

DETERMINATION OF GAS EMISSION CHARACTERISTICS FROM
ANIMAL WASTES USING A MULTIPLEXED PORTABLE
FTIR-SURFACE CHAMBER SYSTEM

by

Pakorn Sutitarnnontr

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Biological Engineering

Approved:

Scott B. Jones, Ph.D.
Major Professor

Anhong Zhou, Ph.D.
Committee Member

Judith L. Sims, M.S.
Committee Member

Randal S. Martin, Ph.D.
Committee Member

Rhonda L. Miller, Ph.D.
Committee Member

Stephen E. Bialkowski, Ph.D.
Committee Member

Richard S. Inouye, Ph.D.
Vice Provost for Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah

2019

Copyright © Pakorn Sutitarnnontr 2019

All Rights Reserved

ABSTRACT

Determination of Gas Emission Characteristics from Animal Wastes

Using a Multiplexed Portable FTIR-Surface Chamber

by

Pakorn Sutitarnnontr, Doctor of Philosophy

Utah State University, 2019

Major Professor: Dr. Scott B. Jones
Department: Biological Engineering

With the trend toward larger and more concentrated production sites as well as population expansion encroaching on rural farming areas, gases emitted from animal feeding operations (AFOs) are rapidly becoming critical issues for the environment, public health, and long-term climate sustainability. This points to the need for cost-efficient, reliable, and easy to maintain measurement and monitoring capabilities to precisely quantify emissions from livestock operations. This research describes and evaluates a novel measurement method based on the multiplexed portable Fourier Transform Infrared (FTIR) spectroscopy analyzer - surface chamber techniques for continuous measurements and monitoring gas emissions from manure sources. The measurement accuracy of the developed system was evaluated under controlled laboratory conditions. Statistical analysis, including ANOVA, was performed to determine the significance of gas flux estimates using the chamber-based estimate. The ANOVA tests indicated no statistically significant differences among estimated fluxes from each of the 12 evaluated chambers, with resulting p-values of 0.54, 0.58, and 0.80

for measurements of three different emission rates. In addition, the multi-chamber system measurements referenced to the gas fluxes estimated with the gradient-based method showed excellent accuracy with measurement biases less than 1%.

A series of soil science measurement techniques were applied to determine a set of fundamental properties of as-excreted dairy cattle manure. The measured water retention characteristic for cattle manure was found to be similar to that of organic peat soil. The saturated hydraulic conductivity was estimated to be about 200 cm day⁻¹. The simulation results suggested that the Richards equation can describe the hydrodynamics taking place in dairy manure relevant to natural drying processes. The thermal conductivities of the dairy manure were found between 0.52 and 0.08 W m⁻¹ °C⁻¹ from saturation to dry conditions. Change of the thermal diffusivity during the manure drying process was observed to be only a small range, approximately from 0.0013 (saturation) to 0.0010 cm² s⁻¹ (dry). The bulk volumetric heat capacity of dairy manure at the saturation point was determined as approximately 3.95 MJ m⁻³ °C⁻¹ and linearly decreased to 0.79 MJ m⁻³ °C⁻¹ for the dry manure sample.

Carbon dioxide (CO₂), methane (CH₄), and ammonia (NH₃) emissions were estimated and characterized using the developed gas emission measurement system. The measurements included four treatments; beef manure, dairy manure, beef compost, and dairy compost. The estimated CO₂, CH₄, and NH₃ emissions from the surface application with dairy manure (452.4 ± 35.4 g m⁻², 1.2 ± 0.1 g m⁻², and 1,786.0 ± 206.7 g m⁻², respectively) were the highest among other treatments. The emissions of CO₂, CH₄, and NH₃ from the surface application with beef compost treatment (210.5 ± 14.4 g m⁻², 0.2 ± 0.02 g m⁻², and 0.07 ± 0.01 g m⁻², respectively) were the lowest. Linear correlations with

the strong coefficients of determination (R^2) were reported between the CO₂ and CH₄ emissions and temperature. Weak linear correlations ($R^2 = 0.39$ for beef and dairy manure treatments and 0.24 for beef and dairy compost treatments) were observed between the NH₃ emissions and temperature. Daily CO₂ and CH₄ emissions and average daily volumetric water content were well correlated and described by an exponential function. An empirical model, based on the Arrhenius equation, was verified with the emission measurement data confirming strong dependency of CO₂ and CH₄ emissions on temperature and moisture content of the soil surface applied with manure source materials. The solubility and adhesive characteristics of the NH₃ molecule most likely affected the accuracy of the NH₃ emission measurements in the study.

(188 pages)

PUBLIC ABSTRACT

Determination of Gas Emission Characteristics from Animal Wastes

Using a Multiplexed Portable FTIR-Surface Chamber

Pakorn Sutitarnnontr

Livestock production is a growing source of air pollution at regional, national, and global scales. Improved livestock manure management has the potential to reduce environmental impacts; however, there is an urgent need for cost-efficient, reliable, and easy to maintain measurement and monitoring capabilities to precisely quantify emissions from livestock manure. This research describes and evaluates a novel measurement method based on the multiplexed portable Fourier Transform Infrared (FTIR) spectroscopy analyzer - surface chamber techniques for continuous measurements and monitoring gas emissions from manure sources. The multiplexing system was designed and developed to automate the chamber network, controlling the movement of chambers and accurately managing chamber air flow distribution. The measurement accuracy of the developed system was evaluated under controlled laboratory conditions. The result of the statistical hypothesis testing showed that there is no statistically significant differences among the measurement results from each of the twelve chambers.

While microbial activity is a key factor for formation of gaseous compounds in manure, the magnitude of gas exchange between manure and the atmosphere largely depends on manure physical characteristics. A series of soil science measurement and modeling techniques were applied to determine a set of fundamental physical, hydraulics,

and thermal properties of cattle manure to support advanced modeling of gas emissions from manure sources. The liquid water retention characteristic for cattle manure was found to be close to that of organic peat soils. The results also suggested that Richards equation can describe the hydrodynamics taking place in cattle manure relevant to natural drying processes. However, the uncertainties of the measurement results could be due to the complexity of shrinkage, surface crust formation, and shrinkage cracks.

Carbon dioxide (CO₂), methane (CH₄), and ammonia (NH₃) emissions were estimated and characterized in field plots using the developed gas emission measurement system. The measurements included four treatments; beef manure, dairy manure, beef compost, and dairy compost. The estimated CO₂, CH₄, and NH₃ emissions from the surface application with dairy manure were the highest among other treatments, while those from the surface application with beef compost were the lowest. Impacts of temperature and water content on gaseous emissions were found to be correlated significantly. Overall, this dissertation provides a solid foundation upon which future research can build in better understanding and modeling animal waste emission processes that impact the environment.

ACKNOWLEDGMENTS

I would like to express my utmost appreciation to my advisor Professor Scott B. Jones for his patience, encouragement, understanding, and continued support. I am privileged to have researched in your environmental soil physics group and my experience working in your research group will surely be unforgettable. I would like to thank my committee members as well, Professor Anhong Zhou, Professor Judith L. Sims, Professor Randal S. Martin, Professor Rhonda L. Miller, and Professor Stephen E. Bialkowski for serving on my PhD committee and all of the assistance, constructive criticism, and contributions to this dissertation.

I would like to offer a special thanks to Professor Markus Tuller at the University of Arizona for his collaboration and guidance he has offered along the way. In addition, Dr. Enzhu Hu has graciously provided guidance for me and his involvement in this research has been invaluable. I especially want to thank the members of the environmental soil physics group, including Bill Mace, Jobie Carlisle, Kashifa Rumana, Dr. Ling Lv, Pawel Szafruga, Ricardo Tejada, J.C. Almonte, Rafael Fernandes and Fabiana Bacalhau for all the technical and laboratory assistance, support, and friendships you all have offered over the years. I would also like to thank the USDA-AFRI and Western SARE to provide funding for this project.

Finally, I would like to thank my wife and son, Dylan, for encouraging me throughout this experience. To my mom and family in Thailand, for the incredibly support all of you have given me all the way, thank you.

Pakorn Sutitarnnontr

CONTENTS

	Page
ABSTRACT	iii
PUBLIC ABSTRACT	vi
ACKNOWLEDGMENTS	viii
LIST OF TABLES	xii
LIST OF FIGURES	xiv
CHAPTER	
1 INTRODUCTION.....	1
1.1 Gas Emissions from Manure Sources	4
1.2 Emission Measurement Methods and Devices	5
1.3 Working Principle of the Multiplexed Portable FTIR and Surface Chamber System	6
1.4 Physical Properties of Manure Affecting Emissions	8
1.5 Research Objectives	9
1.6 Engineering Significance	13
References	15
2 A MULTIPLEXING SYSTEM FOR MONITORING GREENHOUSE AND REGULATED GAS EMISSIONS FROM MANURE SOURCES USING A PORTABLE FTIR GAS ANALYZER	22
2.1 Introduction	23
2.2 System Design Overview	25
2.3 System Component Design and Component Specifications	26
2.4 Data Acquisition	28
2.5 Laboratory Prototype Testing	28
2.6 Conclusion	29
References	29
3 MEASUREMENT ACCURACY OF A MULTIPLEXED PORTABLE FTIR – SURFACE CHAMBER SYSTEM FOR ESTIMATING GAS EMISSIONS	35
3.1 Introduction	36
3.2 Theoretical Considerations	38
3.2.1 Theoretical Gradient-Based Method Computations	38
3.2.2 Gas Diffusion Coefficients in Porous Media	39
3.3 Materials and Methods	40

3.3.1	Experimental Setup	40
3.3.2	Gas Measurement Instrumentation	41
3.3.3	Gas Emission Flux Measurements and Statistical Analyses	42
3.4	Results and Discussion	43
3.4.1	Linear Regression Models for Emission Flux Estimates	43
3.4.2	Measurement Accuracy	44
3.5	Summary	45
	References	46
4	PHYSICAL AND THERMAL CHARACTERISTICS OF DAIRY CATTLE MANURE	60
4.1	Introduction	61
4.2	Theoretical Considerations	66
4.2.1	Physical Properties.....	66
4.2.2	Volumetric Water Content Determination of Dairy Manure.....	66
4.2.3	Water, Solute, and Matric Potentials	67
4.2.4	Water Retention Curve	68
4.2.5	Hydraulic Conductivity.....	68
4.2.6	Thermal Properties.....	70
4.3	Materials and Methods	71
4.3.1	Study Farm and Manure Sampling	71
4.3.2	TDR and GS3 Sensor Calibration in Dairy Manure	72
4.3.3	Manure Water Retention Curve.....	74
4.3.4	Estimated K_s and $K(\theta_v)$ of Dairy Manure using HYDRUS 1-D.....	75
4.3.5	Thermal Properties of Dairy Manure.....	76
4.3.6	Statistical Analyses	77
4.4	Results and Discussions	78
4.4.1	GS3 Sensor Volume of Influence	78
4.4.2	Cattle Manure Dielectric - Moisture Content Relationships.....	79
4.4.3	Dairy Manure Water Retention.....	80
4.4.4	K_s and $K(\theta_v)$ of Dairy Manure.....	82
4.4.5	Thermal Properties.....	84
4.5	Summary and Conclusions	86
	References	87
5	CARBON DIOXIDE, METHANE, AND AMMONIA EMISSIONS FROM SURFACE APPLICATION OF CATTLE MANURE	112
5.1	Introduction	113
5.2	Materials and Methods	115
5.2.1	Manure Samples and Field Setups	115
5.2.2	Field Measurements	116
5.2.3	Gas Flux Emission Calculations	119
5.2.4	Statistical Analyses	120
5.3	Results and Discussions	120
5.3.1	Environmental Conditions	120

5.3.2 Gas Emissions from the Surface Application	120
5.3.3 Surface Soil Moisture Contents	123
5.3.4 Impacts of Temperature on CO ₂ , CH ₄ , and NH ₃ Emissions	124
5.3.5 Impacts of Water Contents on CO ₂ , CH ₄ , and NH ₃ Emissions	125
5.3.6 Impacts of Temperature and Water Contents on CO ₂ , CH ₄ , and NH ₃ Emissions	126
5.4 Summary and Conclusions	126
References	127
6 SUMMARY AND CONCLUSIONS	152
7 RECOMMENDATIONS	156
APPENDICES	159
A. Copyrights and Permissions	160
B. Permission from Authors to Reprint Published Materials.....	164
CURRICULUM VITAE.....	170

LIST OF TABLES

Table		Page
1-1	The National Research Council committee’s scientific evaluation of the importance of AFO emissions, based on pollutant class (NRC 2003)	21
2-1	List of major parts and descriptions used in developing the multiplexing system prototype for monitoring gas emissions from manure sources	31
3-1	Concentration of CH ₄ exhausted from the headspace shown in Figure 3-2, corresponding to the applied flow rate of standard 100 ppm CH ₄ . The concentrations were measured 15 minutes after flow initiation.....	50
3-2	Estimated CH ₄ emission fluxes	51
3-3	Detection ranges and limits of the GASMET DX-4030 FTIR gas analyzer.....	52
3-4	Statistical hypothesis test used for the measurements.....	53
3-5	Goodness-of-fit statistics of linear regression for the change of CH ₄ concentrations over the chamber closure time	54
4-1	Parametric expression and accuracy of the parameters fitted to the measured data to determine the relationship between dielectric permittivity (K_a) and volumetric water content (θ_v).....	99
4-2	Model parameters obtained from fitting the van Genuchten parametric expression to the measurement data compared with the previous studies that investigated those for peat soils.....	100
4-3	Statistical summary of non-linear regression analysis from estimation of the saturated hydraulic conductivity (K_s) with the HYDRUS-1D inverse solution simulation	101
4-4	Parametric expressions and parameters describing the thermal conductivity (λ), thermal diffusivity (κ), and volumetric heat capacity (C) as a function of the volumetric water content (θ_v).....	102
4-5	Summary of thermal properties of dairy and beef cattle manure reported in previous studies	103
5-1	Air temperature (T), relative humidity (RH), wind speed, and solar radiation during field measurements.	133
5-2	Estimated CO ₂ , CH ₄ , and NH ₃ emissions from each treatment	134

5-3	Parametric expression and accuracy of the parameters fitted to the measured water content to determine the relationship between volumetric water content (θ_v) and time (t) in hour	135
5-4	List of coefficients of parametric expression for drying rate of soil surface ($\partial\theta_v/\partial t$)	136
5-5	Coefficients of the linear function $F_s = A \cdot T + B$ demonstrating correlation between percentage of hourly emissions (F_s) and temperature (T) shown in Figure 5-8	137
5-6	Coefficients of the exponential function $F_d = A \cdot e^{B(\theta_{vd})} + C$ for the relation between daily emissions (F_d) and average daily water content (θ_{vd}) shown in Figure 5-9.....	138
5-7	Parameters of the empirical model expressed as $F = A \cdot e^{\left[-\frac{B \cdot \theta_v^2 + C \cdot \theta_v + D}{R \cdot (273.15 + T)} \right]}$ for the relation between emissions (F), water content (θ_v), and temperature (T) as depicted in Figures 5-10, 5-11, and 5-12.	139

LIST OF FIGURES

Figure		Page
2-1	Conceptual diagram of the closed dynamic chamber (CDC) method. Air with a constant flow rate is circulated within a loop between chamber and gas analyzer unit during the measurements by a diaphragm pump.....	32
2-2	Multiplexed gas and sensor measurements with the automated two-chamber setup	33
2-3	Top level system diagram illustrating major components and interface.....	34
3-1	Multiplexed automated-chamber system with five chambers shown in open position.	55
3-2	Sketch of the experimental calibration unit to generate a controllable steady-state gas flux into the surface chamber.	56
3-3	Evolution of CH ₄ concentrations with time inside each of the 12 chambers (a - l) during calibration in Experiment A. The chamber closure time for all 12 chambers was programmed to three minutes and the concentration data were recorded on average in nine-second intervals.	57
3-4	Mean of the methane flux measurements from 12 chambers: (a) Experiment A, (b) Experiment B, and (c) Experiment C. The error bars denote plus and minus one standard deviation. The blue-solid lines depict the mean of the measurements from 12 chambers (n=36) and the red-dashed lines show the methane fluxes estimated with the gradient-based technique.	58
3-5	Comparison of CH ₄ emission fluxes measured with the closed-chamber technique and gradient-based estimates (n = 108). The error bars denote plus and minus one standard deviation and the red-dashed line represents the 1:1 comparison line.	59
4-1	(a) Mean daily evaporation rate (left axis) and cumulative evaporation (right axis) monitored during the evaporation experiments of three dairy manure samples at room temperatures. (b) Daily average of hourly room temperatures. (c) 30-day average of room temperatures recorded on the hour. All error bars denote plus and minus one standard deviation from triplicate sample measurements	104
4-2	(a) End view of the penta-needle heat pulse probe (PHPP) depicting the location of the heater needle and four thermistors (P ₁ , P ₂ , P ₃ , and P ₄). (b) The actual PHPP used for determination of the thermal properties of the dairy manure samples. Prior to the measurements, the electrical components were coated with water resistant epoxy resin.	105

