50. The results indicated that the ethanol emission rate is higher for higher levels of initial ethanol concentration, air temperature and velocity. Once the silage is exposed to air, ethanol emission occurs fast with most of ethanol, it not all, lost within 24 hours. The emission rate varies over time and is the highest at the beginning and then decreases over time. For corn silage, with a moisture content of 45% and an initial ethanol concentration of 1.1 kg/m$^3$ (0.07 lb/ft$^3$), exposed to air velocity ranging from 0.1 to 2 m/s (0.3 to 6.6 ft/s) and temperature from 18-35°C (64.4-95°F), ethanol emission occurs within the first 8 hours, depleting the ethanol present in the silage. Ethanol emission rate varied from high levels at the beginning with the maximum of 10 g/m$^2$ hr to levels close to zero after ten hours of air exposure.

![Figure 46. Measured air temperature and velocity on the dairy farm](image)

![Figure 47. Predicted ethanol concentration in corn silage under farm conditions. Initial silage ethanol concentration was 1.1 kg/m$^3$ (0.07 lb/ft$^3$).](image)
Figure 48. Predicted ethanol emission rate under farm conditions. Initial silage ethanol concentration was 1.1 kg/m³ (0.07 lb/ft³).

Figure 49. Predicted ethanol concentration in silage under farm conditions. Initial silage ethanol concentration was 0.55 kg/m³ (0.035 lb/ft³).
An attempt was made to compare the modeling results of this project with the limited on-farm measurement data available. The emission measurement data available from Krauter et al. (2009) and Schmidt and Card (2009) were examined. These studies use the flux chambers to do the emission measurement and the air flow conditions did not reflect the real conditions that silage was exposed on the farm and also no data were available in these references on the ethanol concentrations in the silage when emission measurements were made. The predicted ethanol emission rate is in the same order of magnitude as the measured emission rate measured by Krauter et al. (2009). More farm measurement data, including the emissions and silage characteristics and environmental conditions are needed in order to perform the emission model calibration and validation in the future. Schmidt and Card (2009) measured non-methane non-ethane VOCs for lagoons using flux chambers and did not measure specific compounds like VFAs. We could not use their results for direct comparison. On-farm emission measurement and monitoring have been conducted for free stall dairy housing by Dr. Frank Mitloehner and his research team at UC Davis as part of National Air Emissions Measurement Study (NEAMS). Ethanol and methanol emissions are among the air pollutants measured but the emission data could not be disclosed and used for the emission model validation at this time.
5.8 Conclusions and Recommendation for Future Research

The kinetics of ethanol emission from corn silage was investigated in this study and a computer model for predicting the ethanol flux from corn silage exposed to open air was developed. With this model, ethanol emission rate and total emission can be estimated for corn silage at different initial ethanol concentrations and under different temperatures and air velocities. The emission measurement data from a laboratory-scale wind tunnel were used to assist the model development. The ethanol emission flux model was validated using the measurement data from an environmental chamber. The model was later used to predict the ethanol emission flux from corn silage exposed to variable environmental conditions that were measured on a dairy farm in the San Joaquin Valley, CA. The results indicated that ethanol emission rate is higher at higher temperatures and air velocities. Once the silage is exposed to air, ethanol emission occurs fast with most of ethanol, if not all, emitted within 24 hours. The emission rate varies over time with the highest at the beginning and then decreases over time. For the corn silage exposed to air velocity ranging from 0.1 to 2 m/s (0.3 to 6.6 ft/s) and temperature from 18-35°C (64.4-95°F), ethanol emission occurs within the first 10 hours, depleting the ethanol in the silage. Ethanol emission rate varies from high levels at a maximum rate of 10 g/m².hr to low levels close to zero.

This model is suitable for predicting ethanol emissions from thin layers of loose silage. Further development and testing of the emission model is needed for application to other scenarios such as ethanol emissions during silage mixing and from deep silage layers or piles. More research is needed to survey the ethanol concentration levels for silages used in California dairies and also study the average air exposure time and conditions of silages. More farm measurement data, including the emissions and silage characteristics and environmental conditions are needed in order to perform the emission model calibration and validation in the future.
6.0 Measurement and Modeling of Volatile Organic Compound Emissions from Free Stall and Corral Housing

6.1 Introduction

Manure collected in free stall housing is one of the emission sources on dairies. For dairies that use flushing or scraping for cleaning the manure in free stalls, the typical residence time of manure is 6 to 24 hours, depending on the cleaning frequency. The most common procedure used in the past by some researchers for assessing the emissions in free stall housing is to use enclosed flux chambers and measure the emissions from small areas. The measurement data were used to estimate the emissions from the whole free stall housing (Ndewga et al., 2008). The drawbacks of using such an empirical approach for estimating the emissions include: (1) high uncertainties created by using the measurement data from a very small area to estimate the emissions from a whole farm (2) inability to estimate the emission rate under the environmental conditions different from the conditions present in the flux chambers. These drawbacks can be overcome by using an emission modeling approach assisted by experimental measurement and validation. Ethanol is one of the major VOCs present in fresh manure and other VOCs include volatile fatty acids, sulfide, amines and mercaptans. Fresh slurry is a source of ethanol emissions on farm (Sun et al., 2008). The main objective of this research was to develop and validate a mathematical model that can be used to predict the emission rate of ethanol from the manure collected in free stalls under different manure and environmental conditions. Moreover, characterization of manure in playing corral is another objective.

6.2. Modeling of Ethanol Emission from Environmental Chamber

A completely mixed system was assumed inside the environmental chamber. A mass balance for ethanol concentration in manure was described by the following equation:

$$V_m \frac{dC_m}{dt} = \left( C_{M0} - C_m \right) \frac{dV_m}{dt} + K \left( C_{M_{max}} - C_m \right) e^{(Kt)} - KL A_m \left( C_m - \frac{C_{air}}{H_{cc}} \right)$$

Where

- $C_M$ = ethanol concentration in manure at time t (kg/m$^3$ or lb/ft$^3$)
- $C_{M0}$ = ethanol concentration in the fresh (i.e., excreted) manure (kg/m$^3$ or lb/ft$^3$)
- $V_m$ = manure volume inside the environmental chamber (m$^3$ or ft$^3$)
- $K$ = rate constant of ethanol generation, (1/sec)
- $C_{M_{max}}$ = maximum ethanol concentration in manure due to generation (kg/m$^3$ or lb/ft$^3$)
- $K_L$ = overall mass transfer coefficient for ethanol, (m/sec or ft/sec)
- $A_m$ = manure surface area (m$^2$ or ft$^2$)
- $C_{air}$ = ethanol concentration in the air inside the chamber (kg/m$^3$ or lb/ft$^3$)
- $H_{cc}$ = Henry's law constant.
A mass balance for ethanol in the chamber air was described by the following equation

\[ V \frac{dC_{\text{air}}}{dt} = \phi_m \left( C_{\text{out-air}} - C_{\text{air}} \right) + K_L A_m \left( C_M - \frac{C_{\text{air}}}{H_{cc}} \right) \]  