4-3	The GS3 sensor and its estimated zone of influence. The dimensions shown on the left are the mean values (in centimeter) from ten replicated independent measurements. The variations of the measurements from ten replicate measurements are shown on the right	106
4-4	Measured water contents (θ_v) versus dielectric permittivity (K_a) determined with GS3 sensors (fitted to solid line) and TDR probes (fitted to dashed line). The Schaap et al. (1996) curve for TDR-measured organic forest soils is also shown for reference	107
4-5	(a) Measured water retention curve of as-excreted cow manure determined by the WP4-T dewpoint potentiometer. The solid line illustrates the van Genuchten hydraulic model with the fitted parameters. The dashed lines show 95% confidence interval of the curve fitting. (b) Water retention curve of dairy manure (dashed line) in comparison with <i>Sphagnum</i> and reed peats in different degrees of decomposition (Paivanen, 1973).....	108
4-6	(a) Simulated θ_v fitted to the measurements during the evaporation experiments. The error bars denote plus and minus one standard deviation. (b) Comparison between the measured and simulated θ_v . The <i>RMSE</i> and <i>R</i> ² value of the model simulation relative to the measured θ_v is 0.020 cm ³ cm ⁻³ and 0.9884, respectively (c) Unsaturated hydraulic conductivity for dairy manure as a function of θ_v , based on the van Genuchten-Mualem model	109
4-7	Changes in (a) thermal conductivity (λ), (b) bulk volumetric heat capacity (<i>C</i>), and (c) thermal diffusivity (κ) with θ_v of dairy manure samples.	110
4-8	Theoretical θ_v estimated from the heat capacity (<i>C_m</i>) using the PHPPs compared with θ_v measured with the GS3 sensors.	111
5-1	Experimental design illustrating four manure treatments with three replicates each	140
5-2	Background temperature, relative humidity (RH), wind speed, and wind direction during measurements	141
5-3	(a) CO ₂ emissions from the surface application with beef and dairy manure (b) Cumulative emission of CO ₂ from beef manure and dairy manure (c) CO ₂ emissions from the surface application with beef and dairy compost, and (d) Cumulative emission of CO ₂ from beef manure and dairy compost.	142
5-4	(a) CH ₄ emissions from the surface application with beef and dairy manure (b) Cumulative emission of CH ₄ from beef manure and dairy manure (c) CH ₄ emissions from the surface application with beef and dairy compost, and (d) Cumulative emission of CH ₄ from beef manure and dairy compost.	143

5-5	(a) NH ₃ emissions from the surface application with beef and dairy manure (b) Cumulative emission of NH ₃ from beef manure and dairy manure (c) NH ₃ emissions from the surface application with beef and dairy compost, and (d) Cumulative emission of NH ₃ from beef manure and dairy compost.	144
5-6	Measured water content vs. time since application for (a) beef manure, (b) beef compost, (c) dairy compost, and (d) dairy manure. The black solid lines are fitted curves with the shaded 95% confidence intervals of the curve fitting	145
5-7	Drying rates of soil surface vs. time for beef manure, beef compost, dairy compost, and dairy manure applications. The black solid line represents the mean from all treatments with shaded standard deviation	146
5-8	(a), (c), and (e) Percentage of hourly CO ₂ , CH ₄ , and NH ₃ emissions vs. temperature from the surface application with beef and dairy manure. (b), (d), and (f) Percentage of hourly CO ₂ , CH ₄ , and NH ₃ emissions vs. temperature from the surface application with beef and dairy compost. All figures show 95% confidence interval and 95% prediction interval from the trend line.	147
5-9	(a), (c), and (e) Daily CO ₂ , CH ₄ , and NH ₃ emissions from the surface application with beef and dairy manure vs. average daily water content. (b), (d), and (f) Daily CO ₂ , CH ₄ , and NH ₃ emissions from the surface application with beef and dairy compost vs. average daily water content. The solid line is the fitted curve with the exponential function. The dashed lines show 95% confidence interval of the curve fitting	148
5-10	Mean measured CO ₂ emissions vs. simulations for (a) Beef manure, (b) Dairy manure, (c) Beef compost, and (d) Dairy compost	149
5-11	Mean measured CH ₄ emissions vs. simulations for (a) Beef manure, (b) Dairy manure, (c) Beef compost, and (d) Dairy compost.....	150
5-12	Mean measured NH ₃ emissions vs. simulations for (a) Beef manure, (b) Dairy manure, (c) Beef compost, and (d) Dairy compost.....	151

CHAPTER 1

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) defines animal feeding operations (AFOs) as agricultural productions where animals are kept and raised in confined situations for a total of 45 days or more in a 12-month period and feed is brought to the animals rather than the animals grazing or seeking feed in pastures, fields, or on rangeland. Concentrated animal feeding operations (CAFOs) are AFOs that meet the regulatory definition by the number of animals at the farm productions, which can be further classified as large, medium, and small CAFOs (40 CFR § 122.23). The emergence of livestock farms that raise animals in confined areas, qualifying them as AFOs, can improve the efficiency of animal production. However, large amounts of animal waste produced by their operations can degrade air quality. The animal feeding industry in the United States has dramatically changed over the last several years. The number of AFOs has decreased while the number of animals confined at each AFO has increased (USDA 2007; USDA 2012).

With the trend toward larger and more concentrated production sites as well as population expansion encroaching on rural farming areas, gases emitted from AFOs are rapidly becoming critical issues for the environment, public health, and long-term climate sustainability. AFOs generate several types of air emissions, including gaseous and particulate compound as both primary and secondary sources. Typical pollutants found in ambient air surrounding AFOs are ammonia (NH₃), hydrogen sulfide (H₂S), methane (CH₄), and particulate matter (PM), specifically “fine” particles - particles less than 2.5 micrometers in diameter (PM_{2.5}). These air pollutants cause respiratory illness, lung

inflammation, and increase vulnerability to respiratory diseases, such as asthma (National Association of Local Boards of Health 2010). Previous studies (Mirabelli, Wing et al. 2005; Sigurdarson and Kline 2006) suggest that AFOs increase asthma in neighboring communities. Children living closer to an AFO have greater risk of asthma symptoms (Barrett 2006). Occupational respiratory diseases such as occupational asthma, acute and chronic bronchitis, and organic dust toxic syndrome can be found as high as 30% in AFO workers (Horrigan, Lawrence et al. 2002).

Aside from degradation of the local-scale air quality, AFOs also emit greenhouse gases contributing to climate change. In addition to carbon dioxide (CO₂) considered as the primary greenhouse gas of concern, manure also emits methane and nitrous oxide (N₂O), which are 23 and 300 times more potent as greenhouse gases than carbon dioxide, respectively. Manure management is ranked the fourth largest source of nitrous oxide emissions and the fifth largest source of methane emissions (USEPA 2012). As the air emissions are perceived as problematic for the environment and public health (NRC 2002; NRC 2003), reduction of gas emissions from farming operations is becoming a significant management policy. To successfully develop appropriate strategies for managing the gas emissions, an accurate measurement system that can be used in quantifying and monitoring gas emissions is a critical element.

It has been well documented that gas emissions from animal manure strongly vary with time and space, resulting from changes in physical, chemical, and biological factors that influence gas emission processes. Several gas emission measurement techniques have been extensively researched and developed in the past few decades. Among these techniques, the most commonly applied for quantifying gaseous emissions from area

sources are surface chambers (Luo and Zhou 2006). The surface chamber methods perform direct measurements of gaseous emissions from ground level area sources. The surface chamber techniques effectively isolate sample sources from external environmental conditions (e.g., wind speed and wind direction). The measurements are not strongly dependent on the meteorological conditions; therefore, they can be directly comparable from day-to-day and site-to-site (Eklund 1992). However, the disadvantage of the surface chamber techniques is that the conditions within the enclosure are momentarily altered from the actual surface conditions around the chamber. For this reason, the time that the chamber seals with the surface is limited to a few minutes for most applications.

Most of the gases emitted to the atmosphere are the products of microbial processes that decompose the complex organic constituents in manure. While the microbial environment determines which gas species are generated, the magnitude of the gas emissions depends primarily on the physical properties of manure (Smith, Ball et al. 2003). From a physical perspective, manure is a heterogeneous, polyphasic, disperse porous medium generally consisting of solid, liquid, and gaseous phases. The solid fraction primarily consists of fibrous material, which may include hay, grain, and silage, creating a complex manure matrix (Sobel 1966; Azevedo 1974; Spellman and Whiting 2007). The liquid phase is mostly water, commonly containing dissolved solutes and organic matter. The gas fraction occupies the empty pores or void space. The manure matrix determines the geometric characteristics of the empty pores that play an important role in the transport of the water and gases (Hillel 1998; Jury and Horton 2004; Horn and Smucker 2005).

1.1 Gas Emissions from Manure Sources

Emissions of concern from AFOs typically include: (a) odors with accompanying non-methane volatile organic compounds (NMVOCs) and hydrogen sulfide (H₂S), (b) particulate matter (PM), (c) ammonia (NH₃), (d) oxides of nitrogen (NO_x), and (e) greenhouse gases (GHGs) primarily consisting of carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O). Concerns over gases listed in Table 1-1 range from the local scale, dealing mostly with odors, to global warming at the regional and global scales. One of the major recommendations identified in the study conducted by National Research Council (NRC) on the air pollutant emissions from AFOs (NRC 2003) is to focus efforts on the measurement of those emissions of major concern.

The major factor affecting the gas emissions from AFOs is the differences in operations and manure management practices among the AFOs, which depend upon the animal type, number of animals, climatic conditions, site locations, farm operations and manure handling practices. Most of the substances emitted are the products of microbial processes resulted from decomposing the complex organic constituents in manure. The biological environment during these processes is a key factor to determine the species of gas released. The differences in operations and manure management practices among the different animal species result in different microbial environments and therefore different emission potentials.

There are limited on-farm emissions data from animal production facilities due to the difficulty and expense in conducting the measurements. Misselbrook and Webb et al. (2006) and Mukhtar et al. (2008) investigated NH₃ emissions from dairy operations using chamber methods in United Kingdom and Texas, respectively. Other studies (Cassel,

Ashbaugh et al. 2005; Rumburg, Mount et al. 2008; Flesch, Harper et al. 2009) employed downwind measurements and modeling techniques to estimate NH_3 emissions from dairy cattle housing. A few studies have determined CH_4 emissions from dairy cattle with different measurement techniques (Kinsman, Sauer et al. 1995; Lassey, Ulyatt et al. 1997; Ulyatt, Lassey et al. 2002; Laubach and Kelliher 2005; Laubach and Kelliher 2005; Sun, Trabue et al. 2008; McGinn, Beauchemin et al. 2009).

Sommer et al. (2000), Amon et al. (2006), and Guarino et al (2006) evaluated the combination of NH_3 , CH_4 , CO_2 , or N_2O emissions from dairy cattle slurry using pilot or laboratory scale techniques. Hellebrand & Kalk (2001) and Hao et al. (2004) determined the combination of NH_3 , CH_4 , CO_2 , and N_2O emissions from composting manure. Laytem et al. (2011) determined the emission of NH_3 , CH_4 , CO_2 , and N_2O from a commercial dairy during multiple seasons using a photoacoustic field gas monitor. Emission data from most of the studies were presented for limited time periods while temporal variations in emissions under different manure management practices were not taken into consideration.

1.2 Emission Measurement Methods and Devices

The methods and techniques selected for measuring gas emissions depend on the type and characteristic of emission (i.e., point source vs. area source). The emission rate from a ground-level area source is commonly determined using micrometeorological or surface chamber techniques. Emissions of gases from area sources are expressed in terms of fluxes with the unit of mass per unit area per unit time. The micrometeorological techniques measure upwind and downwind concentrations and back-calculate of flux using dispersion modeling (Hu, Babcock et al. 2014). Surface chamber techniques can be

classified into two categories: dynamic and static methods, depending on whether air is allowed to circulate through the chamber. The dynamic chamber methods allow air to circulate between the chamber and gas analyzer unit that measures the concentration of target gases. These methods employ one of the current standard gas detection or quantification technologies, including gas chromatography, photo-acoustic-infrared detection, tunable diode laser (TDL), Fourier Transform Infrared (FTIR) spectroscopy, and infrared (IR) gas analyzer to quantify the concentration of the component of interest (Cleemput and Boeckx 2002) and to determine the emission rate based on the volumetric flow rate and surface area. Hu et al. (2014) published a review of these different current techniques for measuring emissions from agricultural and animal production.

In a review of measurement methods and technologies, there have been a number of studies conducted using different techniques in determination of gas emissions from animal facilities. However, it is still unknown to date which method and technology provide results that are the closest to the “actual” gas emissions under the field conditions (Ni and Heber 2008) because a standard technique does not yet exist. Fundamental assumptions and limitations of each technique must be carefully considered in selecting the most appropriate method to fit the desired application.

1.3 Working Principle of the Multiplexed Portable FTIR - Surface Chamber System

The multiplexing system, typically facilitating automation of a network of multiple chambers and management of chamber air flows using a single gas analyzer, is widely used to assess the temporal and spatial variability of gaseous emissions, particularly for continuous monitoring of CO₂ exchange between soils and atmosphere (Liang, Inoue et al. 2003; Liang, Fujinuma et al. 2005; Katsura, Maeda et al. 2006;

Hongxing, Xiaoke et al. 2007). The necessary features of the multiple chamber instrumentation for monitoring gas emissions from animal facilities are: (a) concurrent measurement capability of gaseous fluxes from multiple sources, (b) near real-time and accurate measurement of multiple gaseous components emitted from each source, (c) monitoring system for temperatures inside the chamber and emission source (e.g., soil, manure) for investigating the effects of temperature gradient on gas emissions, (d) monitoring system for relative humidity inside the chamber, (e) monitoring system for moisture content of emission source, (f) automated data collection, (g) integrated fail-safe setup for the solenoid valve manifold to prevent damage that may occur to the sampling pump, and (h) reliable operation and minimum maintenance.

Major components of multiplexing system for monitoring gas emissions from manure sources include a primary control unit, chamber driver circuit, data acquisition unit, and gas stream flow control circuit. A microcontroller serves as the primary control and data acquisition unit. The chamber positioning is accomplished by interfacing the microcontroller with a custom-designed driver circuit. A solenoid valve manifold is designed to coordinate the gas stream direction from the measurement chambers. Temperature and relative humidity (RH) are monitored using a thermistor (10K ohm Yellow Bead Thermistor; Apogee Instruments, Logan, UT) and RH sensor chip (HIH-4021-001; Honeywell, Minneapolis, MN) located inside the chamber. The output voltages from these sensors are transferred to the microcontroller through the analog-to-digital inputs and ultimately sent to the handheld computer for processing and storing via a serial interface.

Linear regression analysis is commonly applied to determine the rate of increasing concentration of the target gas during chamber closure. Computation of the gas emission fluxes from the measured data is based on the mass balance principle together with the ideal gas law:

$$F = \frac{V \cdot P \cdot T_s \cdot MW}{A \cdot P_s \cdot (273.15 + T) \cdot (2.24 \cdot 10^{-2})} \cdot \frac{\partial C}{\partial t} \quad (1)$$

where F is the gaseous flux [$\mu\text{g m}^{-2} \text{s}^{-1}$], V is the total system volume including the chamber headspace [m^3], P is the ambient pressure [kPa], T_s is the standard temperature [273.15 K], MW is the molecular weight of a gas [g mol^{-1}], A is the surface area of the chamber over the emission source [m^2], P_s is the standard pressure [101.33 kPa], T is the temperature ($^{\circ}\text{C}$), $2.24 \cdot 10^{-2}$ is the molar volume of a gas at STP [$\text{m}^3 \text{mol}^{-1}$], and $\partial C/\partial t$ is the gradient of gas concentration changing over time derived from linear regression [ppm s^{-1} or $\mu\text{m}^3 \text{m}^{-3} \text{s}^{-1}$].

1.4 Physical Properties of Manure Affecting Emissions

In order to accurately describe and model the gas emission characteristics, the complex physical properties of manure affecting emissions also need to be determined. While microbial activity is the key factor for formation of gaseous compounds in manure, the magnitude of gas exchange between manure source and the atmosphere largely depends on manure physical characteristics. Microbial metabolism as well as population dynamics (e.g., composition and density) are dramatically influenced by manure temperature (Miller 1992). However, manure moisture content had a greater influence on microbial activity in the manure composting processes than does temperature (Liang, Das et al. 2003). This is in part due to the competing roles water plays in providing an

aqueous environment for microbes while at the same time controlling the rate of gas exchange (i.e., O₂ supply). A comprehensive literature review clearly revealed that while the biological and chemical decomposition of cattle manure has been widely studied (Gerba and Smith 2005; Nennich, Harrison et al. 2005; Liu, Xu et al. 2011; Longhurst, Houlbrooke et al. 2012) with an abundance of reported data, little is known about important physical properties.