(12)

Where

- \( V \) = volume of the environmental chamber, m³
- \( \phi_m \) = volumetric air flow rate inside the environmental chamber (m³/sec or ft³/sec)
- \( C_{\text{out-air}} \) = ethanol concentration in the air inlet of the environmental chamber (kg/m³ or lb/ft³)

Ethanol emission rate from manure (\( F_{\text{Eth}} \), kg/m².sec or lb/ft².sec) was calculated as follows:

\[ F_{\text{Eth}} = \frac{\phi_m (C_{\text{air}} - C_{\text{out-air}})}{A_m} \]  

(13)

The developed model was validated using the experimental data collected from an environmental chamber. Experiments are described in the next section. The parameters used in the simulations are shown in Table 6. The manure density and excretion rate were obtained from ASABE (2003). Mass transfer coefficient of ethanol (\( K_L \)) inside the environmental chamber was estimated using the lsqnonlin routine in Matlab (The Math Works Inc., Natick, MA, USA) as described by Sleutels (2002). The differential equations were solved using ODS15s routine in Matlab.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of cows,</td>
<td>3</td>
</tr>
<tr>
<td>Average weight of cow, kg</td>
<td>783</td>
</tr>
<tr>
<td>Manure surface area, m²</td>
<td>23.94</td>
</tr>
<tr>
<td>Manure excretion rate, kg/1000 kg[live weight]-day</td>
<td>86</td>
</tr>
<tr>
<td>Manure density, kg/m³</td>
<td>990</td>
</tr>
<tr>
<td>Environment chamber volume, m³</td>
<td>129.36</td>
</tr>
<tr>
<td>Air flow rate, m³/hr</td>
<td>2107</td>
</tr>
<tr>
<td>( K_L ), m/s</td>
<td>3.07×10⁻⁷</td>
</tr>
</tbody>
</table>

### 6.3. Experimental Research Methods

#### 6.3.1 Quantification of ethanol emissions from manure

To quantify ethanol emissions from manure collected in free stalls, three cows were kept inside an environmental chamber for one day (Figure 51). The same environmental chamber used for corn silage was also used in this experiment. The average weight of cows was 783 kg (1726 lb). The cows were fed the ration shown in Table 7. The temperature inside the environmental chamber was recorded every 10 min using a HOBO sensor (Onset Computer, Bourne, MA).
Figure 51. Three cows kept inside an environmental chamber

Table 7. Ingredient and chemical composition of the cows feed

<table>
<thead>
<tr>
<th>Ingredient, as fed bases</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain mix (%)</td>
<td>37.51</td>
</tr>
<tr>
<td>Alfalfa hay, chopped (%)</td>
<td>36.15</td>
</tr>
<tr>
<td>Almond hulls (%)</td>
<td>11.97</td>
</tr>
<tr>
<td>Whole cottonseed (%)</td>
<td>9.58</td>
</tr>
<tr>
<td>Soybean meal (%)</td>
<td>2.08</td>
</tr>
<tr>
<td>Mineral mix (%)**</td>
<td>1.60</td>
</tr>
<tr>
<td>EnerG (%)**</td>
<td>0.80</td>
</tr>
<tr>
<td>Salt (%)</td>
<td>0.32</td>
</tr>
</tbody>
</table>

*Grain mix contained (% as-fed of grain mix) steam flaked corn (38.0), rolled barley (20.0), bakery product (16.0), beet pulp (12.7), dried distillers grain (6.0), wheat mill run (5.0), fat (2.2), and mold inhibitor (0.1).

**Mineral mix contained: Calcium 8.5%, Magnesium 6.4%, Phosphorus 4.4%, Sodium (max) 12.5%, Potassium 1.0%, Zinc 3250 ppm, Manganese 2000 ppm, Copper 500 ppm, Selenium 16.8 ppm, Vitamin A 180,000 IU/lb, Biotin 20 mg/lb, Rabon 1960 g/ton.

***EnerG II, Vitrus Nutrition (vitrusnutrition.com), Fairlawn, OH.

The environmental chamber was ventilated at a rate of 2107 m³/hr (74400 ft³/hr). Ethanol concentrations in the inlet and outlet air were measured using INNOVA (Model 1412, LummaSense Technologies, Ballerup, Denmark). No flushing was applied for manure during this experiment that was last for one day. The manure accumulated on the chamber floor was sampled to measure ethanol concentration in manure. During sampling, the chamber floor was divided into 6 sections. One sample of about 100 g (3.53 oz) was taken from each section. Samples were transferred immediately to the laboratory on blue ice. All the six samples were mixed and a composite sample was taken for analyses. Ethanol, TS and VS contents were measured in duplicate. Ethanol and VFAs were measured after diluting samples 10 times using deionized water and then mixed for 30 minutes on a wrist action shaker (Burrell Corporation, Pittsburgh, PA, USA). The mixed samples were centrifuged for 10 min at 5000 rpm, and then
filtered using 0.45 µm membrane filters. The filtered samples were acidified using ortho-
phosphoric acid (10%) to a pH < 2 before injection into the GC. The GC conditions are the same
as those used for silage analysis. The TS and VS were measured using the standard methods
(APHA, 1998). All the measurements were done in duplicate.

6.3.2 Quantification of ethanol generation from manure

The generation rate of ethanol in manure is an important term in formulating mathematical
model for ethanol emissions from manure. It was not possible to use the data from the manure
inside the environmental chamber to quantify the generation of ethanol under different
temperatures due to the small range of temperature inside the chamber (19-22°C) (66.2-71.6°F).
Therefore, laboratory experiments were carried out. A certain amount of manure was incubated
under different temperatures (15, 25 and 35°C) (59, 77 and 95°F) in the presence of air over
manure surface. Fresh feces and urine was collected from UC Davis experimental farm in early
morning directly after cows defecated. Feces and urine were equally mixed based on wet base.
The characteristics of this mixture are shown in Table 8.