Numerical models are required to simulate complex transformation and translocation processes such as with carbon and nitrogen, which involve both liquid and gas phases. There are a number of these models including large-scale land surface models (Parton, Hartman et al. 1998; Del Grosso, Parton et al. 2006; Grosso, Parton et al. 2008; Oleson, Niu et al. 2008) and point scale models (Simunek, Jacques et al. 2006; Toride and Chen 2011) that are continually being improved as more detail is made available; however, physical properties of manure have not been defined for use with these models. An accurate simulation model that can describe solute and gas transport from manure sources at a range of scales is mandatory for estimation of quality and quantity of manure leachate and gas emission characteristics.

1.5 Research Objectives

The specific objectives of this research are to:

- (1) develop an automated multi-gas emission measurement system, based on the multiplexed portable FTIR-surface chamber network for continuous measurements and monitoring of target gas emissions, which initially include CH₄, CO₂, NH₃, NO_x, and N₂O,

- (2) evaluate the determined accuracy of gaseous emission fluxes using the multiplexed portable FTIR and surface chamber system under controlled laboratory conditions,
- (3) measure and model physical, hydraulic, and thermal properties of as-excreted dairy manure that primarily affect flow of liquid water and gas exchange and transport of dissolved constituents, and
- (4) quantify emissions of the target gases from different manure sources in field experiments using the developed system.

The research plan proceeded in four phases reflecting the specific objectives as follows. The first phase involved the development of the multiplexed portable FTIR-surface chamber system. The multiplexed chambers were integrated with a FTIR gas spectroscopy analyzer (Gasmeter Technologies Oy, Helsinki, Finland) capable of monitoring concentrations of 15 pre-programmed gases simultaneously.

The second phase was to evaluate the multiplexed surface chamber-based gas measurement accuracy. This phase included evaluation of the accuracy in determination of emission fluxes from each chamber to ensure there was no bias in the data collection and analysis. A method, based on Fick's laws of diffusion, to simulate a controllable diffusive gas source while it diffuses upward through a dry sand layer was developed to determine the base-line flux in order to compare with the flux measurement from each chamber. The computed fluxes were statistically analyzed with the general ANOVA module of the R statistical software package (R Development Core Team 2011). The statistical hypothesis testing for the evaluation was to verify that there was no difference

in emission fluxes measured from all chambers. This phase laid the groundwork for the fourth phase, which involves the emission measurements in the field.

Techniques commonly applied for soil analysis were applied in the third phase of the research plan to examine physical, hydraulic, and thermal properties of as-excreted dairy cattle manure. Water potential of dairy manure was measured with the WP4-T Dewpoint Potentiometer (Decagon Devices, Inc., Pullman, WA) to investigate the structural and functional relation between the volumetric water content (θ_v) and water potential (ψ_w) under equilibrium conditions. The solute potential (ψ_s) of the manure was then estimated and subtracted from ψ_w to generate the relationship between θ_v and the matric potential (ψ_m), which is known as the water characteristic or water retention curve. The saturated hydraulic conductivity (K_s) and the unsaturated hydraulic conductivity function $K(\theta_v)$ of the dairy manure samples were determined by means of an inverse solution simulation technique as an alternative to direct measurement. Changes in manure moisture content during the drying process was numerically simulated with HYDRUS 1-D (Šimůnek, van Genuchten et al. 2008), a software package for simulating transient water movement in one-dimensional variably-saturated media with a robust inverse modeling capability. The thermal properties, including the thermal conductivity (λ), thermal diffusivity (κ), and bulk volumetric heat capacity (C) of drying dairy manure were measured with the penta-needle heat pulse probes (PHPPs) to investigate and identify relationships between these thermal properties and θ_v during the drying process.

The last phase of the research plan was to evaluate the measurement system in the field applications. Gas emission characteristics from different types of manure sources and manure management practices were evaluated under the field experiments in this

phase. The field experiments initially were conducted to characterize individual gas emission rates from manure as a function of temperature, manure water content and time. Evaporation rates, changes in manure water content, and temperature were also continuously monitored over the course of the experiments to define the degree of temporal variability affected by these factors.

Four cattle manure types including dairy manure, beef manure, dairy compost, and beef compost, were used as the sources of gaseous emissions in the experiments. The dairy and beef manures are collected from Utah State University's Caine Dairy Farm (Central Coordinates: 41° 39' 22" N; 111° 53' 57" W) and Animal Science Farm (Central Coordinates: 41° 40' 6" N; 111° 53' 17" W) in Wellsville, UT, respectively. The measurements were set up in a field at Greenville Research Farm in North Logan, UT (Central Coordinates: 41° 45' 57" N; 111° 48' 43" W). The elevation is about 1,355 m (4,445 ft.) with the prevailing winds flowing from east to west. A meteorological station, located within the Greenville Research Farm approximately 480 feet to the east of the measurement field recorded air temperature, barometric pressure, and rainfall amount during the experimental period. Twelve 1.70 m by 1.20 m plots was prepared for four manure types (or treatments), each with three replicate samples to determine the assay statistics. The location of each treatment is statistically independent (i.e., assigned randomly), using a true random number generator. Gas emissions from the manure sources were continuously monitored for 15 days to investigate the diurnal pattern in detail. The effect of manure type, water content and temperature, monitored as part of the in-situ instrumentation, were correlated with the gas emissions to evaluate the most significant factor(s) contributing to the variation in emissions.

The remainder of this dissertation is organized as follows: Chapter 2 introduces the framework for the development of an automated multi-gas emission measurement system, based on the multiplexed portable FTIR-surface chamber network for continuous measurements and monitoring of target gas emissions. Chapter 3 describes measurement accuracy of the measurement system under controlled laboratory conditions in comparison to a gradient-based technique for the reference gas flux (CH_4). In Chapter 4, physical, hydraulic, and thermal properties of dairy manure, that primarily affect flow of liquid water and gas exchange and transport of dissolved constituents were evaluated. Chapter 5 presents the measurements of gas emissions from different manure sources in field experiments using the measurement system. An overall summary and conclusions is in Chapter 6.

1.6 Engineering Significance

The work of this dissertation stands apart from previous research in measuring gaseous emissions from AFOs due to the unique design and development of the multiplexed portable FTIR - surface chamber system and the potential impact the instrument could have on AFO gaseous emission regulations and the development of management strategies that minimize gaseous emissions. Reliable measurements of gas emissions from animal wastes generated by AFOs are often difficult and inaccurate. The unique design presented provides an avenue for fully automated continuous monitoring necessary for in situ assessment of long-term gas dynamics in animal operations at the farm scale.

Typical point-scale chamber techniques have significant limitations. While chamber techniques are commonly employed to measure gas emissions from point

sources and can be versatile in some scenarios, micrometeorological methods are applicable for measurements from larger footprints that more realistically represent emissions at the farm level. However, micrometeorological methods requiring complex setup are cost-prohibitive and more representative when weather conditions are stable with uniform wind direction and speed. Because of considerable differences between animal varieties and spatial heterogeneity of animal urine and feces depositions, multiple chambers are required to accurately capture all potential emission sources and spatial heterogeneity.

The multiplexed chambers integrated with the FTIR gas spectroscopy analyzer presented in this work addresses the limitations typically associated with the chamber techniques. The developed gas emission measurement system will be beneficial for assessment of gas emissions from manure sources. The multiplexing system, which facilitates automation of multiple chambers and management of chamber air flow, can be employed to assess the temporal and spatial variability of emissions from different manure sources or farming practices. Application of the developed measurement system can also be extended for other agricultural management or natural ecosystems.

The resulting physical, hydraulic, and thermal properties of cattle manure that primarily affect the transport of liquid water and gas within the manure presented in Chapter 4 of this dissertation provide a solid foundation upon which future research can build in better modeling and understanding cattle manure processes that impact the environment. By characterizing the physical and hydraulic properties of cattle manure using well established analytical models, advanced modeling of gaseous emissions, in addition to water, solute and colloid transport processes can be simulated using analytical and

advanced numerical modeling. The thermal properties of cattle manure are likely to be used for development of heat transport models to identify the optimal conditions for manure composting processes as well as for prediction of manure water content and the movement of solutes and water from manure sources in addition to microbial activity and gas generation.

References

- Amon, B., V. Kryvoruchko, et al. (2006). Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. *Agriculture, Ecosystems & Environment* 112(2-3): 153-162.
- Azevedo J. (1974). Farm animal manures: An overview of their role in the agricultural environment. University of California Agricultural Experiment Station, Berkeley, CA.
- Barrett, J. R. (2006). Hogging the air: CAFO emissions reach into schools. *Environmental Health Perspectives* 114(4): A241.
- Cassel, T., L. Ashbaugh, et al. (2005). Ammonia flux from open-lot dairies: developments of measurement methodology and emission factors. *Journal of the Air & Waste Management Association* 55: 816-825.
- Cleemput, O. V. and P. Boeckx (2002). Measurement of greenhouse gas fluxes. *Encyclopedia of Soil Science*. R. Lal, Marcel Dekker, Inc. New York, NY.
- Del Grosso, S. J., W. J. Parton, et al. (2006). DAYCENT national-scale simulations of nitrous oxide emissions from cropped soils in the United States. *Journal of Environmental Quality* 35(4): 1451-1460.
- Eklund, B. (1992). Practical guidance for flux chamber measurements of fugitive volatile organic emission rates. *Journal of the Air Waste Management Association* 42: 1583-1591.
- Flesch, T. K., L. A. Harper, et al. (2009). Inverse-dispersion calculation of ammonia emissions from Wisconsin dairy farms. *Transactions of the ASABE* 52(1): 253-265.

- Gerba, C. P. and J. E. Smith (2005). Sources of pathogenic microorganisms and their fate during land application of wastes. *Journal of Environmental Quality*. 34(1): 42-48.
- Grosso, S. J. D., W. J. Parton, et al. (2008). DAYCENT simulated effects of land use and climate on county level N loss vectors in the USA. *Nitrogen in the environment: Sources, problems, and management*, Academic Press/Elsevier. Cambridge, MA.
- Guarino, M., C. Fabbri, et al. (2006). Evaluation of simplified covering systems to reduce gaseous emissions from livestock manure storage. *Transactions of the ASABE* 49(3): 737.
- Hao, X., C. Chang, et al. (2004). Carbon, nitrogen balances and greenhouse gas emission during cattle feedlot manure composting. *Journal of Environmental Quality*. 33(1): 37-44.
- Hellebrand, H. J. and W. D. Kalk (2001). Emission of methane, nitrous oxide, and ammonia from dung windrows. *Nutrient Cycling in Agroecosystems* 60(1-3): 83-87.
- Hillel, D. (1998). *Environmental soil physics*, Academic Press, San Diego, CA.
- Hongxing, Z., W. Xiaoke, et al. (2007). Multichannel automated chamber system for continuous monitoring of CO₂ exchange between the agro-ecosystem or soil and the atmosphere. *Acta Ecologica Sinica* 27(4): 1273-1282.
- Horn, R. and A. Smucker (2005). Structure formation and its consequences for gas and water transport in unsaturated arable and forest soils. *Soil and Tillage Research* 82(1): 5-14.
- Hu, E., E. L. Babcock, et al. (2014). Methods and techniques for measuring gas emissions from agricultural and animal feeding operations. *Critical Reviews in Analytical Chemistry* 44(3): 200-219.
- Jury, W. A. and R. Horton (2004). *Soil physics*, John Wiley & Sons, Inc., Hoboken, NJ.
- Katsura, K., S. Maeda, et al. (2006). A multichannel automated chamber system for continuous measurement of carbon exchange rate of rice canopy. *Plant Production Science* 9(2): 152-155.

- Kinsman, R., F. D. Sauer, et al. (1995). Methane and carbon dioxide emissions from dairy cows in full lactation monitored over a six-month period. *Journal of Dairy Science* 78(12): 2760-2766.
- Lassey, K. R., M. J. Ulyatt, et al. (1997). Methane emissions measured directly from grazing livestock in New Zealand. *Atmospheric Environment* 31(18): 2905-2914.
- Laubach, J. and F. M. Kelliher (2005). Measuring methane emission rates of a dairy cow herd (II): Results from a backward-Lagrangian stochastic model. *Agricultural and Forest Meteorology* 129(3-4): 137-150.
- Laubach, J. and F. M. Kelliher (2005). Methane emissions from dairy cows: Comparing open-path laser measurements to profile-based techniques. *Agricultural and Forest Meteorology* 135(1-4): 340-345.
- Leytem, A. B., R. S. Dungan, et al. (2011). Emissions of ammonia, methane, carbon dioxide, and nitrous oxide from dairy cattle housing and manure management systems. *Journal of Environmental Quality* 40(5): 1383-1394.
- Liang, C., K. C. Das, et al. (2003). The influence of temperature and moisture contents regimes on the aerobic microbial activity of a biosolids composting blend. *Bioresource Technology* 86(2): 131-137.
- Liang, N., Y. Fujinuma, et al. (2005). Measurement of wood CO₂ efflux using a multichannel automated chamber system. *Phyton-Annales Rei Botanicae* 45(4): 109-115.
- Liang, N., G. Inoue, et al. (2003). A multichannel automated chamber system for continuous measurement of forest soil CO₂ efflux. *Tree Physiology* 23: 825-832.
- Liu, J., X. H. Xu, et al. (2011). Effect of microbiological inocula on chemical and physical properties and microbial community of cow manure compost. *Biomass and Bioenergy* 35(8): 3433-3439.
- Longhurst, B., D. Houlbrooke, et al. (2012). Characterizing dairy manures and slurries. Advanced nutrient management: Gains from the past - goals for the future. Occasional Report No. 25. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand.
- Luo, Y. and X. Zhou (2006). *Soil respiration and the environment*, Academic Press, San Diego, CA.

- McGinn, S. M., K. A. Beauchemin, et al. (2009). Performance of a dispersion model to estimate methane loss from cattle in pens. *Journal of Environmental Quality*. 38(5): 1796-1802.
- Miller, F. C. (1992). Composting as a process based on the control of ecologically selective factors. *Soil microbial ecology: Applications in agricultural and environmental management*. J. F. Blaine Metting. Marcel Dekker, Inc., New York, NY: 515-544.
- Mirabelli, M. C., S. Wing, et al. (2005). Race, poverty, and potential exposure of middle-school students to air emissions from confined swine feeding operations. *Environmental Health Perspectives* 114(4): 591-596.
- Misselbrook, T. H., J. Webb, et al. (2006). Ammonia emissions from outdoor concrete yards used by livestock-quantification and mitigation. *Atmospheric Environment* 40(35): 6752-6763.
- Mukhtar, S., A. Mutlu, et al. (2008). Seasonal and spatial variations of ammonia emissions from an open-lot dairy operation. *Journal of the Air & Waste Management Association* 58(3): 369-376.
- National Association of Local Boards of Health (2010). Understanding concentrated animal feeding operations and their impact on communities. National Association of Local Boards of Health, Bowling Green, OH.
- Nennich, T. D., J. H. Harrison, et al. (2005). Prediction of manure and nutrient excretion from dairy cattle. *Journal of Dairy Science* 88(10): 3721-3733.
- Ni, J-Q., A. J. Heber (2008). Sampling and measurement of ammonia concentration at animal facilities – A review. *Advances in Agronomy* 98: 201-269.
- NRC (2002). The scientific basis for estimating air emissions from animal feeding operations. Interim Report. National Academy Press, Washington, DC.
- NRC (2003). Air emissions from animal feeding operations: Current knowledge, future needs. National Academies Press, Washington, DC.
- Oleson, K. W., G. Y. Niu, et al. (2008). Improvements to the community land model and their impact on the hydrological cycle. *Journal of Geophysical Research: Biogeosciences* 113(G1): G01021.

- Parkin, T. B. and T. C. Kaspar (2004). Temporal variability of soil carbon dioxide flux: effect of sampling frequency on cumulative carbon loss estimation. *Soil Science Society of America Journal* 68(4): 1234-1241.
- Parton, W. J., M. Hartman, et al. (1998). DAYCENT and its land surface submodel: description and testing. *Global and Planetary Change* 19(1-4): 35-48.
- R Development Core Team (2011). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria.
- Rumburg, B., G. H. Mount, et al. (2008). Measurement and modeling of atmospheric flux of ammonia from dairy milking cow housing. *Atmospheric Environment* 42(14): 3364-3379.
- Sigurdarson, S. T. and J. N. Kline (2006). School proximity to concentrated animal feeding operations and prevalence of asthma in students. *Chest* 129(6): 1486-1491.
- Simunek, J., D. Jacques, et al. (2006). Multicomponent geochemical transport modeling using HYDRUS-1D and HP1. *Journal of the American Water Resources Association* 42(6): 1537-1547.
- Simunek, J., M. T. van Genuchten, et al. (2008). Development and applications of the HYDRUS and STANMOD software packages and related codes. *Vadose Zone Journal* 7(2): 587-600.
- Smith, K. A., T. Ball, et al. (2003). Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *European Journal of Soil Science* 54(4): 13.
- Sobel, A. T. (1966). Physical properties of animal manures associated with handling. *Proceedings National Symposium on Animal Waste Management, ASAE, East Lansing, MI*
- Sommer, S. G., S. O. Petersen, et al. (2000). Greenhouse gas emission from stored livestock slurry. *Journal of Environmental Quality* 29(3): 744-751.
- Spellman, F. R. and N. E. Whiting (2007). *Environmental management of concentrated animal feeding operations (CAFOs)*, CRC Press, Boca Raton, FL.