Table 8. Characteristics of manure used in ethanol generation experiments
(Standard deviations are given in parentheses)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol (mg/kg wet)</td>
<td>8.01 (5.15)</td>
</tr>
<tr>
<td>Ethanol (mg/kg wet)</td>
<td>60.85 (23.17)</td>
</tr>
<tr>
<td>Acetic acid (mg/kg wet)</td>
<td>2095.73 (414.73)</td>
</tr>
<tr>
<td>Propionic acid (mg/kg wet)</td>
<td>975.58 (465.93)</td>
</tr>
<tr>
<td>Iso-Butyric acid (mg/kg wet)</td>
<td>107.24 (57.14)</td>
</tr>
<tr>
<td>Butyric acid (mg/kg wet)</td>
<td>771.90 (294.75)</td>
</tr>
<tr>
<td>Valeric acid (mg/kg wet)</td>
<td>213.62 (127.28)</td>
</tr>
<tr>
<td>Total VFA (mg/kg wet)</td>
<td>4164.07 (1359.83)</td>
</tr>
<tr>
<td>pH (-)</td>
<td>8.07 (0.01)</td>
</tr>
<tr>
<td>TS (% wet base)</td>
<td>9.32 (0.01)</td>
</tr>
<tr>
<td>VS/TS, %</td>
<td>74.23 (0.68)</td>
</tr>
</tbody>
</table>

At each studied temperature, 18 bottles were used and each bottle had a total volume of 300 ml.
In the beginning of the experiments, 40 g (1.41 oz) of manure mixture was added in each bottle.
Then the bottle was sealed with a plastic cover under a screw cab. Periodically, two bottles were
sacrificed, at each studied temperature, as destructive samples. The concentration of ethanol in
the bottle head space was measured using an ethanol sensor (Model Alco-Sensor IV; Intoximeters, St. Louis, MO) by inserting the needle of ethanol sensor through the plastic cover
of bottle. After measuring the ethanol in the head space, bottles were opened and manure was
diluted 5 times with deionized water and ethanol was measured using the GC. The cumulative
concentration of ethanol in manure, at any time, due to generation was calculated by subtracting
the initial ethanol concentration originally presented in manure from the summation of ethanol
concentration in the manure and in the head space. The amount of ethanol in the headspace was
calculated based on the concentration of ethanol in the headspace and the volume of the
headspace. The calculated ethanol amount in the headspace was divided by the amount of
manure to express this amount as a portion of the ethanol concentration in manure. The cumulative ethanol in the manure due to generation was modeled using the following equation:

\[ E_g = C_{max} \left(1 - \exp(-Kt)\right) \]  

(10)

Where

- \( E_{gen} \) = Cumulative ethanol concentration due to generation (kg/m³ or lb/ft³)
- \( C_{max} \) = Maximum cumulative ethanol concentration (kg/m³ or lb/ft³)
- \( K \) = Rate constant of ethanol generation (1/sec)

Herrera et al. (2004) used a similar approach to model acetic acid concentration during the diluted acid hydrolysis of sorghum straw. The parameters \( C_{max} \) and \( K \) were estimated using the nlinfit routine in Matlab (The Math Works Inc., Natick, MA, USA).

### 6.3.3 Characterization of manure in corral

Manure in playing corral was sampled during one day in summer 2009. Samples were randomly collected from different locations in a farm corral located in the San Joaquin Valley, CA. During sample collections, some aged manure on the ground had a crust layer under which moist manure was found. Manure was mixed manually on the ground before taking samples. Samples were kept on blue ice and transferred directly to the lab for analysis. TS, VS, VFAs and ethanol were measured as described above.

### 6.4. Results and Discussion

#### 6.4.1. Ethanol generation at different temperatures

The measured ethanol concentrations in manure and in the bottle head space at different temperatures are shown in Figures 52 and 53. The data in Figure 52 were calculated as kg of ethanol per cubic meter of manure using a manure density of 990 kg/m³ (61.8 lb/ft³) (ASABE, 2003). As can be seen there was a slight increase of ethanol concentrations at the lowest temperature (15°C (59°F)). On the other hand, there was a large increase in ethanol concentrations at 25 (77°F) and 35°C (95°F) until 20 hours. Then there was a decrease in ethanol concentrations that might be due to the consumption of ethanol by microorganisms or due to the conversion of ethanol to other compounds (e.g., acetaldehyde).
Figure 52. Ethanol concentrations in manure at three different temperatures

Figure 53. Ethanol concentrations in the head space of storage bottles at three different temperatures

The calculated cumulative concentrations of ethanol due to generation were fitted to equation 10. Due to the low concentrations measured in some samples at 15°C (59°F), some of the data points showed cumulative negative generation. These data points were excluded from model fitting. The results of ethanol generation model are shown in Figures 54-56.
Figure 54. Cumulative ethanol generation in dairy manure stored at 15°C (59°F).

Figure 55. Cumulative ethanol generation in dairy manure stored at 25°C (77°F).

Figure 56. Cumulative ethanol generation in dairy manure stored at 35°C (95°F).
The estimated $K$ and $C_{\text{max}}$ at different temperatures are shown in Table 9. As can be seen there is no clear relation between generation rate constant of ethanol and temperature. The reason behind this phenomenon is not clear. Theoretically, Arrhenius equation could be used to describe this relation (e.g., Yu and Fang, 2003). Moreover, there is no clear relation between maximum accumulative ethanol and temperature. More experiments are needed to find out the reason behind these phenomena.

### Table 9. Model results of ethanol generation model

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>$K$ (1/sec)</th>
<th>$C_{\text{max}}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>$1.144 \times 10^{-5}$</td>
<td>0.0484</td>
<td>0.820</td>
</tr>
<tr>
<td>25</td>
<td>$7.219 \times 10^{-6}$</td>
<td>0.417</td>
<td>0.900</td>
</tr>
<tr>
<td>35</td>
<td>$2.398 \times 10^{-5}$</td>
<td>0.228</td>
<td>0.926</td>
</tr>
</tbody>
</table>

### 6.4.2. Results of ethanol emission model

Measured and predicted ethanol emission rates from the manure collected in the environmental chamber are shown in Figure 57. Ethanol emissions increase over the experimental time. This is due to both accumulation of manure inside the environmental chamber and the generation of ethanol in the manure over the experimental time. It should be mentioned that, in these simulations, the estimated values of $C_{\text{max}}$ and $K$ at 15°C (59°F) and 25°C (77°F) were used to interpolate the values for the measured temperatures inside the environmental chamber. This is because there was no clear correlation between these two parameters and the temperature.

![Figure 57. Measured and predicted ethanol emission rates from dairy manure collected in an environmental chamber.](image)

The cumulative ethanol emissions from the environmental chamber are shown in Figure 58. As can be shown, unlike ethanol concentration in the manure (Figure 59), a good agreement between measured and predicted values of cumulative ethanol emissions. The cumulative
emissions of ethanol were 0.126, 0.182, 0.31 and 0.73 g/m² after 6, 8, 12 and 24 hours. Therefore, when flushing manure three times a day at 8 hours interval, ethanol emission per cow could account for 0.245 g/cow-hr. Although the good agreement between measured and predicted ethanol emissions for the environmental chamber, the model needs to be calibrated using more experimental data under different experimental conditions. Moreover, the model needs to be calibrated and validated with farm measurement data.

![Cumulative ethanol emissions from the environmental chamber](image1.png)

Figure 58. Cumulative ethanol emissions from the environmental chamber

![Measured and predicted ethanol concentration in manure inside the environmental chamber](image2.png)

Figure 59. Measured and predicted ethanol concentration in manure inside the environmental chamber
6.5. Characteristics of Manure Collected from Corral

Measured ethanol and VFAs concentrations in manure samples, collected from corral, as functions of moisture contents are shown in Figures 60 and 61. As can be seen the higher the moisture contents the higher the concentrations of these compounds. Moisture content was used as an indicator of the age of manure on corral. Lower moisture content means that manure was standing on the ground for a longer period of time that was not exactly known. Theoretically, the potential of VOCs (e.g., ethanol) emissions increases as the concentrations of these VOCs increase in manure. Therefore, it is expected that higher emission rates of VOCs are expected from wet manure as compared with the dried manure. The measured VS/TS ratios as a function of TS are shown in Figure 62. As can be seen that as manure dried out, lower VS/TS ratios were measured. The reduction in VS content indicates that manure undergone biological and possibly some physical changes (e.g., diffusion of some compounds into the ground).

![Figure 60. Ethanol concentrations of corral manure at different moisture contents](image)

![Figure 61. Total VFAs concentration of corral manure at different moisture contents](image)
The measurement data for manure in the corral raised many research questions that should be answered as part of developing a mathematical model for ethanol emission from corral. Some of the research questions are as flows:

- How many cows stay in corral and for how long?
- The effect of weather conditions (temperature, rain, shad, etc.) and farm practice (e.g., feeding and milking) on cows behavior on corral need to be determined.
- It was also not possible to judge whether the reduction of moisture content was due to merely evaporation or loss to the ground or both. This should be determined.
- The time required to develop the crust layer on manure need to be determined under different conditions.
- The effect of crust layer on the emission rates of VOC needs to be determined.
- The effect of manure moisture content and open weather conditions on the degradation/generation rates and mass transfer coefficients of different VOCs needs to be determined experimentally.

It was not possible to answer these questions, unfortunately, with the time and fund constraints of this project. Therefore, we are seeking more funds to research the processes and factors that affect the emissions from corral and other open feedlot sources. Better scientific understanding and quantification are needed for these issues before we could develop and validate a mathematical model for VOC emissions from corral.
6.6 Conclusions and Future Research

Ethanol emission from manure in free stalls was measured and modeled using an environmental chamber that housed three dairy cows. Manure was allowed to accumulate for 24 hour. The generation and accumulation of ethanol in fresh manure over a 24-hour period were measured and modeled at three temperatures (15 (59°F), 25 (77°F) and 35°C (95°F)). No clear correlation was found between maximum accumulated ethanol in manure and the rate constant of ethanol generation and temperature. The reason is not clear and needs further investigation. A smaller temperature range may be needed in the future experiments to determine the generation of ethanol and other VOCs in the manure. The oxygen level that the manure is exposed to during the storage may have an effect on the ethanol generation and more research is needed in this direction. The modeling of ethanol emissions from environmental chamber showed good agreement between the measured and predicted cumulative emissions. The estimated cumulative emissions of ethanol were 0.13, 0.18, 0.31 and 0.73 g/m² after 6, 8, 12 and 24 hours, respectively, under the conditions tested in the environmental chamber. The model needs to be calibrated and validated using more experimental and farm measurement data. More research questions need to be answered to enable the development and validation of mathematical models for VOCs emissions from corral and open feedlot sources.
7.0 Measurement and Modeling of Volatile Organic Compounds Emission from Manure Storage

7.1 Introduction

Manure storage under anaerobic conditions is a common practice on dairies. The total solids (TS) content of the manure under storage is 1-3% for dairies that use flush systems for manure collection and 4% or higher for dairies that use scrape systems. Due to the high organic content of manure, anaerobic conditions naturally form in storages unless aeration is provided to increase the oxygen content. The VFAs and alcohols are among the major VOCs produced from the microbial degradation of dairy manure. The objectives of this research were to quantify the changes in VFAs and alcohols concentration in liquid manure during anaerobic storage at different conditions and to develop mathematical models to predict the generation and emissions of these compounds from manure storages.

7.2 Research Methods

7.2.1 Manure collection and preparation

Fresh feces and urine was collected from UC Davis experimental farm in early morning directly after cows defecated. Feces (50%) and urine (50%) were mixed. This mixture had a TS content of about 9.1% and a VS/TS content of 81%. This mixture was diluted to 2% and 4% TS using tap water.

7.2.2 Manure storage experiments

The temperature and initial TS content of the manure were investigated as major factors that influence the manure degradation. Three levels of each factor were tested: 15±2, 25±1 and 35°C±1 (59±33.8, 77±33.8 and 95±33.8°F) for temperature and 2%, 4% and 9% for manure TS. Manure storage experiments were carried out using 1-L bottles for 30 days after which concentrations of VFAs and alcohols in the manure became stable. For each TS tested, four bottles were used. The first two bottles had working volumes of 500ml. These two bottles were kept closed for measuring the amount and composition of biogas produced. The other two bottles had working volumes of 800 ml. Samples were taken periodically from these two bottles. In the start up of these experiments, after adding the required amount of manure, bottles were flushed with argon gas for three min to assure anaerobic conditions. Bottles were manually shaken once daily to provide mixing of bottle contents.

7.2.3 Measurements and analyses

The daily amount of biogas produced from each container was calculated after measuring the daily increase of pressure in the storage head space using a WAL-BMP pressure gauge (Type 3150, Wal, Germany).
Biogas composition (H₂, CH₄ and CO₂ contents) was measured periodically using a gas chromatography (HP5890A, Avondale, PA, USA) that was equipped with a thermal conductivity detector (TCD). A 1.8 m × 0.32 mm Alltech carbospher column (Alltech Associates Inc., USA) was used. Oven, inlet, and detector temperatures were 100 (212°F), 120 (248°F) and 120°C (248°F), respectively. Argon was used as a carrier gas. Volatile fatty acids, methanol and ethanol and pH were measured in the liquid phase. The measurements were done every day during the first three days, then twice a week for the second week and finally once a week until the end of the 30 day storage period. The TS and VS were measured using the standard methods (APHA, 1998). The pH was measured using Accumet AR50 (Fisher Scientific, USA). VFA, methanol and ethanol were measured as indicated above. All measurements were done in duplicate.