- Sun, H., S. L. Trabue, et al. (2008). Alcohol, volatile fatty acid, phenol, and methane emissions from dairy cows and fresh manure. *Journal of Environmental Quality* 37(2): 615-622.
- Toride, N. and D. Chen (2011). Fate and transport of nitrogen and organic matter in soils based on a coupled nitrogen-carbon cycling model using the HP1 program. ASA CSSA SSSA International Annual Meetings, San Antonio, TX.
- Ulyatt, M. J., K. R. Lassey, et al. (2002). Methane emission from dairy cows and wether sheep fed subtropical grass-dominant pastures in midsummer in New Zealand. *New Zealand Journal of Agricultural Research* 45(4): 227-234.
- USDA (2007). Profits, costs, and the changing structure of dairy farming (ERR-47). Department of Agriculture. Economic Research Service, Washington, DC.
- USDA (2012). Animal feeding operations (AFO) and confined animal feeding operations (CAFO). Natural Resources Conservation Service, Washington, DC.
- USEPA (2012). Inventory of U.S. greenhouse gas emissions and sinks: 1990 – 2010. EPA Publication No. EPA 430-R-12-001. U.S. Environmental Protection Agency, Washington, DC.

Table 1-1. The National Research Council committee's scientific evaluation of the importance of AFO emissions, based on pollutant class (NRC 2003)

Species	Criteria Pollutant	Hazardous Air Pollutant (HAP)	Greenhouse Gas	Regulated Air Pollutant
NH ₃	-	-	-	X
N ₂ O	-	-	X	-
NO _x	X	-	-	X
CH ₄	-	-	X	-
NMVOCs	-	X	-	X
H ₂ S	-	-	-	X
PM ₁₀	X	-	-	X
PM _{2.5}	X	-	-	X
Odor	-	-	-	X

CHAPTER 2
A MULTIPLEXING SYSTEM FOR MONITORING GREENHOUSE AND
REGULATED GAS EMISSIONS FROM MANURE SOURCES
USING A PORTABLE FTIR GAS ANALYZER[†]

Abstract: Gas emissions from animal feeding operations (AFOs) degrade air quality and may be threats to public health. Animal manure is a significant emission source, which is highly dependent on temperature and moisture content varying both spatially and temporally. We present the design and operational features of an automated multiplexing system for chamber-based monitoring of greenhouse and regulated gas emissions from animal manure sources using a Fourier Transformed Infrared (FTIR) spectroscopy analyzer. The multiplexing system allows users to automate the chamber network, controlling the movement of chambers and accurately managing chamber air flow distribution. Chamber positioning was achieved with two 12-volt actuators with limit switches at the end of each cycle. Low-power latching solenoid valves were programmed to distribute air streams in concert with chamber placement. The sampled air stream was ultimately analyzed using an FTIR spectroscopy analyzer, which is capable of monitoring 15 pre-programmed gases simultaneously. System design, control circuit and system operating algorithms as well as data collection management are

[†] The material for this chapter was previously published as: Suttarnontr, P., Miller, R., Bialkowski, S., Tuller, M., & Jones, S. B. (2012). A multiplexing system for monitoring greenhouse and regulated gas emissions from manure sources using a portable FTIR gas analyzer. In ASABE Annual International Meeting 2012, ASABE 2012 (Vol. 4, pp. 2782-2788). American Society of Agricultural and Biological Engineers, St. Joseph, MI. Reprinted with permission from ASABE Paper No. 121337982 © 2012 ASABE Annual Meeting.

presented in this paper. The multiplexing system is anticipated to increase data collection efficiency and decrease the uncertainty associated with spatial variations in gas emission measurements from manure sources.

2.1 Introduction

Air pollutants from animal feeding operations (AFOs) cause public health and environmental problems, becoming critical issues for farm workers and population living near livestock production sites. Accurate on-farm determination of emission rates that reflect the site-specific conditions is essential for understanding the scale of the emissions and for development and implementation of regulations and policies necessary for mitigating the impact of AFOs on the environment. However, there are only limited on-farm emission data available from livestock production facilities that are useful from a regulatory and environmental protection standpoint due to the complexity inherent to measuring gaseous emissions from AFOs (Leytem et al., 2011).

It has been well documented that gaseous emissions from animal manure strongly vary with time and space, resulting from changes in physical, chemical, and biological factors that influence gaseous emission processes. Several gas emission measurement techniques have been extensively researched and developed in the past few decades. Among these techniques, the most commonly applied for quantifying gaseous emissions from area sources are surface chambers (Luo and Zhou, 2006). Surface chamber methods perform direct measurements of gaseous emissions from ground level area sources. The surface chamber techniques effectively isolate sample sources from external environmental conditions (e.g., wind speed and wind direction). The measurements are not strongly dependent on the meteorological conditions; therefore, they can be directly

comparable from day-to-day and site-to-site (Eklund, 1992). However, the disadvantage of the surface chamber techniques is that the conditions within the enclosure are momentarily altered from the actual surface conditions around the chamber. For this reason the time that the chamber seals with the surface is limited to a few minutes for most applications.

Surface chamber techniques can be classified into two categories: dynamic and static methods, depending on whether air is allowed to circulate through the chamber. The dynamic chamber methods allow air to circulate between the chamber and gas analyzer unit that measures the concentration of target gases. The closed dynamic chamber (CDC) method measures changes in gas concentration inside the chamber that is part of a closed loop system operating over a short time period (Figure 2-1). Most of the commercially available surface chambers for measurement of gaseous emissions from ground level area sources are developed using the fundamentals of the CDC method. Gases emitted from the source build up inside the chamber, creating a temporal gradient during the measurement. A gradual increase in gas concentration inside the chamber typically can be fitted with a linear regression equation over a time frame of a few minutes.

However, the gaseous concentration gradients between the subsurface and chamber diminish with time due to the build-up of gases in the chamber, thereby resulting in an apparent reduction in gas flux as time progresses. Several non-linear regression models have been developed to correct the apparent reduction in gas emission rates from the source by increasing gas concentrations inside the chamber (Davidson et

al., 2002; Hutchinson and Mosier, 1981; Venterea, 2010; Venterea and Baker, 2008; Wagner et al., 1997).

A network of automated surface chambers with a multiplexing system is commonly used to assess the temporal and spatial variability of gaseous emissions, particularly for continuous monitoring of CO₂ exchange between soils and atmosphere (Hongxing et al., 2007; Katsura et al., 2006; Liang et al., 2005; Liang et al., 2003). The multiplexing system typically facilitates automation of multiple chambers and management of chamber air flow, using a single gas analyzer. Our multiplexing system prototype was designed based on microcontroller technology, providing flexibility for future system expansion.

A Fourier Transform Infrared (FTIR) spectroscopy gas analyzer (Gasmeter DX-4030; Gasmeter Technology Oy, Helsinki, Finland), capable of monitoring concentration of up to 15 pre-programmed gaseous components simultaneously, was used as the gas analyzer unit to measure concentration of the target gases. Our target gases include typical gaseous compounds and greenhouse gases emitted from manure, namely ammonia (NH₃), carbon dioxide (CO₂), and methane (CH₄). Sample air is drawn into the FTIR gas analyzer by a built-in diaphragm pump with a flow rate of two liters per minute. The FTIR gas analyzer is operated with a handheld computer (Trimble/TDS Recon) via Bluetooth protocol. Gas concentration results are stored in the handheld computer.

2.2 System Design Overview

The most important features of our multiple chamber instrumentation are: (a) concurrent measurement capability of gaseous fluxes from multiple sources, (b) near real-

time and accurate measurement of multiple gaseous components emitted from each source, (c) monitoring system for temperatures inside the chamber and emission source (e.g., soil, manure) for investigating the effects of temperature gradient on gas emissions, (d) monitoring system for relative humidity inside the chamber, (e) equalizing pressure in the chamber with atmospheric pressure, particularly in windy conditions, (f) providing well-mixed air sample in the chamber, (g) monitoring system for moisture content of emission source, (h) automated data collection, (i) integrated fail-safe setup for the solenoid valve manifold to prevent damage that may occur to the diaphragm pump, and (j) reliable operation and minimum maintenance. A diagram of the multiplexed chamber setup with two chambers is illustrated in Figure 2-2. Depending on multiplexer configuration, additional chambers can be accommodated with our design for future expansion.

2.3 System Component Design and Component Specifications

Major components of multiplexing system for monitoring gas emissions from manure sources include a primary control unit, chamber driver circuit, data acquisition unit, and gas stream flow control circuit. Figure 2-3 outlines the system architecture and interface between the main components. A microcontroller serves as the primary control and data acquisition unit. The chamber positioning is accomplished by interfacing the microcontroller with a custom-designed driver circuit. A solenoid valve manifold is designed to coordinate the gas stream direction from the measurement chambers. Temperature and relative humidity (RH) are monitored using a thermistor (10K ohm Yellow Bead Thermistor; Apogee Instruments, Logan, UT) and RH sensor chip (HIH-4021-001; Honeywell, Minneapolis, MN) located inside the chamber. The output

voltages from these sensors are transferred to the microcontroller through the analog-to-digital inputs and ultimately sent to the handheld computer for processing and storing via a serial interface. The main parts used in developing the multiplexing system and their descriptions are listed in Table 2-1.

LICOR 8100 Series chambers were initially used as the measurement chambers for demonstrating our system prototype. The chambers are initially designed, developed, and widely used for long term measurements of carbon dioxide fluxes from soils. The built-in drive system used in actuating the chamber is based on Transistor-Transistor Logic (TTL). Two additional driver circuits were used in interfacing the microcontroller for this application. One of the circuits is for multiple-chamber positioning and the other one is for controlling the solenoid valves for gas flow stream. The multiple-chamber positioning driver circuit was built based on metal-oxide-semiconductor field-effect transistors (MOSFETs; IRFD120). The solenoid valve driver circuit was based on integration of MOSFETs and a decoder (MM74HC4514). The decoder was used for translating the signal from the microcontroller to the gate pin of the MOSFETs driving the solenoid valves. MOSFETs were used as switching devices in this application due to low power consumption and low voltage at the gate while switching.

The Gaset DX4030 FTIR gas analyzer samples air with a flow rate of two liters per minute. Using the multiplexing system in monitoring gas emissions, the solenoid valve manifold distributes air streams in concert with chamber placement. For each measurement chamber, the air flow (a) from the chamber to gas analyzer and (b) from the gas analyzer to chamber, in order to complete a closed path during a measurement, is controlled by a pair of two solenoid valves. The first valve allows air flow from the

chamber to gas analyzer and the second valve allows air flow from the gas analyzer to the chamber. When the chamber is sealed, the control unit switches the solenoid valves accordingly to ensure the closed path of gas stream flow is accomplished during the measurement.

To prevent damage that may occur to the internal diaphragm pump, the valve manifold is programmed so that the solenoid valves corresponding to the chamber that previously measured remain opened until the valves coordinated with the chamber currently measuring are opened. This programming approach ensures at least one pair of valves remain opened at any given time.

2.4 Data Acquisition

Voltages that are proportional to the chamber temperatures and RH are measured by the thermistor and RH sensor chip located inside the chamber and sent to the handheld computer by the microcontroller. The moisture content, temperatures, and RH are ultimately computed, based on the output voltages. A C# program, installed in the handheld computer, computes, displays, and stores the temperature and RH data. All data collected during the measurement are recorded and stored in the handheld computer with the timestamp as the gas concentrations are being monitored by the FTIR gas analyzer.

2.5 Laboratory Prototype Testing

The multiplexing system prototype has been satisfactorily tested in the laboratory environment. We tested and verified the system function with repeated measurement cycles. The default measurement cycling time in using two chambers with the multiplexer was 12 minutes, including three minutes for each chamber measurement in

addition to time required for chamber repositioning. This default values can be simply modified to fit specific applications in emission measurement.

2.6 Conclusion

The multiplexing system for the CDC method offers a capability for simultaneously monitoring multi-gas emissions, decreasing the uncertainty associated with spatial variations in gas emission measurements from manure sources. With the multi-gas emission measurement and expandable sensor network capabilities, the presented system is more flexible than the commercially available ones. The system prototype was initially designed and developed using the advanced microcontroller technology. With the multiplexing system, data collection and management in gas emission measurement are anticipated to be much more efficient than using a single chamber. The system can be used to evaluate gas mitigation strategies for AFOs (e.g., use of manure amendments, comparing manure incorporation methods, changes in animal diet), as well as to investigate the factors affecting gaseous emission mechanisms from manure sources. Although the system prototype has been successfully tested in the laboratory environment, it is essential to test the system in the field condition and evaluate the system precision.

References

- Davidson, E. A., K. Savage, L. V. Verchot, and R. Navarro (2002). Minimizing artifacts and biases in chamber-based measurements of soil respiration. *Agricultural and Forest Meteorology* 113(1-4):21-37.
- Eklund, B (1992). Practical guidance for lux chamber measurements of fugitive volatile organic emission rates. *Journal of the Air & Waste Management Association* 42: 1583-1591.

- Hongxing, Z., W. Xiaoke, F. Zongwei, S. Wenzhi, L. Wenzhao, and O. Zhiyun (2007). Multichannel automated chamber system for continuous monitoring of CO₂ exchange between the agro-ecosystem or soil and the atmosphere. *Acta Ecologica Sinica* 27(4):1273-1282.
- Hutchinson, G. L., and A. R. Mosier (1981). Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Science Society of America Journal* 45(2): 311-316.
- Katsura, K., S. Maeda, T. Horie, and T. Shiraiwa (2006). A multichannel automated chamber system for continuous measurement of carbon exchange rate of rice canopy. *Plant Production Science* 9(2): 152-155.
- Leytem, A. B., R. S. Dungan, D. L. Bjorneberg, and A. C. Koehn (2011). Emissions of ammonia, methane, carbon dioxide, and nitrous oxide from dairy cattle housing and manure management systems. *Journal of Environmental Quality* 40(5): 1383-1394.
- Liang, N., Y. Fujinuma, and G. Inoue (2005). Measurement of wood CO₂ efflux using a multichannel automated chamber system. *Phyton-Annales Rei Botanicae* 45(4): 109-115.
- Liang, N., G. Inoue, and Y. Fujinuma (2003). A multichannel automated chamber system for continuous measurement of forest soil CO₂ efflux. *Tree Physiology* 23: 825-832.
- Luo, Y., and X. Zhou (2006). *Soil respiration and the environment*. Academic Press, Cambridge, MA.
- Venterea, R. T (2010). Simplified method for quantifying theoretical underestimation of chamber-based trace gas fluxes. *Journal of Environmental Quality* 39(1): 126-135.
- Venterea, R. T., and J. M. Baker (2008). Effects of soil physical nonuniformity on chamber-based gas flux estimates. *Soil Science Society of America Journal* 72(5): 1410-1417.
- Wagner, S. W., D. C. Reicosky, and R. S. Alessi (1997). Regression models for calculating gas fluxes measured with a closed chamber. *Agronomy Journal* 89(2): 279-284.

Table 2-1. List of major parts and descriptions used in developing the multiplexing system prototype for monitoring gas emissions from manure sources

Part	Description
1. C8051F020 Microcontroller (Silicon Laboratories Inc., Austin, TX)	Programmable control unit, used in control and communication with other devices (e.g., temperature and RH sensors, chamber movement signals)
2. LICOR 8100-101 and 8100-104 Chambers (LI-COR Biosciences, Lincoln, NE)	Measurement chambers used for system demonstration
3. Gasmeter DX4030 FTIR Gas Analyzer (Gasmeter Technology Oy, Helsinki, Finland)	Gas analyzer unit, capable of monitoring concentration of up to 15 pre-programmed gaseous components simultaneously
4. Trimble/TDS Recon 400 64/256 Handheld Computer (Tripod Data Systems, Corvallis, OR.)	Data collection and analysis unit
5. Solenoid Valves GL2015 (Precision Dynamics, Inc, CA)	Major component of the valve manifold, used in distributing air streams in concert with chamber placement.

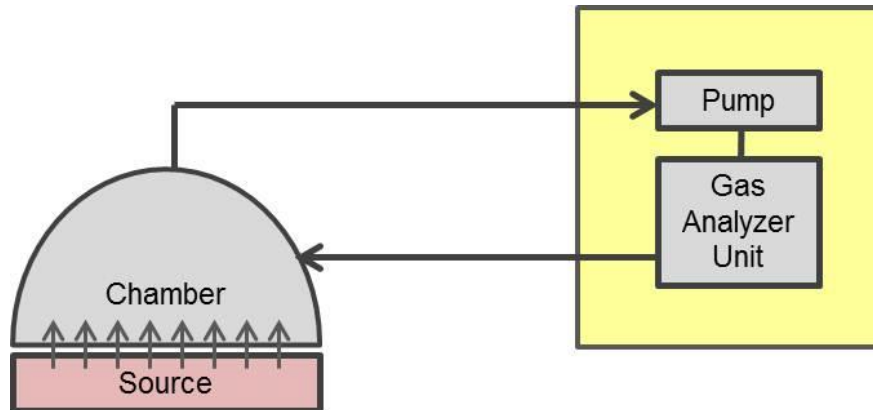


Figure 2-1. Conceptual diagram of the closed dynamic chamber (CDC) method. Air with a constant flow rate is circulated within a loop between chamber and gas analyzer unit during the measurements by a diaphragm pump.