### 7.2.4 Modeling of acetic acid emission from manure storage

Because acetic acid was the major VFAs present in the manure storages, mathematical models were developed to calculate the emission rate and cumulative emission of acetic acid from a dairy manure lagoon. The following equation is used to calculate the emission rate of acetic acid ($F_{AC}$):

$$F_{AC} = K_L f C_m \quad (14)$$

Where

- $F_{AC}$ = emission rate of acetic acid (kg/m².hr or lb/ft².hr)
- $K_L$ = overall mass transfer coefficient for acetic acid (m/hr or ft/hr)
- $f$ = dissociated fraction of acetic acid.
- $C_m$ = concentration of acetic acid in the manure at time t (kg/m³ or lb/ft³)

Assuming the concentration of acetic acid in air equals zero, the following equations are used to calculate the concentration of acetic acid in the lagoon storing manure from a given number of cows at a given time:

$$V_m \frac{dC_m}{dt} = (C_0 - C_m) \frac{dV_m}{dt} + K_h (C_{max} - C_m) V_m - K_L A_m f C_m \quad (15)$$

$$\frac{dV_m}{dt} = \frac{N \cdot W_c \cdot (M_{cr} + W_a)}{C (3600)(24) \rho} \quad (16)$$

Where

- $C_m$ = concentration of acetic acid in the manure at time t (kg/m³ or lb/ft³)
- $C_0$ = concentration of acetic acid in the fresh (e.g., flushed) manure (kg/m³ or lb/ft³)
- $V_m$ = volume of manure in lagoon (m³ or ft³)
- $t$ = time, hr
- $K_h$ = rate constant of acetic acid generation (1/hr)
- $C_{max}$ = maximum concentration of acetic acid due to generation (kg/m³ or lb/ft³)
 overall mass transfer coefficient for acetic acid (m/hr or ft/hr)
A_m = surface area of manure (m² or ft²)
f = dissociated fraction of acetic acid
C_{air} = concentration of acetic acid in the air above manure surface (kg/m³ or lb/ft³)
N = number of cows
W_c = average weight of a cow (kg or lb)
M_{cr} = excretion rate of manure (kg/hr.1000 kg (live weight)) or (lb/hr.2000 lb (live weight)). The value of M_{cr} was obtained from ASABE (2003).

W_a = amount of water added to manure before delivering to the lagoon (kg/hr.1000 kg (live weight)) or (lb/hr.2000 lb (live weight))
C = constant that is equal to 1000 when using the W_a as kg/hr.1000 kg (live weight) or 2000 when using the W_a as lb/hr.2000 lb (live weight)
ρ = manure density, kg/m³. It was assumed to be 1000 kg/m³ (62.4 lb/ft³).

The values of K_h as a function of temperature was calculated based on the Arrhenius equation using the estimated parameters from storage experiments. Overall mass transfer coefficient, K_L, was calculated based on the equation presented by Parker et al. (2008).

\[ K_L = \frac{k_{Lf} k_{Gf} H_{cca}}{k_{Lf} + k_{Gf} H_{cca}} \]  \hspace{1cm} (17)

Where

k_{Lf} = liquid-film mass transfer coefficient (m/hr or ft/hr)
k_{Gf} = gas-film mass transfer coefficient (m/hr or ft/hr)
H_{cca} = Henry law constant of acetic acid, dimensionless

The liquid film mass transfer coefficient (k_{Lf}) was calculated as follows:

\[ k_{Lf} = 0.2 \left( \frac{32}{M_{Wa}} \right)^{0.5} \]  \hspace{1cm} (18)

Where M_{Wa} = molecular weight of acetic acid, g/mole

The gas film mass transfer coefficient (k_{Gf}) was calculated as follows:

\[ k_{Gf} = \frac{170 V_{surf}}{24} \left( \frac{18}{M_{Wa}} \right)^{0.25} \]  \hspace{1cm} (19)

Where V_{surf} = wind velocity over lagoon surface, m/s

Temperature of manure surface was calculated as a function of air temperature (Preud'homme and Stefan's, 1993).
\[ T_{\text{surf}} = 2.9 + 0.86 T_{\text{air}} \]  \hspace{1cm} (20)

Where

\( T_{\text{surf}} \) = temperature of manure surface, °C

\( T_{\text{air}} \) = temperature of air, °C

The measured wind speed data taken from a weather station were used to calculate the wind speed over the manure surface using a surface roughness length of 0.01 m (0.4 inch) (Parker et al., 2008) and the average manure depth in the lagoon. The dissociated fraction of acetic acid was calculated using the equation presented by Zhang et al. (1993) and Schwarzenbach et al. (2003):

\[ f = \frac{1}{1 + 10^{(pH - pKa)}} \]  \hspace{1cm} (21)

Where

\( f \) = dissociated fraction of acetic acid

\( pKa \) = average acidity constant

An average acidity constant of 4.677 was used in these calculations. The pH of the manure in the lagoon was estimated from the batch experimental data, which varied from 6.4 to 7.5.

The developed model was used to simulate a lagoon storing manure produced from 1000 cows located near Davis, CA. The manure is assumed to have 2% TS. Two months were selected to run the emission simulation, March and August, which represent cool and warm weather conditions, respectively. The weather data used for the lagoon model was from the California Irrigation Management Information System (CIMIS), which has a web site from which hourly weather data for over 120 sites in California can be downloaded. (http://wwwcimis.water.ca.gov/cimis/welcome.jsp). The weather site we used is from Station 6, and is located on the Campbell Tract field research facility at UC Davis. In these simulations, it was assumed that manure was accumulated in the lagoon for one month. The emission models can be used to calculate the emission from the lagoon for any periods of time, depending on the lagoon management practices. The parameters used in the simulation are shown in Table 10.
Table 10. Parameters used for the simulated dairy lagoon

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of cows</td>
<td>1000</td>
</tr>
<tr>
<td>Average weight, kg</td>
<td>783</td>
</tr>
<tr>
<td>Manure excretion, kg/1000 kg/live weight/day</td>
<td>86</td>
</tr>
<tr>
<td>Total solids content of manure excreted, %</td>
<td>12</td>
</tr>
<tr>
<td>Total solid content of manure entering the lagoon, %</td>
<td>2</td>
</tr>
<tr>
<td>Bottom width of lagoon, m</td>
<td>30.48</td>
</tr>
<tr>
<td>Bottom length of lagoon, m</td>
<td>182.9</td>
</tr>
<tr>
<td>Side slope of lagoon</td>
<td>3</td>
</tr>
</tbody>
</table>

7.3 Results and Discussion

7.3.1 Volatile fatty acid and alcohol concentrations in the manure during storage

The concentrations of total VFAs and acetic acid for the manure initially stored at 2% TS and at different temperatures are shown in Figures 63 and 64. As can be seen, VFAs started to increase right away after incubation. At 35°C (95°F), total VFAs and acetic acid increased till about day 6 and then decreased. The maximum VFAs concentration averaged 5.5 g/L. Acetic acid represented 60% of the total VFAs. At 25°C (77°F), the increase of VFAs continued until day 15 and then decreased. The maximum total VFAs was 6 g/L and acetic acid represented 56%. The reduction of VFAs after day 6 may indicate the establishment of methanogenic consortia that consumed VFAs and produced biogas (Figure 77). On the other hand, at 15°C (59°F), VFAs still increased after the 6th day. The accumulation of VFAs caused the decrease of pH as shown in Figure 65. Temperature is an important factor affecting the decomposition of organic matter under anaerobic conditions and it is expected that reaction rates increase with temperature provided that no inhibitory conditions are present.