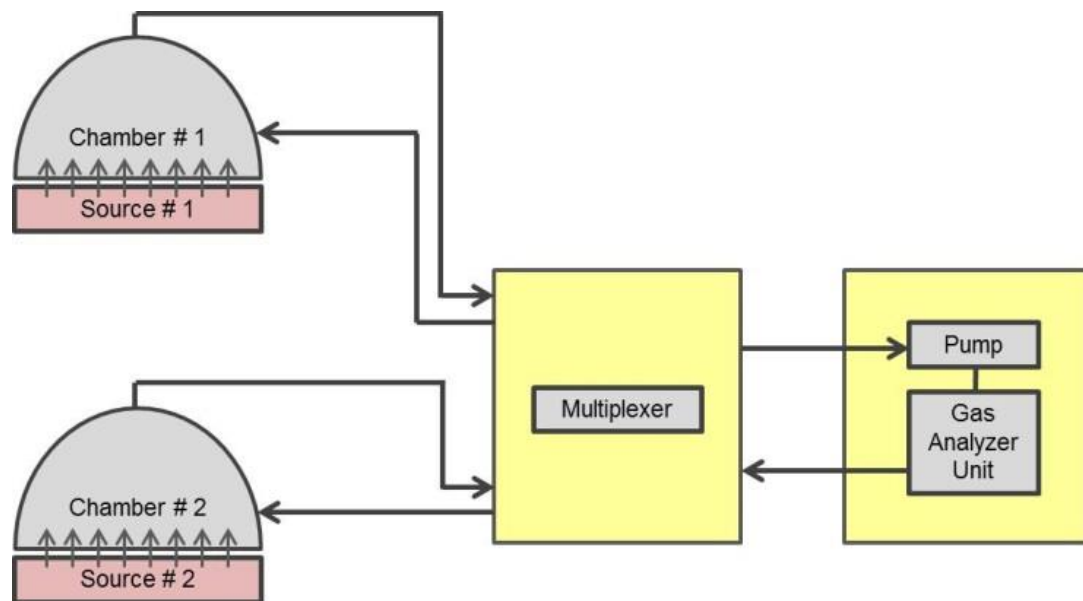


Figure 2-2. Multiplexed gas and sensor measurements with the automated two-chamber setup

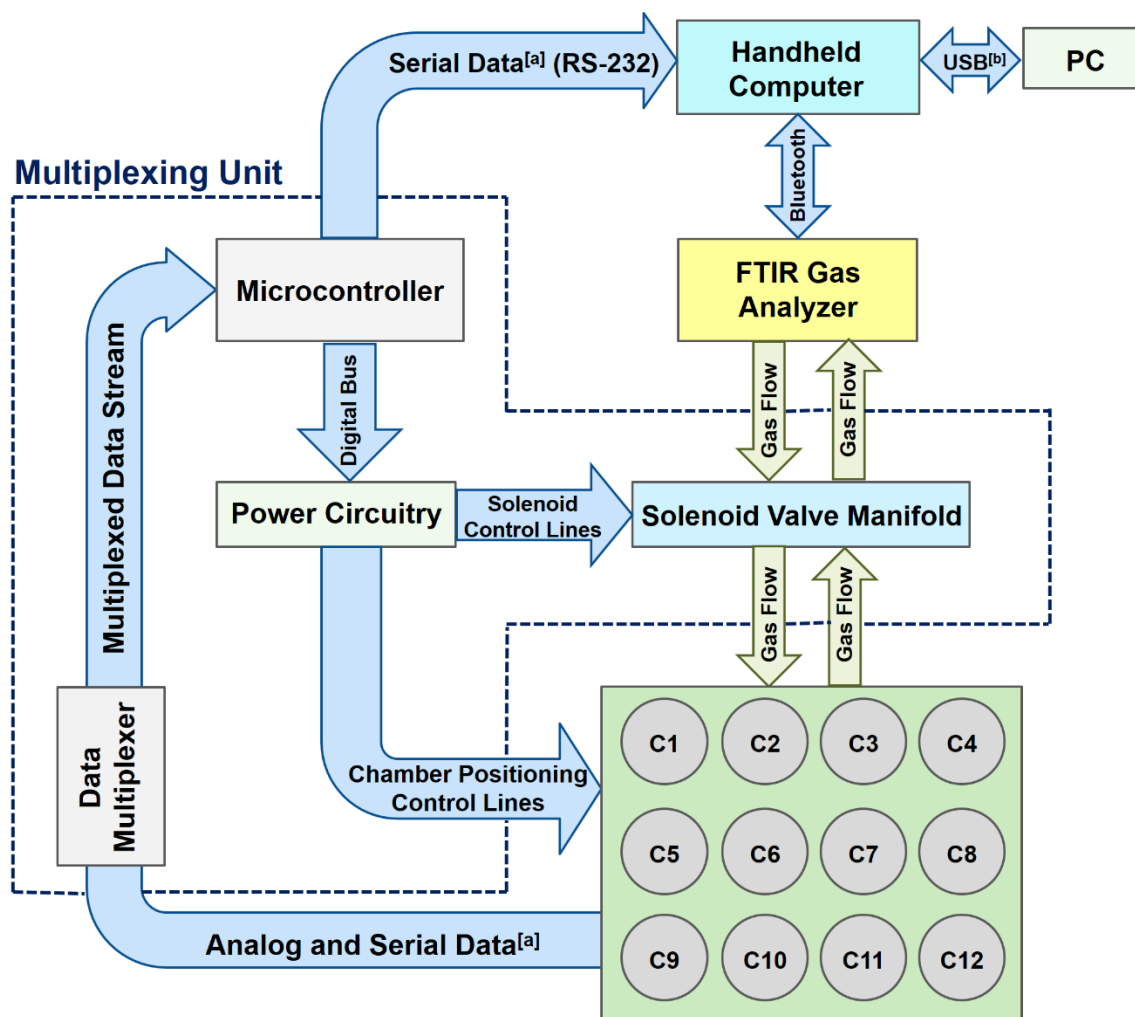


Figure 2-3. Top level system diagram illustrating major components and interfaces
^[a] Analog and serial data includes temperatures, relative humidity (RH), dielectric permittivity, and electrical conductivity (EC). ^[b] USB connection is used for downloading data from handheld computer to PC. Abbreviation: PC = Personal computer; C1-C12 = The numbers of the chambers in the system.

CHAPTER 3

MEASUREMENT ACCURACY OF A MULTIPLEXED PORTABLE FTIR –
SURFACE CHAMBER SYSTEM FOR ESTIMATING GAS EMISSIONS[†]

Abstract: Reliable and accurate monitoring systems for greenhouse gas emissions from animal feeding operations (AFOs) are crucial for establishment and enforcement of gas emission mitigation strategies. An automated multiplexing system for chamber-based monitoring of greenhouse and regulated gas emissions from manure sources was developed to examine spatial and temporal variability of emissions associated with manure management practices. The measurement system uses a Fourier Transformed Infrared (FTIR) spectroscopy analyzer for determination of up to 15 pre-programmed gas fluxes. Multiple chambers provide estimates of variance for emissions from different management practices. The objective of this paper is to demonstrate the robustness and reliability of the described system for monitoring gas emissions from AFOs. Evaluation of system performance was based on laboratory experiments using methane gas (CH₄) to assess the accuracy of the chamber-based measurement system. We developed a method to generate constant emission of methane gas using a gradient-based technique for the reference gas flux. Three different emission rates were simulated. Statistical analysis, including ANOVA, was performed to determine the significance of gas flux estimates using the chamber-based estimate. A p-value ≤ 0.05 was considered to be statistically significant. The ANOVA tests indicated no statistically significant differences among

[†] The material for this chapter was previously published as: Suttarnnontr, P., Hu, E., Miller, R., Tuller, M., & Jones, S. B. (2013). Measurement accuracy of a multiplexed portable FTIR - surface chamber system for estimating gas emissions. In ASABE Annual International Meeting 2013, ASABE 2013 (Vol. 6, pp. 4634-4645). American Society of Agricultural and Biological Engineers, St. Joseph, MI. Reprinted with permission from ASABE Paper No. 131620669 © 2013 ASABE Annual Meeting.

estimated fluxes from each of the 12 evaluated chambers, with resulting p-values of 0.54, 0.58, and 0.80 for measurements of three different emission rates. In addition, the multi-chamber system measurements referenced to the gas fluxes estimated with the gradient-based method showed excellent accuracy with measurement biases less than 1%.

3.1 Introduction

Gas emissions from animal feeding operations (AFOs) create detrimental impacts on air quality ranging from short-term local effects, particularly odor, to long-term large-scale effects such as global warming. Most emissions from AFOs are from area sources such as cattle feedlots, wastewater lagoons, or from agricultural fields amended with manure or sewage, causing complications for emission measurements. Spatial and temporal variations from these sources are found to be challenging for quantifying the amount of gases released to the atmosphere. Emissions of gases from area sources are commonly expressed in terms of fluxes (i.e. mass emission rates per unit area perpendicular to the direction of the flux). Gas emission fluxes can be measured at a range of scales, including small, surface layer, and mixed-layer scales (NRC, 2003). Gas fluxes from a ground-level area source can be determined using enclosures (flux chambers) or micrometeorological techniques by measuring upwind and downwind concentrations and back calculating fluxes with a dispersion model.

A number of enclosure techniques have been widely used for area flux estimates at small-scales. When micrometeorological techniques are inappropriate due to the required the required complex and expensive instrumentation, chamber-based methods are used to measure gaseous emissions at the farm-scale (DeSutter and Ham, 2005; Laguee et al., 2005; Park et al., 2010; Safley and Westerman, 1988, 1992).

Chambers have also been employed for measuring gas fluxes to evaluate manure management practices in controlled pilot-scale experiments at research facilities (Amon et al., 2006; Petersen et al., 2009; VanderZaag et al., 2009, 2010; Wood et al., 2012). Advantages of chamber-based methods include their cost effectiveness and ease of use. However, it is important to consider the potential impacts of discrete sampling in space and time associated with chambers, particularly when using the measured flux data to estimate total emissions over extended time periods.

Spatial and temporal variability issues relative to chamber techniques have been discussed extensively for soil gas emissions (Hutchinson and Livingston, 2002; Livingston and Hutchinson, 1995; Rochette et al., 2005). However, few studies have addressed issues related to chamber-based techniques for measuring emissions from manure sources at AFOs (Wheeler et al., 2011). We designed, constructed, and tested a multiplexed automated-chamber system for determination of gaseous emissions from surface sources from a variety of animal waste treatment practices (Sutitarnnontr et al., 2012). The multiplexing system, based on the closed dynamic chamber principle, includes state-of-the-art moisture content sensors, thermistors, and relative humidity sensors to monitor and examine the primary physical factors directly influencing gas production and transport mechanisms.

The multiplexed chambers are integrated with a Fourier Transformed Infrared (FTIR) gas spectroscopy analyzer (Gaset Technologies Oy, Helsinki, Finland) capable of monitoring concentrations of 15 pre-programmed gases simultaneously. The capability of measuring multiple gases simultaneously is particularly important for studying factors affecting gas production and transport processes; for example, raising the temperature

may increase the emission rate of one gas, while having the opposite effect (i.e. decreasing the emission rate) on another gas.

The objective of this study was to evaluate the accuracy of determination of methane emission fluxes using the multiplexed portable FTIR and surface chamber system under controlled laboratory conditions (Figure 3-1). To accomplish this goal, we developed a method to generate controllable diffusive gas sources to be used as reference emission fluxes. The accuracy of measurements was evaluated using identical sources for each chamber, and comparing the measurement results by means of statistics. Evaluation procedures were refined by examining (a) measurements from each chamber at three different emission rates and (b) by comparing chamber-based measurements with fluxes estimated with a gradient-based technique. Finally, we discuss the use of the multiplexing system for determination of gas emissions from manure sources in AFOs.

Laboratory testing of the chamber-system performance was carried out under controlled conditions where environmental parameters such as temperature, relative humidity, surface air velocity were controlled. This is an important step for calibration and validation of the chamber systems measurement capability since it is difficult to obtain repeatable data under field conditions.

3.2 Theoretical Considerations

3.2.1 Theoretical Gradient-Based Method Computations

Gas transport through a porous medium mainly occurs by molecular diffusion and/or advection through the pores. In fine grained materials such as soils, gas moves predominantly by molecular diffusion (Glinski and Stepniewski, 1985; Hillel, 1998). For

steady-state conditions, the diffusive transport can be described by Fick's law, which in one dimension is given as:

$$J = -D_s \frac{dC}{dz} \approx -D_s \frac{\Delta C}{\Delta z} \quad (1)$$

where J is the flux of gas species [$\text{g m}^{-2} \text{s}^{-1}$], $D_s = D_a(n, \theta)$ is the gas diffusion coefficient [$\text{m}^2 \text{s}^{-1}$] in the porous medium that is dependent on the total porosity (n) and volumetric water content (θ), C is the mass concentration of gas [g m^{-3}], and z is the depth [m]. For flux determination, the gradient (dC/dz) is estimated by discrete differences in gas concentration, ΔC , across distance, Δz .

Based on the ideal gas law, the mass concentration of gas can be converted from the volume or molar concentration using the relation below:

$$C = C_{ppm} \cdot \frac{P \cdot M_W}{R \cdot T} \quad (2)$$

where C is the mass concentration of gas [g m^{-3}], C_{ppm} is the volume or molar concentration [ppm], P is the ambient pressure [atm], M_W is the molecular weight of gas [g gmol^{-1}], R is the ideal gas law constant [$82.06 \times 10^{-6} \text{ atm m}^3 \text{ gmol}^{-1} \text{ K}^{-1}$], and T is the temperature in degrees Kelvin [K].

3.2.2 Gas Diffusion Coefficients in Porous Media

The fraction of air or air-filled porosity (ϕ), defined as the relative content of air in soils, is related to the total porosity (n) and volumetric water content (θ):

$$\phi = n - \theta \quad (3)$$

As ϕ determines the gas diffusion coefficient, a number of models have been proposed to relate the total porosity (n) and water content (θ) to the gas diffusion

coefficient in soils (Werner et al., 2004). Moldrup et al. (2000) developed a simple relationship that yielded excellent predictions of the soil-gas diffusion coefficient (D_s) as a function of n and θ for sieved and repacked soils:

$$D_s = D_a \frac{(n - \theta)^{2.5}}{n} \quad (4)$$

where D_a is the diffusion coefficient for a particular gas in free air. For methane, $D_a \approx 0.16 \text{ cm}^2 \text{ s}^{-1}$ at 0 °C, 1 atm pressure (Thibodeaux, 1996).

When the soil is oven-dry ($\theta \approx 0 \text{ cm}^3 \text{ cm}^{-3}$ and $\phi = n$), Eq. (4) can be simplified:

$$D_s = D_a n^{1.5} = D_a \phi^{1.5} \quad (5)$$

3.3 Materials and Methods

3.3.1 Experimental Setup

We developed a method to simulate a controllable diffusive gas source while it diffuses upward through a dry sand layer and applied this technique to determine the accuracy of the automated multiplexed chamber system. Figure 3-2 depicts the experimental setup. A PVC column (11.5-cm length, 20.32-cm diameter) was sealed with a PVC plate at the bottom. A 1-mm thick steel grate with a geotextile fabric filter was placed inside the column 3.5 cm above the bottom plate to create the headspace for gas diffusion.

A certified standard 100 ppm methane gas (CH_4) was used as the gas source in our experiment. The CH_4 concentration in the headspace was dependent on the flow rate of the standard CH_4 gas diluted with 99.999% nitrogen gas (N_2), controlled by a gas mixing system (Series 4000, Environics Inc., Tolland, CT). Table 3-1 shows the flow rates of the certified 100 ppm CH_4 supplied to the headspace with the measured CH_4

concentrations exhausted from the headspace after equilibration. While the majority of the gas molecules travel to a fume hood through a flexible polyethylene duct hose (3-m length, 3.18-cm diameter), some diffuse upward through the porous medium (sand) above the headspace at a constant rate, producing a steady-state gas flux. The exhaust rate of the fume hood was maintained at $2.72 \text{ m}^3 \text{ min}^{-1}$ ($96 \text{ ft}^3 \text{ min}^{-1}$). Wedron sand (99% quartz, Wedron Silica Company, Wedron, IL) was used as the porous medium through which CH_4 would diffuse upward into the chamber. The sand was oven-dried at $105 \text{ }^\circ\text{C}$ for 24 hours prior to the measurements. The dry bulk density (ρ_b) of the sand was determined to be $1.53 \pm 0.012 \text{ g cm}^{-3}$, resulting in an estimated total porosity of $0.42 \text{ cm}^3 \text{ cm}^{-3}$.

Three experiments were setup to cover a range of gas fluxes anticipated under field conditions: (A) $2,000 \text{ cm}^3 \text{ min}^{-1}$ of the standard methane gas diluted with $645 \text{ cm}^3 \text{ min}^{-1}$ of nitrogen gas with 2 cm sand depth, (B) $300 \text{ cm}^3 \text{ min}^{-1}$ of the standard methane gas diluted with $324 \text{ cm}^3 \text{ min}^{-1}$ of nitrogen gas with 2 cm sand depth, (C) $300 \text{ cm}^3 \text{ min}^{-1}$ of the standard methane gas diluted with $324 \text{ cm}^3 \text{ min}^{-1}$ of nitrogen gas with 4 cm sand depth. Table 3-2 summarizes the conducted experiments and lists the gas fluxes that were theoretically determined with the gradient-based method (Eq. (1)).

3.3.2 Gas Measurement Instrumentation

Multi-gas concentration measurement was accomplished with a Fourier transform infrared (FTIR) spectrometer (model DX-4030, Gaset Technologies Oy, Helsinki, Finland). The instrument was designed for on-site measurements of various organic and inorganic gaseous compounds at low concentrations in ambient air. The detection ranges and detection limits for specific gases of interest are listed in Table 3-3. Results presented in this paper focus on methane concentrations since methane is one of the major gaseous

components released from manure sources in AFOs and, therefore, of primary interest for our affiliated studies that are based on the presented measurement platform. The Gaset DX-4030 provides rapid and accurate measurements with calibration-stability for multiple gases. According to the Gaset DX-4030 instruction and operating manual, span calibrations are not required and the cross-references are automatically compensated for during automated calculation of the gas fluxes due to the FTIR technology. Fifteen gaseous compounds can be simultaneously analyzed and the results can be averaged, displayed and recorded within nine seconds.

Prior to the measurement, a zero calibration was performed using 99.999% nitrogen gas (N_2) with a flow rate of 2 L min^{-1} to improve accuracy of very low concentration readings. During the measurement, an air sample is continuously drawn into the measurement chamber with an approximate flow rate of 2 L min^{-1} by an external diaphragm pump (model D737-23-01, Parker-Hannifin Corp., Mooresville, NC). The air sample is filtered through a PTFE $2\text{-}\mu\text{m}$ membrane (part 450-25-3, Savillex Corp., Eden Prairie, MN) to prevent solid particles from accumulating in the sample cell, which would deteriorate measurement quality. PTFE tubing (6-mm OD) was used for the gas sampling lines in the closed-loop system.

3.3.3 Gas Emission Flux Measurements and Statistical Analyses

The gas flux measurements were performed in a well-controlled laboratory setting with an average temperature of $21.84 \pm 0.9 \text{ }^\circ\text{C}$ and an average barometric pressure of 0.84 atm. Three replicate measurements were performed for each chamber to determine the assay statistics. Linear regression analysis was applied to determine the rate of increasing concentration of CH_4 during chamber closure. Computation of the CH_4 emission fluxes

from the measured data is based on the mass balance principle together with the ideal gas law:

$$J = \frac{V \cdot P \cdot T_s \cdot M_W}{A \cdot P_s \cdot (273.15 + T) \cdot (2.24 \cdot 10^{-2})} \cdot \frac{\partial C}{\partial t} \quad (2)$$

where J is the flux of CH₄ gas [$\mu\text{g m}^{-2} \text{s}^{-1}$], P is the measured ambient pressure [atm], V is the total system volume including the chamber headspace [m^3], T_s is the standard temperature [273.15 K], P_s is the standard pressure [atm], S is the surface area of the chamber on top of the emission source [m^2], T is the temperature in degree Celsius, $2.24 \cdot 10^{-2}$ is the molar volume of a gas [$\text{m}^3 \text{mol}^{-1}$], and $\partial C/\partial t$ is the gradient of gas concentration changing over time derived from linear regression [ppm s^{-1} or $\mu\text{m}^3 \text{m}^{-3} \text{s}^{-1}$]

The computed fluxes were statistically analyzed with the general ANOVA module of the R statistical software package version 2.14.1 (R Development Core Team, 2011). For all analyses, a p-value of 0.05 or smaller was considered significant. The statistical hypothesis testing for our study is summarized in Table 3-4.

3.4 Results and Discussion

3.4.1 Linear Regression Models for Emission Flux Estimates

Examples for measured CH₄ concentrations and the fitted linear regression model are shown in Figure 3-3. The goodness-of-fit statistics from all measurements are summarized in Table 3-5. In general, all of the measured data fit well with the linear regression models. The largest variation of the statistical coefficients of determination (R^2) was observed for Experiment C where the system was evaluated with the smallest CH₄ flux simulation.

Although, the application of linear regression is appropriate for estimating CH₄ fluxes in this study, due to the well-controlled laboratory setting, care must be taken when the non-linear nature of gas concentrations over time in closed chambers is observed in field settings. Covering the emission sources with a closed chamber over a long period of time can disturb the natural gaseous emission fluxes by altering the concentration gradient between the emission source and the air inside the chamber. Using the linear regression for determination of the gaseous fluxes may lead to underestimation of the actual fluxes. Several non-linear regression models have been developed to correct the apparent reduction in gas emission rates from the source by increasing gas concentrations inside the chamber (Davidson et al., 2002; Hutchinson and Mosier, 1981; Kutzbach et al., 2007; Venterea, 2010; Venterea and Baker, 2008; Wagner et al., 1997).

3.4.2 Measurement Accuracy

A series of one-way analyses of variance (ANOVAs) were performed to examine the mean differences among the CH₄ flux measurements with 12 chambers in three experiments, reflecting the measurement accuracy of the system. The means and standard deviations of all measurements are presented in Figure 3-4(a)-(c). All three analyses revealed that there were no significant differences across the chambers; $F(11, 24) = 0.92$, ns in Experiment A, $F(11, 24) = 0.87$, ns in Experiment B, and $F(11, 24) = 0.62$, ns in Experiment C. The largest measurement variation across chambers occurred in Experiment A, where the highest emission fluxes were anticipated.

A comparison between gradient-based surface CH₄ flux estimates and closed-chamber measurements (Figure 3-5) shows excellent agreement. The mean of the flux measurements ($n = 36$) in Experiments A, B, and C was within 0.79%, 0.47%, and 0.37%

of the gradient-based flux estimates, respectively. The largest bias in the mean of the measurements was 3.85%, observed for Chamber 11 in Experiment A (Figure 3-4(a)). Despite the excellent agreement between the multi-chamber measurements and the gradient-based estimates, it is important to note that the experiments were conducted in a well-controlled laboratory environment. Measuring gas fluxes under field conditions will potentially be more complicated because of spatially and temporary varying physical, chemical, and biological factors as suggested by Turcu et al. (2005), who measured CO₂ fluxes in greenhouse soil columns.

3.5 Summary

The multiplexed portable FTIR-surface chamber measurement platform with fully automated data collection provides a potential new method for near real-time monitoring of multi-gas emissions from manure sources. The complex nature and multiple factors influencing gaseous emissions from manure sources require measurement capabilities that are accurate, reliable and repeatable. The multiple-surface chamber platform, designed and built based on the closed dynamic chamber principle, exhibits these characteristics, providing defensible measurement capabilities, which are crucial for understanding production, flux and fate of gases from biologically active porous media such as manure and soil. Comparisons of CH₄ emission measurements from the same sources were used to evaluate the measurement accuracy of the system with statistical one-way ANOVA tests with a level of significance of 0.05. Analyses revealed that there were no significant differences across the twelve chambers with resulting p-values of 0.54, 0.58, and 0.80 in Experiments A, B, and C, respectively proving the null hypothesis is true. The system accuracy was observed as relative percentage differences between the

mean of the CH₄ fluxes determined by the system and the fluxes estimated using the gradient-based technique. Overall, the measurement biases were less than 1%.

In addition to decreasing the uncertainties associated with spatial variations, the multiplexed surface chamber platform is valuable for investigating relationships between factors affecting gaseous emissions from biologically active porous media such as manure sources, leading to improvement of best management practices (BMPs) to minimize gaseous emissions from farm operations. The system can be employed for evaluation of gaseous mitigation strategies such as comparison of manure incorporation methods, effect of various bedding materials, and effects of animal diet as well as for investigating factors that cause uncertainties in gas emissions such as manure surface crusting. Although the multiplexing system was successfully evaluated for a single test gas in a controlled laboratory environment, testing under field conditions is essential and part of our ongoing research.

References

- Amon, B., V. Kryvoruchko, T. Amon, and S. Zechmeister-Boltenstern (2006). Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. *Agriculture, Ecosystems & Environment* 112(2-3): 153-162.
- Davidson, E. A., K. Savage, L. V. Verchot, and R. Navarro (2002). Minimizing artifacts and biases in chamber-based measurements of soil respiration. *Agricultural and Forest Meteorology* 113(1-4): 21-37.
- DeSutter, T. M., and J. M. Ham (2005). Lagoon-biogas emissions and carbon balance estimates of a swine production facility. *Journal of Environmental Quality* 34(1): 198-206.
- Glinski, J., and W. Stepniowski (1985). *Soil aeration and its role for plants*. CRC Press Inc., Boca Raton, FL.

- Hillel, D (1998). *Environmental soil physics*. Academic Press, San Diego, CA.
- Hutchinson, G. L., and G. P. Livingston (2002). Soil-atmosphere gas exchange. In *Methods of Soil Analysis: Part 4 Physical Methods*, 1159-1182. J. H. Dane, and G. C. Topp, eds. Soil Science Society of America, Madison, WI.
- Hutchinson, G. L., and A. R. Mosier (1981). Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Science Society of America Journal* 45(2): 311-316.
- Kutzbach, L., J. Schneider, T. Sachs, M. Giebels, H. Nykanen, N. J. Shurpali, P. J. Martikainen, J. Alm, and M. Wilmking (2007). CO₂ flux determination by closed-chamber methods can be seriously biased by inappropriate application of linear regression. *Biogeosciences* 4(6): 1005-1025.
- Laguee, C., E. Gaudet, J. Agnew, and T. A. Fonstad (2005). Greenhouse gas emissions from liquid swine manure storage facilities in Saskatchewan. *Transactions of the ASAE* 48(6): 2289-2296.
- Livingston, G. P., and G. L. Hutchinson (1995). Enclosure-based measurement of trace gas exchange: applications and sources of error. In *Biogenic trace gases: Measuring emissions from soil and water*, 14-51. P. A. Matson and R. C. Harriss, eds. Blackwell Science Ltd., Oxford, England.
- Moldrup, P., T. Olesen, J. Gamst, P. Schjonning, T. Yamaguchi, and D. E. Rolston (2000). Predicting the gas diffusion coefficient in repacked soil water-induced linear reduction model. *Soil Science Society of America Journal* 64(5): 1588-1594.
- NRC (2003). *Air emissions from animal feeding operations: current knowledge, future needs*. National Academies Press, Washington, DC.
- Park, K.-H., C. Wagner-Riddle, and R. J. Gordon (2010). Comparing methane fluxes from stored liquid manure using micrometeorological mass balance and floating chamber methods. *Agricultural and Forest Meteorology* 150(2): 175-181.
- Petersen, S. O., M. Skov, P. Droscher, and A. P. S. Adamsen (2009). Pilot scale facility to determine gaseous emissions from livestock slurry during storage. *Journal of Environmental Quality* 38(4): 1560-1568.
- R Development Core Team (2011). *R: A language and environment for statistical computing*. R Foundation for Statistical Computing, Vienna, Austria.

- Rochette, P., G. L. Hutchinson, J. L. Hatfield, J. M. Baker, and M. K. Viney (2005). Measurement of soil respiration in situ: chamber techniques. In *Micrometeorology in Agricultural Systems*, Agronomy Monograph 47: 247-286.
- Safley, L. M., and P. W. Westerman (1988). Biogas production from anaerobic lagoons. *Biological Wastes* 23(3): 181-193.
- Safley, L. M., and P. W. Westerman (1992). Performance of a dairy manure anaerobic lagoon. *Bioresource Technology* 42(1): 43-52.
- Sutitarnnontr, P., Miller, R., Bialkowski, S., Tuller, M., & Jones, S. B. (2012). A multiplexing system for monitoring greenhouse and regulated gas emissions from manure sources using a portable FTIR gas analyzer. In *ASABE Annual International Meeting 2012, ASABE 2012 (Vol. 4, pp. 2782-2788)*. American Society of Agricultural and Biological Engineers, St. Joseph, MI.
- Thibodeaux, L. J (1996). *Environmental chemodynamics: Movement of chemicals in air, water, and soil*. John Wiley & Sons, Inc, Hoboken, NY.
- Turcu, V. E., S. B. Jones, and D. Or (2005). Continuous soil carbon dioxide and oxygen measurements and estimation of gradient-based gaseous flux. *Vadose Zone Journal* 4(4): 1161-1169.
- VanderZaag, A. C., R. J. Gordon, R. C. Jamieson, D. L. Burton, and G. W. Stratton (2009). Gas emissions from straw covered liquid dairy manure during summer storage and autumn agitation. *Transactions of the ASABE* 52(2): 599-608.
- VanderZaag, A. C., R. J. Gordon, R. C. Jamieson, D. L. Burton, and G. W. Stratton (2010). Permeable synthetic covers for controlling emissions from liquid dairy manure. *Applied Engineering in Agriculture* 26(2): 287-297.
- Venterea, R. T (2010). Simplified method for quantifying theoretical underestimation of chamber-based trace gas fluxes. *Journal of Environmental Quality*. 39(1): 126-135.
- Venterea, R. T., and J. M. Baker (2008). Effects of soil physical nonuniformity on chamber-based gas flux estimates. *Soil Science Society of America Journal* 72(5): 1410-1417.
- Wagner, S. W., D. C. Reicosky, and R. S. Alessi (1997). Regression models for calculating gas fluxes measured with a closed chamber. *Agronomy Journal* 89(2): 279-284.

- Werner, D., P. Grathwohl, and P. Hohener (2004). Review of field methods for the determination of the tortuosity and effective gas-phase diffusivity in the vadose zone. *Vadose Zone Journal* 3(4): 1240-1248.
- Wheeler, E. F., P. A. Topper, R. C. Brandt, N. E. Brown, A. Adviento-Borbe, R. S. Thomas, and G. A. Varga (2011). Multiple-chamber instrumentation development for comparing gas fluxes from biological materials. *Applied Engineering in Agriculture* 27(6): 1049-1060.
- Wood, J. D., R. J. Gordon, C. Wagner-Riddle, K. E. Dunfield, and A. Madani (2012). Relationships between dairy slurry total solids, gas emissions, and surface crusts. *Journal of Environmental Quality* 41(3): 694-704.

Table 3-1. Concentration of CH₄ exhausted from the headspace shown in Figure 3-2, corresponding to the applied flow rate of standard 100 ppm CH₄ mixed with 99.999% nitrogen gas. The concentrations were measured 15 minutes after flow initiation.

CH ₄ flow rate (cm ³ min ⁻¹)	CH ₄ concentration (ppm)†
300	48.10±0.78
2,000	75.61±0.62

† The concentrations shown represent the mean and standard error (n = 20)

Table 3-2. Estimated CH₄ emission fluxes

Experiment	Flow rate of certified 100 ppm CH ₄ (cm ³ min ⁻¹)	Sand depth (cm)	Estimated CH ₄ emission flux (μg m ⁻² s ⁻¹)
A	2,000	2	8.63
B	300	2	5.42
C	300	4	2.69

Table 3-3. Detection ranges and limits of the GASMET DX-4030 FTIR gas analyzer (Source: Gasmet Technologies Oy, Helsinki, Finland)

Gas component	Formula	Detection range	Theoretical detection limit†
Water vapor	H ₂ O	5%	NA‡
Carbon dioxide	CO ₂	5,000 ppm	NA‡
Carbon monoxide	CO	100 ppm	0.25 ppm
Methane	CH ₄	100 ppm	0.11 ppm
Nitrous oxide	N ₂ O	50 ppm	0.02 ppm
Ammonia	NH ₃	100 ppm	0.13 ppm
Nitrogen dioxide	NO ₂	50 ppm	0.37 ppm
Nitrogen monoxide (Nitric oxide)	NO	200 ppm	0.29 ppm
Ethanol	C ₂ H ₅ OH	200 ppm	0.20 ppm
Acetic acid	CH ₃ COOH	100 ppm	0.04 ppm
Phenol	C ₆ H ₅ OH	50 ppm	0.17 ppm
m-Cresol (3-Methyl phenol)	3-CH ₃ C ₆ H ₅ OH	50 ppm	0.06 ppm
n-Decane	C ₁₀ H ₂₂	50 ppm	0.03 ppm
n-Undecane	C ₁₁ H ₂₄	50 ppm	0.02 ppm
Ethane	C ₂ H ₆	200 ppm	0.13 ppm

† Theoretical detection limits are defined as the peak height that corresponds to three times the standard deviation of the signal-to-noise of the spectrum and based on 60-second measurement time with one component in the N₂ peak height.

‡ Theoretical detection limits of measuring H₂O and CO₂ are not specified due to potentially high changes in H₂O and CO₂ concentrations in the ambient air. Estimated theoretical detection limit for H₂O and CO₂ is in a range greater than 100 ppm and 10 ppm, respectively.