![Figure 63](image.png)

Figure 63. Average concentrations of total VFAs in manure storage at 2% initial TS at different temperatures
Figure 64. Average concentrations of individual VFAs in manure storage at 2% initial TS at different temperatures

Figure 65. Average pH in manure storage at 2% initial TS and at different temperatures

The average concentrations of methanol and ethanol in the storage of 2% TS manure over the storage time are shown in Figure 66. Ethanol concentrations increased to 140 mg/L after 4 days of storage at 15 (59°F) and 25°C (77°F), then declined to a level of close to zero, then increased to 40 mg/L. At 35°C (95°F), there was a little increase of ethanol to about 75 mg/L at day 10, then it
declined. This may indicate higher rates of conversion of ethanol to VFAs at higher temperatures. Lower levels of methanol were measured with an oscillation pattern in some cases. The oscillation pattern in methanol and ethanol (after day 10) might be the error encountered during sample dilution and preparation. During a study of the digestion of dairy wastewater at thermophilic conditions, Yu and Fang (2001) mentioned that while ethanol was produced at high concentrations methanol was found in lesser amounts.

![Figure 66. Average concentrations of methanol and ethanol in manure storage at 2% TS](image)

The measured concentrations of VFAs, ethanol and methanol in manure storage at 4% TS and at different temperatures are shown in Figs 67, 68 and 69. As can be seen higher rates of degradation are also evident at the higher temperature. The VFAs concentrations were still increasing after 30 days of storage at both 35°C (95°F) and 25°C (77°F) with maximum concentrations of near 12 g/L at 35°C (95°F). At 15°C (59°F), VFAs increased to 6 g/L, and then remained constant at that level. The measured pH showed an opposite relation to VFAs concentrations (Figure 70). The accumulation of VFAs was accompanied by lower pH values and negatively affected methanogenesis (Asinari di san marzano et al., 1981). Although the suppression of methanogenesis is beneficial from reducing methane emission from manure storage, it may increase the emissions potential of VFAs.
Ethanol concentrations increased to 210 and 170 mg/L after 4 days of storage, at 15 \( (59^\circ F) \) and 25\(^{\circ} \)C \( (77^\circ F) \), respectively, and then declined. After day 10, there was an increase to 40 mg/L. On the other hand, at 35\(^{\circ} \)C \( (95^\circ F) \), there was an increase of ethanol to about 100 mg/L in the first 2 days and then declined. Low levels of methanol of about 30 mg/L were measured in these
In the storage of manure with 9% TS, substantial increases of VFAs were found at 25°C (77°F) and 35°C (95°F) (Figures 71 and 72). At 35°C (95°F), VFAs continued to increase until about day 10 leveling off at about 17 g /L. This might indicate that acidogenesis was also negatively affected or that all biodegradable organic matter was converted to VFAs. No data is available for manure used in current storage systems. At 25°C (77°F), VFAs continued its increase reaching almost the same level that was obtained at 35°C (95°F) on day 30. A maximum VFAs concentration of about 12.5 g/L could be measured after about 2 weeks of storage and it remained constant afterwards. Similar to manure storage at 2% and 4% TS, pH decreased as VFAs accumulated. However, it should be noted that relatively higher pH values were measured at the higher temperatures (i.e., higher VFAs concentrations). This might indicate that these systems had higher buffer capacity. The latter might be an indication of increased hydrolysis.
rates of protein at the higher temperature and therefore higher ammonia concentrations might be present. Comparing the storage at the three studied TS, it can be seen that at a TS of 9% the lower pH values were about 6.6 as compared with about 6.0 and 6.4 at TS of 2% and 4% respectively (Figure 73). This may indicate that the systems had higher buffer at higher the higher TS.

Figure 71. Average concentrations of total VFAs in manure storage at 9% TS and at different temperatures

Figure 72. Average concentrations of individual VFAs in manure storage at 9% TS and at different temperatures
Similar to the storage at 4% TS, ethanol concentrations increased to about 230 and 170 mg/L after 4 days of storage, respectively at 15 (59°F) and 25°C (77°F) then declined (Figure 74). On the other hand at 35°C (95°F), there was a decrease of the initial ethanol concentrations during the first 3 days then ethanol concentration increased to about 130 mg/L for about 3 days decreasing afterwards. Low levels of methanol of about 30 mg/L were measured in these storages. These low levels of methanol and again the oscillations in ethanol after day 10th might be due to sample dilution and preparation.
Biogas yields at different temperatures and different initial TS contents are shown in Figure 75. Higher biogas yields were obtained at higher temperatures at each studied TS level. The highest biogas yield (318 ml/g VS) was obtained at 35°C (95°F) and 2% TS. This is may be due to the positive effective of the higher temperature on methanogenic activity and low VFAs concentrations present under this storage conditions (Figure 63). The lower biogas yields were obtained at 15°C (59°F) with a lowest value of about 25 ml/gVS at 9% TS. At the same storage temperature, lower biogas yields were obtained at the higher initial TS. These results indicate that methanogenic activity in the manure is inversely affected by manure TS content in the storage.

![Figure 75. Biogas yield at different temperatures and different initial total solids](image)

Methane contents of the biogas are shown in Figure 76. Again the methane content was higher at the lower TS. At 35°C (95°F) and 2%, methane content increased over the storage time reaching 70% on day 18, then remained constant while VFAs concentrations declined (Figure 63). It can be noticed that in the storage at 15°C (59°F), methane increased to about 15% in the first few days, then declined. This may indicate that the methanogenic archea, originally present in manure, were able to survive for a few days, then negatively affected by either the low temperature or the accumulation of VFAs. At 25°C (77°F), there was a slight decrease of methane content after the first few days. The methane content stabilized for about two weeks, and then started to increase again. These results might indicate that a period of time is required either for establishing new methanogenic consortia in manure storage or for adaptation of methanogenic archea to lower temperature. Studies on manure storages for longer times are
underway to determine the fate of the accumulative VFAs and the biogas, especially methane, production from these storages.