Table 3-4. Statistical hypothesis test used for the measurements

Null hypothesis (H ₀)	Alternative hypothesis (H _a)
There is no difference in CH ₄ emission fluxes measured from all 12 chambers.	The CH ₄ emission flux determined from at least one of twelve chambers differs from the others.

Table 3-5. Goodness-of-fit statistics of linear regression for the change of CH₄ concentrations over the chamber closure time

Experiment	Estimated CH ₄ flux ($\mu\text{g m}^{-2} \text{ s}^{-1}$)	R ² Statistics				
		Mean	Min	Max	SD	n
A	8.63	0.9962	0.9915	0.9988	0.00174	36
B	5.42	0.9942	0.9905	0.9970	0.00164	36
C	2.69	0.9918	0.9847	0.9964	0.00262	36



Figure 3-1. Multiplexed automated-chamber system with five chambers shown in open position.

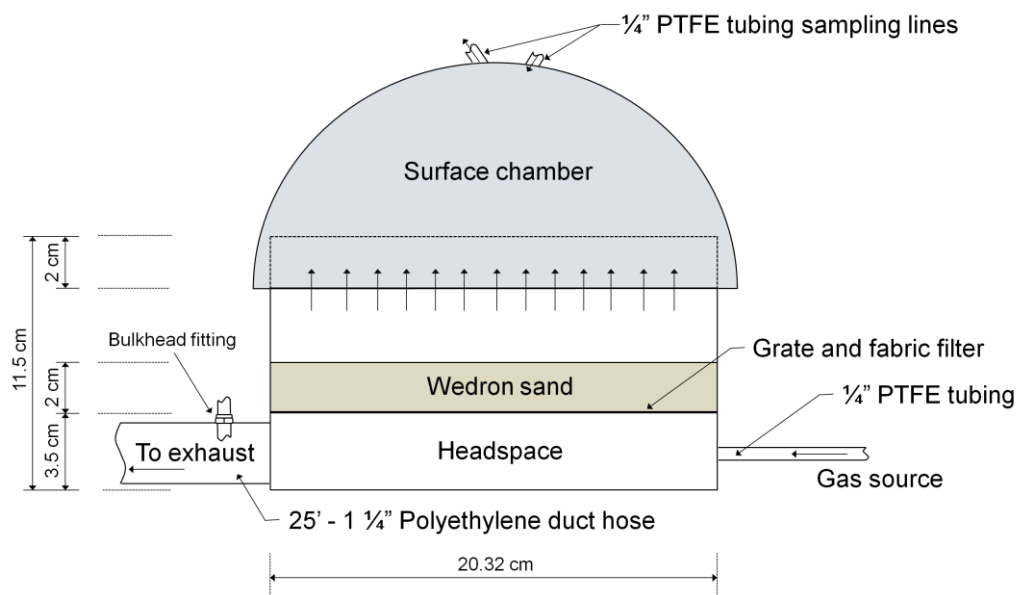


Figure 3-2. Sketch of the experimental calibration unit to generate a controllable steady-state gas flux into the surface chamber. Methane (CH_4) mixed with nitrogen gas (N_2) was continuously fed through the headspace with a constant flow rate resulting in an equilibrium gas concentration within the headspace. The bulkhead fitting was for $\frac{1}{4}$ " PTFE sampling tube to determine the concentration of CH_4 exhausted from the headspace. Methane gas diffused from the headspace into the uniform dry Wedron sand with at a constant rate. Fluxes of CH_4 from the sand were measured during closure of the flux chamber. The depth of the sand layer and gas flow rate can be adjusted to produce the desired gas fluxes.

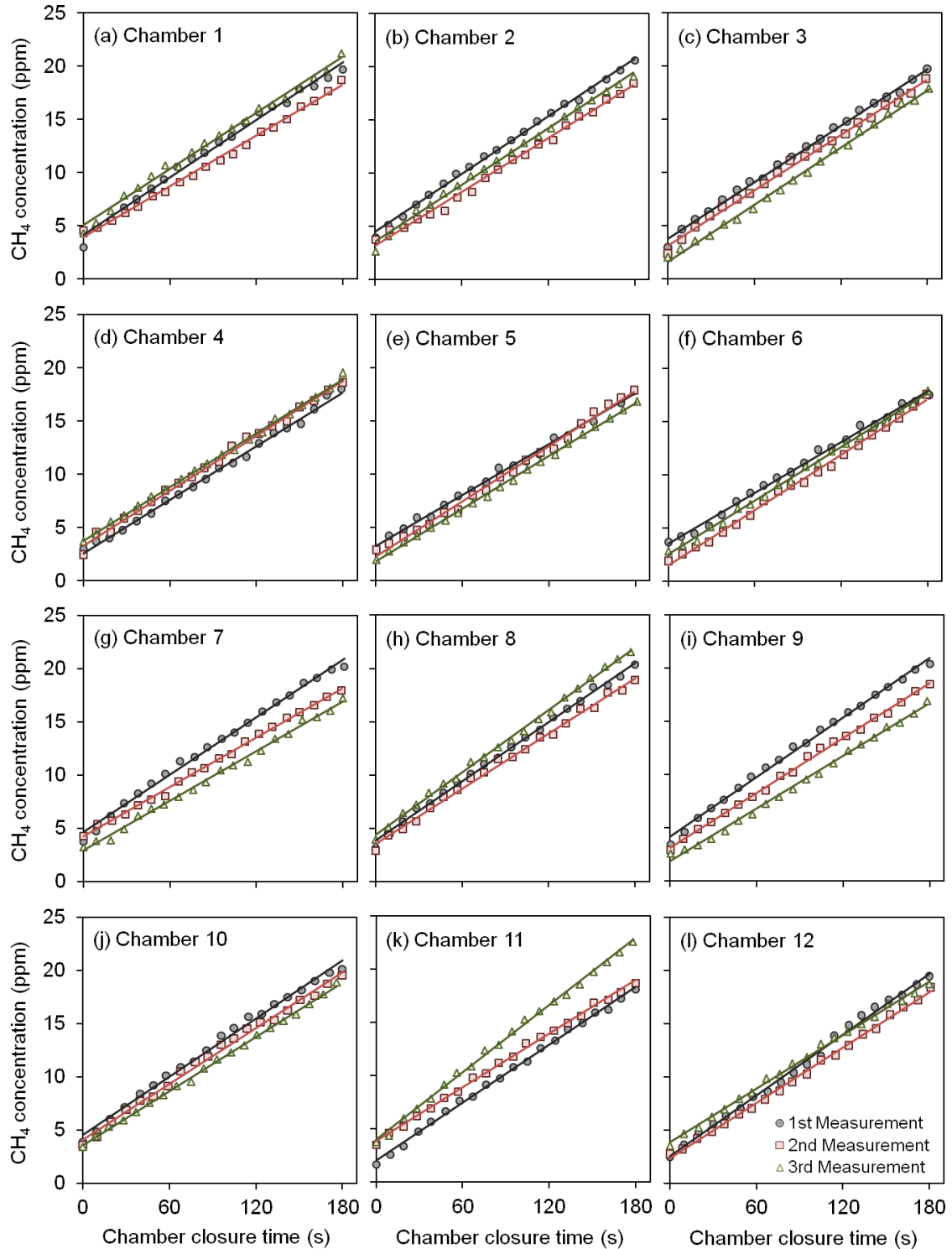


Figure 3-3. Evolution of CH₄ concentrations with time inside each of the 12 chambers (a – l) during calibration in Experiment A. The chamber closure time for all 12 chambers was programmed to three minutes and the concentration data were recorded on average in nine-second intervals.

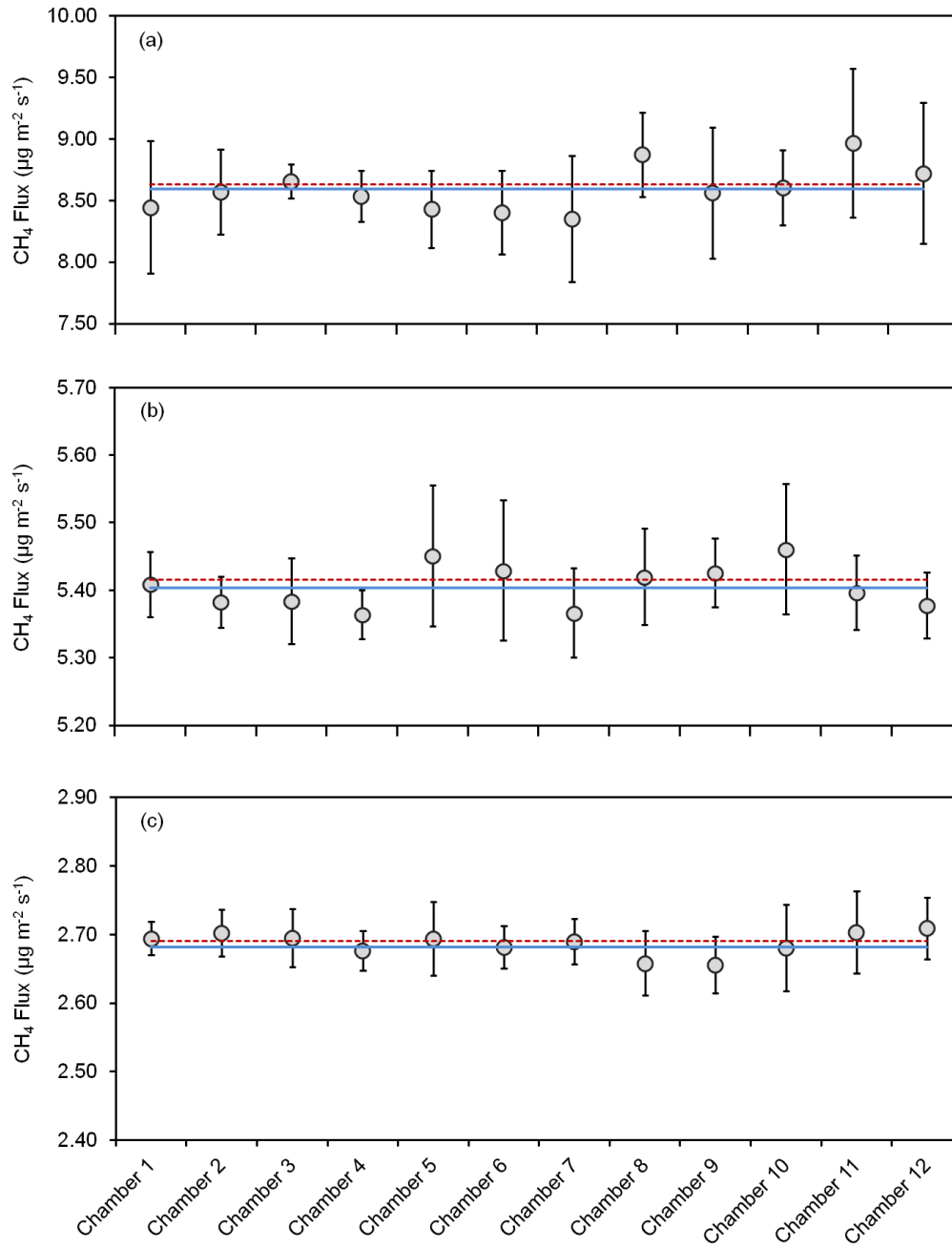


Figure 3-4. Mean of the methane flux measurements from 12 chambers: (a) Experiment A, (b) Experiment B, and (c) Experiment C. The error bars denote plus and minus one standard deviation. The blue-solid lines depict the mean of the measurements from 12 chambers (n=36) and the red-dashed lines show the methane fluxes estimated with the gradient-based technique.

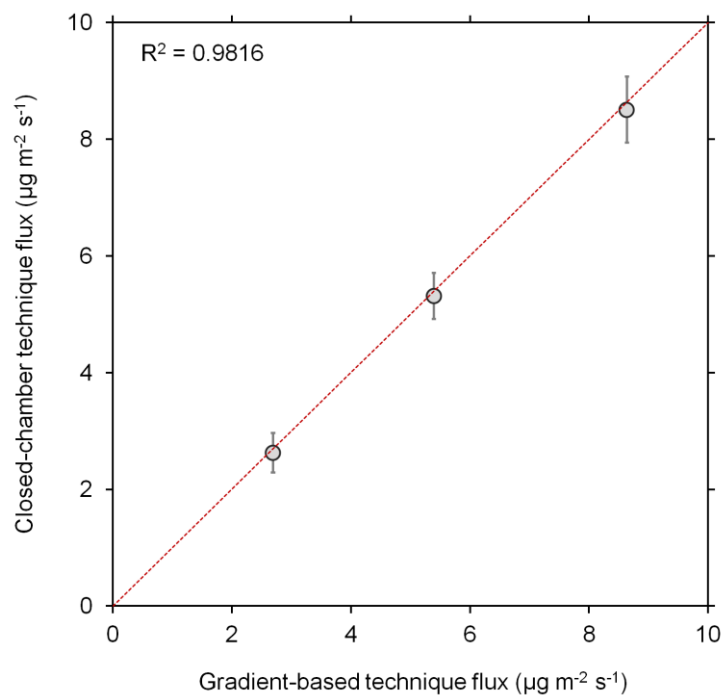


Figure 3-5. Comparison of CH₄ emission fluxes measured with the closed-chamber technique and gradient-based estimates ($n = 108$). The error bars denote plus and minus one standard deviation and the red-dashed line represents the 1:1 comparison line.

CHAPTER 4

PHYSICAL AND THERMAL CHARACTERISTICS OF DAIRY CATTLE MANURE[†]

Abstract: Greenhouse and regulated gas emissions from animal waste are naturally mediated by moisture content and temperature. As with soils, emissions from manure could be readily estimated given the physical, hydraulic, and thermal properties are described by models and microbes and nutrients are not limiting factors. The objectives of this study were to measure and model physical, hydraulic, and thermal properties of dairy manure to support advanced modeling of gas and water fluxes in addition to solute, colloid and heat transport. A series of soil science measurement techniques were applied to determine a set of fundamental properties of as-excreted dairy cattle manure.

Relationships between manure dielectric permittivity (K_a) and volumetric water content (θ_v) were obtained using time-domain reflectometry (TDR) and capacitance-based dielectric measurements. The measured water retention characteristic for cattle manure was found to be similar to that of organic peat soil. The unsaturated hydraulic conductivity function $K(\theta_v)$ of dairy manure was inferred from inverse numerical fitting of laboratory manure evaporation results. The saturated hydraulic conductivity (K_s) was estimated to be about 200 cm day^{-1} . These simulation results suggest that the Richards equation can describe the hydrodynamics taking place in dairy manure relevant to natural drying processes. The thermal properties of dairy manure, including thermal conductivity, thermal diffusivity, and bulk volumetric heat capacity, were also determined using three penta-needle heat pulse probes (PHPPs). The thermal

[†] The material for this chapter was previously published as: Sutitaranontr P., Hu E., Tuller M., Jones S.B. (2014). Physical and thermal characteristics of dairy cattle manure. *Journal of Environmental Quality* 43: 2115-2129. DOI: 10.2134/jeq2014.05.0212.

conductivities (λ) of the dairy manure were found between 0.52 and 0.08 W m⁻¹ °C⁻¹ from saturation to dry conditions. Change of the thermal diffusivity (κ) during the manure drying process was observed to be only a small range, approximately from 0.0013 (saturation) to 0.0010 cm² s⁻¹ (dry). The bulk volumetric heat capacity (C) of dairy manure at the saturation point was determined as approximately 3.95 MJ m⁻³ °C⁻¹ and linearly decreased to 0.79 MJ m⁻³ °C⁻¹ for the dry manure sample. The accuracy of the measurements was determined from a comparison of theoretical volumetric water content, estimated from the measured thermal properties with that determined by the capacitance-based dielectric measurement. These data represent a novel and unique contribution for advancing prediction and modeling capabilities of gas emissions from cattle manure, while the uncertainties of the results can be due to the complexity of shrinkage, surface crust formation, and shrinkage cracks.

4.1 Introduction

Livestock manure is widely applied to land in agricultural production as the nutrient and organic matter content of manure is beneficial for plant growth, long-term fertility, and soil structure in agronomic systems (Klop et al., 2012; Schröder et al., 2013). However, runoff and infiltration from feedlots and barnyards, land applied manure, and from pastures where livestock are grazing can result in transfer of nutrients, pathogens, pharmaceuticals and organic matter to aqueous systems including both ground and surface waters (Christian et al., 2003; Sharpley et al., 1998). Numerical models are required to simulate complex transformation and translocation processes such as with carbon and nitrogen, which involve both liquid and gas phases. There are a number of these models including large-scale land surface models (Del Grosso et al., 2006; Grosso

et al., 2008; Oleson et al., 2008; Parton et al., 1998) and point scale models (Simunek et al., 2006; Toride and Chen, 2011), which are continually being improved as more detail is made available, but physical properties of manure have not been defined for use with these models. An accurate simulation model that can describe solute transport from manure sources at a range of scales is mandatory for estimation of quality and quantity of manure leachate.