![Graph showing biogas composition at different temperatures and initial total solids](image)

**Figure 76. Biogas composition at different temperatures and different initial total solids**

### 7.3.2 Modeling of acetic acid generation in dairy manure

Since acetic acid is the major VFA, mathematical models were constructed to calculate the net cumulative acetic acid concentration in manure storage due to generation and conversion (measured concentration at time (t) – measured concentration at time (0)). This was fitted to a first order equation in the form:

\[ Y_{gen} = C_{max} (1 - \exp(-Kt)) \]  

(16)

Where
- \( Y_{gen} \) = Net cumulative acetic acid concentration in the liquid phase (g/L)
- \( C_{max} \) = Empirical constant, represents the maximum net accumulative acid (g/L)
- \( K \) = Rate constant of acid generation (1/day)

Then the concentration in each storage (\( Y_T \)) could be calculated as follows:

\[ Y_T = Y_{gen} + C_0 \]  

(17)

Where \( C_0 \) is the initial concentration of acetic acid (g/L)

Examples of data fitting are shown in Figures 77 and 78. The results of the parameters estimation are shown in Table 11. The value of \( K \) increases with the increase of temperature except for
manure stored with 4% TS at 25°C (77°F). The reason behind this is not clear and needs to be investigated.

Figure 77. Measured and predicted acetic acid concentration in manure storage at initial TS of 2% and a temperature of 25°C (77°F)

Figure 78. Measured and predicted acetic acid concentration in manure storage at initial TS of 9% and a temperature of 35°C (95°F)

The effect of temperature on the rate constant of acetic acid generation was quantified using Arrhenius equation (e.g., Yu and Fang, 2003):

\[ K = K_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \]  

(18)

Where

- \( K_0 \) = Constant or frequency factor (1/day),
- \( E_a \) = Activation energy, kCal/mole
- \( R \) = universal gas constant, k Cal/mole.K
Plotting the natural logarithm of the rate constant against the reciprocal of absolute temperature of manure storage gives a straight line with a slope equals to $(E_a/R)$ and an intercept equals to the value of $\ln (K_0)$ (e.g., Yu and Fang, 2003).

The data obtained from the storage at 2% and 9% TS were fitted to this model. As can be seen from Table 11 that the calculated values of activation energy were 19.52 and 8.09 kCal/mole for the storage stayed at 2% and 9% TS, respectively. The low value of the activation energy implies that acidogenic consortia cope more easily with temperature variations than the methanogenic archea (Yu, and Fang, 2003; Dinopoulou et al., 1988).

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* Not determined.

### 7.3.3 Modeling of acetic acid emission from manure storage

Simulations for the acetic acid emissions from a dairy manure lagoon located near Davis, CA were shown for two months, March and August and the influence of wind speed and temperature on the emissions are clearly observed. March represents a cold and August represents a warm month. The temperature of manure surface in the lagoon was calculated from the air temperature and is shown in Figure 79. The wind speed over the manure surface in the lagoon was calculated from the wind speed data obtained from CIMIS (2003) and is shown in Figure 80.

The results of acetic acid emission rates from manure stored at 2% TS are shown in Figure 81. As can be seen, the emissions rates are higher in August than in March because of the higher temperatures in August. On daily basis, emissions are following the temperature profile with higher emissions rates around noon. Lower emissions rates are shown in the beginning of each month simulations because of the lower acetic acid concentration in stored manure (Figure 82). For the lagoon receiving the manure of 2% TS, the highest emission rate was about 0.096 and 0.057 g/m².hr respectively in August and March. Cumulative acetic acid emission per cow
(Figure 83) over one month period is about 4.8 and 11.2 g/cow for March and August, respectively.

Figure 79. Calculated manure surface temperatures in a simulated lagoon in August and March

Figure 80. Calculated wind speed over the surface of a lagoon receiving 2% TS manure in August and March
Figure 81. Predicted acetic acid emission rate from a lagoon storing dairy manure of 2% TS for one month

Figure 82. Predicted acetic acid concentration in the lagoon storing dairy manure of 2% TS for one month
Although the emission model can give prediction of the acetic acid emissions under different weather conditions, more research is needed to further develop this model by including other processes, such as rain fall and water evaporation from lagoon, which may influence the lagoon volume and surface area. On-farm measurement data are needed in order to validate the emission model. The measurement data shall include the emission rate, manure characteristics (pH, TS and VS contents, concentrations of acetic acid and other VFAs, and temperature), air velocity over the manure surface and air temperature.
7.4 Conclusions and Recommendations for Future Research

Manure naturally contains various microorganisms and undergoes dynamic microbial and enzymatic degradation during storage. Among many compounds produced during the microbial degradation process, VFAs and alcohols are major volatile organic products. Biogas consisting of methane and carbon dioxide is also produced. The research results of this study indicate that the initial solids content in the manure and storage temperature are significant factors that affect the microbial activities and their products. The amounts of VFAs (especially acetic acid) were over 10 times higher than the amounts of alcohols (mainly ethanol). The highest concentration of acetic acid in the manure reached 8, 6, 3.5 g/L for the manure with 9%, 4% and 2% initial TS content, respectively, at 35°C (95°F). The acetic acid and VFA concentrations in the manures with 9% and 4% initial TS continuously increased over the storage time and reached at stable levels at 30 days but the VFAs increased and then decreased for the manure with 2% initial TS content. It is believed that the decrease was caused by the increased activities of methanogens as evidenced by increased biogas and methane production. The results indicate that the methanogenic activity was inhibited in the manure that had 4% and 9% TS. From the experimental results, it is difficult to develop a correlation between the production of VFAs and alcohols with initial solids content as the microbial activities are influenced by the solids content. More research is needed to investigate the influence of solids content on the microbial activities and their products including VFAs and alcohols. The influence of temperature on the production of VFAs and alcohols is clear and higher temperature levels resulted in higher concentrations of VFAs in the manure.

Based on the experimental data, mathematical correlations were developed for predicting the cumulative acetic acid concentration in the manure as a function of time and temperature. The data were used to develop mathematical correlations of VFA generation rates with storage temperature and time at different TS content of the manure. An emission model was developed to calculate the emission rate and cumulative emission of acetic acid from manure storage lagoons under different manure and environmental conditions. Future research is needed to collect field measurement data for the emission rate of acetic acid and other VFAs from dairy lagoons and other storage structures for validation of the emission models developed in this project. The emission models can be further developed to include other VFAs (e.g. propionic acid and butyric acid) and other compounds for emission rate and total emission calculations.
8.0 Overall Conclusions and Recommendations for Future Research

In this project, in-depth analyses and investigations were conducted on the emissions of VOCs in silages and dairy manure by using a combination of experimental measurements, mathematical modeling and computer simulation. The results allowed better understanding of the major compounds emitted from different silage and manure sources and identify the key processes and parameters that control and influence the VOC emission rates. The emission models were successfully developed for predicting the emission rate and total emissions of alcohols and VFAs from silages and manure storages under different conditions. The models can be further expanded in the future to include other compounds so that the emissions of individual compounds as well as a group of compounds from various sources on dairies can be estimated more accurately in different time and spatial scales. Such results will lead to improvement of VOC emission inventories for dairies. The emission models and computer algorithms developed in this project are currently being incorporated into a windows based computer modeling software for dairy emissions, which is supported by a research grant from the National Milk Producers Federation. The major conclusions from this research are summarized as follows.

• Silage and manure emit multitude of VOCs. Up to 20 VOCs were identified in this research for corn and alfalfa silage and dairy manure samples. Ethanol, methanol, acetic acid, acetaldehyde and acetone were the major compounds emitted from both silages and manure samples. Ethanol is the predominant compound for silages and acetic acid is for dairy manure.

• The VOC emissions from silages are mainly controlled by mass transfer processes. A computer model was developed for predicting ethanol emission from silage exposed to an open air environment. Based on the input parameters of silage exposure surface area, silage density, ethanol concentration in the silage, air velocity and temperature, the model calculates the ethanol emission rate and total emission over time. For example, the model was used to predict ethanol emission from corn silage exposed to variable environmental conditions on a dairy farm located in the San Joaquin Valley, CA. The results show that ethanol emission is a fast, dynamic process. Once a thin layer of silage is exposed to air, most of ethanol is emitted within 24 hours. Different types of silages have different emission kinetics due to the differences in ethanol concentration and other characteristics, such as density. Corn silage was found to have a higher ethanol emission rate than alfalfa silage. More research is needed to characterize different types of silages used on dairies so that silage characteristic data can be used to further develop and calibrate the ethanol emission models for their applications to a wide range of silages. Further studies are also needed to investigate the ethanol emissions during silage mixing and from deep silage layers or piles so that the ethanol emission models could be expanded to cover those operations.

• The VOC emissions from dairy manure are controlled by both microbial generation processes and mass transfer processes. Experimental data showed that ethanol generation in fresh manure increased with the temperature and the time elapsed after manure excretion. A model was developed to estimate ethanol emissions from dairy free stalls. The developed model was validated using the data collected from an environmental chamber housing three
dairy cows. A good agreement was found between the measured and estimated ethanol emissions from the environmental chamber. The model needs to be calibrated and validated using more experimental data, under different experimental conditions, and farm measurement data.

- The dairy manure characteristics (volatile solids, ethanol and volatile fatty acids contents) in corrals were measured and found to be dependent on moisture content of manure, which is influenced by the manure residence time and environmental conditions. Animal feeding and management practices and animal behavior have large influences on the manure distribution and residence time in corrals. It will take a significant study to investigate the manure characteristics and emissions in relationship to these factors and processes before a useful emission model can be developed. This is beyond the time and funding resources available in this project.

- Experimental results showed that the solids content of manure and storage temperature were significant factors affecting microbial activities and their products. Higher solids content and temperature resulted in more production of VFAs and alcohols in the manure. The concentrations of VFAs (especially acetic acid) in the stored manure were more than 10 times higher than the concentrations of alcohols (mainly ethanol). The results indicate that alcohol emissions from dairy manure can be important during the first five days after excretion from animals and become negligible after the manure goes into storages. Emissions of VFAs, especially acetic acid, are predominant for manure storages. Computer models were developed to quantify the generation and emission rates of acetic acid from manure storages that receive manure of different solids content and exposed to different environmental conditions. The models can be expanded in the future to include other VOCs generated in the manure storages.

- Measurement data on dairy farms for the emissions of specific compounds are needed in order to fully calibrate and validate the emission models. The measurement data should include the characteristics and environmental conditions of emission sources as well as the emission rates and cumulative emissions over time.

- The VOC emissions from various sources on dairies, including silage and manure, are very complicated, especially with the analytical identification and quantification. In order to develop process-based or source based emission models, we need to know the concentrations of specific compounds both in the source and the emission rate at least under certain known environmental and source characteristic conditions. Most of the VOC compounds that we and other researchers identified were present in such low concentrations that could only be measured in one phase (the source or air) due to the limitation of the analytical procedures and instruments. Therefore, after extensive effort in measuring and quantifying those compounds in this project, we decided to focus on the major compounds that we could measure at high certainties. It will be very difficult to model all the VOC compounds but the emission models for major compounds, like the ones we developed in this project, allowed us to analyze the influence of key factors and estimate the emissions under different conditions and will provide a range of emission values for the conditions encountered on dairy farms.
Because each of the emission sources on dairies has its own characteristics and emission profile, and different sources emit different types and amounts of VOCs, it is important to characterize and understand the physical, chemical and biochemical conditions in the sources that influence the generation and emissions and determine the compounds that are emitted from the source. Due to the large number of compounds emitted, individually modeling each of the dozens of VOCs emitted from dairy sources does not appear to be practical because of the magnitude of the task and limited resources. Emission modeling effort should be focused on the key compounds that have significant impact on the air quality, such as ozone formation, either by emission mass quantities or reactivities. The emissions of total VOCs may be estimated from the emissions of key compounds that can be modeled and the knowledge of their relative magnitude to the total VOC emissions, which could be determined through the measurements. For the cases where significant VOCs cannot be modeled, research effort should be made to determine the correlation between the emission of such compounds and the emission of the compounds that can be modeled. The threshold for this analysis (possibly 5%, 10%, or 25% of total emissions) should be determined by evaluation of how much variation is expected for these compounds and the variation observed in such emissions by other studies. Process-based emission models are mostly useful for estimating the emissions of key compounds under variable conditions, understanding the changes of emissions under different conditions, and determining the conditions that are responsible for most of the emissions. In order to estimate the emissions of total VOCs, both models and measurement data are needed.

The advantages of process-based emission models are well recognized by scientific community and livestock industry as well as research sponsors, such as US Department of Agriculture, US Environmental Protection Agency, California Air Resources Board, and National Milk Producers Federation. It will take more significant resources and time to develop a processed based VOC emission modeling package that can be used to estimate the emissions, with reasonable accuracies, from individual sources as well as the whole farm but the undertaking and results of this project are significant accomplishments toward the overall goal.
9.0 References


Publications Produced

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