Accurately describing fluid flow and transport mechanisms in porous media requires extensive knowledge and understanding of physical, chemical, and microbiological processes and properties. Similar to other porous media, the transport and fate of dissolved nutrients in manure depends on the magnitude and direction of the water flux (e.g., infiltration, runoff), which is primarily influenced by the hydraulic gradient (Hillel, 1998; Jury and Horton, 2004). While the Richards equation is widely applied in simulations of the fluid transport in unsaturated porous media, it requires the physical and hydraulic properties as the primary input parameters in the model development. As the accumulation of dairy cattle manure in feedlots, storage areas or in pastures generates large amounts of dissolved solutes mobilized by water transport, the physical and hydraulic properties of cattle manure are key requirements in the model development to accurately describe manure leachate transport mechanisms and response from point to field and feedlot scales.

From a physical perspective, manure is a heterogeneous, polyphasic, disperse porous medium generally consisting of solid, liquid, and gaseous phases. The solid fraction primarily consists of fibrous material, which may include hay, grain, and silage, creating a complex manure matrix (Azevedo, 1974; Sobel, 1966; Spellman and Whiting,

2007). The liquid phase is mostly water, commonly containing dissolved solutes and organic matter. The gas fraction occupies the empty pores or void space. The manure matrix determines the geometric characteristics of the empty pores that play an important role in the transport of the water and gases (Hillel, 1998; Horn and Smucker, 2005; Jury and Horton, 2004).

Livestock manure is responsible for approximately 7.5% of methane (CH₄) and 4.7% of nitrous oxide (N₂O) emissions in the US (United States Department of State, 2010). While microbial activity is a key factor for formation of gaseous compounds in manure, the magnitude of gas exchange between manure and the atmosphere largely depends on manure physical characteristics. Microbial metabolism as well as population dynamics (e.g., composition and density) are dramatically influenced by manure temperature (Miller, 1992). However, manure moisture content had a greater influence on microbial activity in the manure composting processes than does temperature (Liang et al., 2003). This is in part due to the competing roles water plays in providing an aqueous environment for microbes while at the same time controlling the rate of gas exchange (i.e., O₂ supply). The effects of microbial-bacterial growth on the physical and hydraulic characteristics of soil matrix structure in the unsaturated zone are significant (Or et al., 2007). Microbial existence in the soil matrix was found to decrease the evaporative water losses due to an evaporation-retarding barrier, potentially formed by microbes (Chenu and Roberson, 1996; Sutherland, 2001).

Surface crusting has been identified to have a significant impact in decreasing the hydraulic conductivities in infiltration and evaporation processes in soils (Assouline, 2004; Ruan et al., 2001; Touma et al., 2011). Similar principles should apply to surface

crust forming processes of cattle manure, which occur at the surface through shrinkage. With drying, capillary forces become more negative, pulling the solid phase fibers closer together, effectively shrinking the pore structure and filling open pore spaces with microbially-generated polymeric substances that have cementation properties. Following crust formation, development of random shrinkage cracks is commonly observed on the cattle manure surface, increasing the difficulty of model predictions. The volume of the sample is known to have an effect on the magnitude of shrinkage cracks (Chertkov, 2013); the larger the manure sample, the more shrinkage cracking is likely to occur. Or (1996) introduced a model of liquid phase sintering of glass compacts to describe wetting induced densification of aggregated soil that could be potentially adopted for crust formation in cattle manure. The model requires information on geometrical and density parameters of cattle manure, which could be obtained from direct measurements while the viscosity of saturated manure, as the unknown parameter, could be estimated using a curve fitting technique. However, more research is needed to evaluate and verify the accuracy of adopting this model to describe crust formation on manure surfaces.

Thermal properties of dairy cattle manure also play a significant role in the drying process. These parameters, including the volumetric heat capacity, thermal conductivity, and thermal diffusivity, are used in the heat flow equation to describe the spatial and temporal temperature variations, allowing prediction of the movement of thermal energy and water (Sailor et al., 2008; Scott, 2000). Heat pulse probes have been developed to determine soil thermal properties with high accuracy (Ham and Benson, 2004; Heitman et al., 2003; Knight et al., 2012; Young et al., 2008). The measurement is based on the theory of radial heat dissipation from an infinite line source. Temperature rise associated

with a heat pulse applied to the line source is measured at an approximate distance of 6 mm from the line source. The probes normally consist of two parallel needles; one needle providing the heat source and the other containing a thermistor or thermocouple for the temperature measurement.

Heat pulse probes have been successfully used to determine thermal properties and water content, in addition to water flux density of porous media (Gao et al., 2006; Kamai et al., 2008). The penta-needle heat-pulse probes (PHPPs) used in this study employ a novel inverse fitting method for determining soil thermal properties and heat flux density (Sakai et al., 2011; Yang and Jones, 2009; Yang et al., 2013).

A comprehensive literature review clearly revealed that while the biological and chemical decomposition of cattle manure has been widely studied (Gerba and Smith, 2005; Liu et al., 2011; Longhurst et al., 2012; Nennich et al., 2005) with an abundance of reported data, little is known about important physical and thermal properties. The objectives of this study were to measure and model physical, hydraulic, and thermal properties of as-excreted dairy manure, that primarily affect flow of liquid water and gas exchange and transport of dissolved constituents. As-excreted manures were selected for characterization because they are not contaminated with foreign materials such as bedding materials or flushed water; therefore, considered to be the most reliable data. (Spellman and Whiting, 2007). By characterizing physical, hydraulic, and thermal properties of dairy manure using well established analytical models, advanced modeling of greenhouse gas emissions, in addition to water, solute and colloid transport processes can be simulated using analytical and advanced numerical modeling.

4.2 Theoretical Considerations

Critical properties of porous media (manure) and analytical and numerical models used in characterizing and estimating these properties are discussed below..

4.2.1 Physical Properties:

Particle density of organic matter typically ranges between 0.9 to 2.0 g cm⁻³ (Boyd, 1995; Boyd, 2000; Cater et al., 2007; Chen and Avnimelech, 1986). The particle (solid fraction) density of dairy manure was reported within a range of 1.41 to 1.84 g cm⁻³ and was largely dependent on mineral content of manure (Hafez et al., 1974). The dry bulk density of organic substrates may range from 0.05 to 0.30 g cm⁻³ (Chen and Avnimelech, 1986). Due to some swelling and significant shrinkage, variations in the bulk density of manure and other organic materials are normally substantial when compared to particle density. Total porosity in most organic materials is commonly greater than 80% by volume (Chen and Avnimelech, 1986).

4.2.2 Volumetric Water Content Determination of Dairy Manure:

In this study, the water or moisture content of dairy manure (i.e., the quantity of water contained in a manure sample) is described in terms of volumetric water content (θ_v) that is the volume of water contained within a specified bulk volume of manure, which for dielectric sensor-based measurements is inherently given by the sensor output. A large number of techniques have been used to determine θ_v in porous media. Due to a strong correlation between the dielectric permittivity (K_a) and θ_v , sensors are able to estimate θ_v by measuring the apparent K_a (Davis and Chudobiak, 1975). Two different measurement approaches employing electromagnetic (EM) sensing of K_a were used in

this study: 1) travel time analysis using time domain reflectometry (TDR) and 2) capacitance-based measurement using a commercial dielectric sensor (GS3, Decagon Device Inc., Pullman, WA).

A function to describe the relationship between K_a and θ_v can be developed empirically (Malicki et al., 1996; Schaap et al., 1997; Topp et al., 1980) or based on a physical approach employing dielectric theory, which combines constituent dielectric constants and volume fractions of each component (i.e., solid, liquid, and gas). Additional details on TDR measurements are given in Jones et al. (2002) and Robinson et al. (2003). Schaap et al. (1997) derived an empirical relationship between K_a and θ_v for five different organic forest soils using TDR measurements. The empirical calibration equation based on 505 measurements is given as

$$\theta_v = \left(A\sqrt{K_a} - B \right)^C \quad (1)$$

where $A = 0.133 \pm 0.002$, $B = 0.146 \pm 0.002$, and $C = 0.885 \pm 0.018$.

In addition, four potential error sources from TDR calibrations in organic forest soils were described in Schaap et al. (1997). The error sources include decomposition of organic matter during the measurement, residual water after drying, temperature effects, and shrinking of the samples while drying. Among these sources, shrinkage was found to be the most significant factor affecting reliability of the TDR measurements.

Nevertheless, because the corrections for θ_v and K_a were approximately comparable, the shrinkage effects on the calibration parameters were insignificant.

4.2.3 Water, Solute, and Matric Potentials:

The WP4-T Dewpoint Potentiometer (Decagon Devices, Inc., Pullman, WA) determines water potential (ψ_w) of porous media in the laboratory using the chilled mirror

dewpoint technique (Gee et al., 1992; Scanlon et al., 2002), which is based on fundamental thermodynamic relationships and precise measurements of temperature (Campbell et al., 2007). The value of ψ_w measured by the WP4-T is the sum of the osmotic potential (or solute potential, ψ_s) and matric potential, ψ_m , of the porous medium. As the dewpoint method measures the sum of ψ_s and ψ_m , we estimated the contribution of ψ_s using a correlation between ψ_s and electrical conductivity (EC) of the sample solution, corrected for water content (United States Salinity Laboratory Staff, 1954), given as

$$\psi_s (\theta_v) = -EC_e \left(\frac{\theta_s}{\theta_v} \right) \cdot 0.036 \quad (2)$$

where $\psi_s (\theta_v)$ is the water content dependent osmotic potential [MPa], EC_e is the electrical conductivity of the saturation extract [dS m⁻¹], θ_s/θ_v is the ratio of saturated and actual water contents [cm³ cm⁻³], and 0.036 is a conversion coefficient [MPa dS⁻¹ m].

4.2.4 Water Retention Curve:

The experimental water retention data were characterized by fitting the van Genuchten model (van Genuchten, 1980) to each data set using

$$\Theta (\psi_m) = \frac{\theta_v - \theta_r}{\theta_s - \theta_r} = \left[\frac{1}{1 + (\alpha |\psi_m|)^n} \right]^m \quad (3)$$

where Θ is the degree of saturation, ψ_m is the matric potential [-cm], θ_s and θ_r are the saturated and residual water contents [cm³ cm⁻³], respectively, while α , m , and n ($m = 1 - 1/n$) are the shape parameters related to the pore-size distribution.

4.2.5 Hydraulic Conductivity:

Numerical analyses of transient water transport problems including infiltration, redistribution and evaporation have been widely used to determine hydraulic parameters

of soils with high accuracy (Hopmans et al., 2002; Ritter et al., 2003; Schwarzel et al., 2006; Si and Kachanoski, 2000; Šimůnek et al., 1998). Kosugi et al. (2001) effectively used inverse simulations to characterize the unsaturated water flow in four types of forest soils, indicating the Richards equation can describe the unsaturated water flow in organic forest floors.

In this study, the HYDRUS 1-D software package (Šimůnek et al., 2008) containing the inverse modeling capability was used to estimate the saturated hydraulic conductivity and unsaturated hydraulic conductivity function. An objective function, including deviations between measured and simulated variables (i.e., water contents) at different times during manure drying, was minimized. Optimization of the objective function was accomplished using the Levenberg-Marquardt nonlinear minimization (Marquardt, 1963). The unsaturated hydraulic conductivity function was estimated from three evaporation experiments during dairy manure drying using the HYDRUS 1-D inverse modeling function. Details of transient flow parameter optimization techniques are described by Hopmans et al. (2002). The van Genuchten hydraulic conductivity model (van Genuchten, 1980) describing unsaturated hydraulic conductivity is given by

$$K(h) = K_s \Theta^l \left[1 - \left(1 - \Theta^{1/m} \right)^m \right]^2 \quad (4)$$

$$m = 1 - 1/n, \quad n > 1 \quad (5)$$

where K_s is the saturated hydraulic conductivity [cm day^{-1}] and l is the pore-connectivity parameter. Schaap and Leji (2000) recommended using $l = -1$ for most soil textures.

Additional information on the numerical solution of the variably saturated flow equation and parameter optimization is given in Simunek et al. (2009).

4.2.6 Thermal Properties:

Manure is composed of solid, liquid and gaseous phases and its thermal conductivity (λ) is dependent primarily on the volume fractions of these components, the size and arrangement of the solid particles, and the interfacial contact between the solid and liquid phases (Jury and Horton, 2004). Thermal diffusivity (κ) is a parameter indicating the rate of change of temperature with time as the result of a thermal gradient. An inverse method for optimizing λ and κ of a porous medium from temperature rise measurements was implemented in the FORTRAN program, INV-WATFLX (Yang and Jones, 2009; Yang et al., 2013). Based on the Newton-Gauss-Levenberg-Marquard method, the INV-WATFLX code simultaneously fits temperature rise emitted from a central heater needle as sensed by four thermistor needles surrounding the heater. The theory of the analytical solution and implementation of the inverse parameter optimization method are given in Yang and Jones (2009) and Yang et al. (2013).

Bulk volumetric heat capacity (C) is defined as the ratio of λ over κ and was determined by fitting of λ and κ values. The bulk volumetric heat capacity of the dairy manure can also be estimated, based on the volume fraction and density of solid organic matter (som) and water (w) composing the dairy manure (the density of air is negligible in comparison with that of solid organic matter and water), given as

$$C_m = \rho_{som}\theta_{som}c_{som} + \rho_w\theta_w c_w \quad (6)$$

where C_m is the bulk volumetric heat capacity of manure [$\text{J m}^{-3} \text{ }^\circ\text{C}^{-1}$], ρ_{som} and ρ_w are the density of solid organic matter and water, respectively [kg m^{-3}], θ_{som} and θ_w are the volume fraction of solid organic matter and water, respectively [$\text{m}^3 \text{ m}^{-3}$], and c_{som} and c_w are the specific heat capacity per unit mass or specific heat of solid organic matter and

water, respectively [$\text{J kg}^{-1} \text{ }^\circ\text{C}^{-1}$]. The specific heat capacity of solid organic matter was estimated to be $1,925 \text{ J kg}^{-1} \text{ }^\circ\text{C}^{-1}$ (Hillel, 1998; Jury and Horton, 2004).

4.3 Materials and Methods

Techniques commonly applied for soil analysis were applied in this study to examine physical, hydraulic, and thermal properties of as-excreted dairy cattle manure. First, the relationship between θ_v and K_a was determined with TDR and the capacitance-based GS3 moisture sensor. Secondly, water potential of dairy manure was measured with the WP4-T Dewpoint Potentiometer to investigate the structural and functional relation between θ_v and ψ_w under equilibrium conditions. The ψ_s of the manure was then estimated and subtracted from ψ_w to generate the relationship between θ_v and ψ_m , which is known as the water characteristic or water retention curve. Third, K_s and the unsaturated hydraulic conductivity function $K(\theta_v)$ of the dairy manure samples was determined by means of an inverse solution simulation techniques as an alternative to direct measurement. Changes in manure moisture content during the drying process were numerically simulated with HYDRUS 1-D, a software package for simulating transient water movement in one-dimensional variably-saturated media with a robust inverse modeling capability. Lastly, the thermal properties λ , κ , and C of drying dairy manure were measured with PHPPs to investigate and identify relationships between these thermal properties and θ_v during the drying process.

4.3.1 Study Farm and Manure Sampling:

Dairy manure samples used in this study were collected from the Utah State University Caine Dairy Teaching and Research Center in Wellsville, UT (central

coordinates: 41° 39' 22" lat; 111° 53' 57" long). The milking cows were young, early lactation Holsteins with an average bodyweight of 771 kg and a growth rate of 0.45 kg d⁻¹ (1.00 lb d⁻¹). In a feedlot barn, the milking cows were fed a total mixed ration with an approximate crude protein content of 17% and a dry matter intake (DMI) of 27.67 kg cow⁻¹ d⁻¹ (61.0 lb cow⁻¹ d⁻¹). The average milk production for the herd was 40.82 kg cow⁻¹ d⁻¹. The manure samples were collected as excreted and mixed together in containers. Composite samples were then placed in one-gallon plastic heavy-duty zip lock bags approximately half full, squeezed to remove excess air, sealed and delivered to the lab directly (Peters et al., 2003).

4.3.2 TDR and GS3 Sensor Calibration in Dairy Manure:

The relationship between θ_v and K_a of manure was characterized at an ambient temperature of about 22 °C. The TDR sensing system included a TDR cable tester (1502B Metallic Cable Tester, Tektronix Inc., Beaverton, OR) connected via a coaxial multiplexer (SDMX50SP, Campbell Scientific Inc., Logan, UT) to three custom three-rod probes with 0.08-m long, 3.20-mm diameter rods and 12.0-mm rod spacing. The waveforms measured with the Tektronix TDR were captured and interpreted for travel time with WinTDR waveform analysis software (Or et al., 2004) on a personal computer. Three GS3 moisture sensors were connected to a data logger (CR1000, Campbell Scientific Inc., Logan, UT) and a personal computer for monitoring K_a . In addition to K_a , the output from the GS3 sensor included the sample temperature and electrical conductivity (EC).

Three manure samples were prepared for testing with the TDR system and three samples were prepared for testing with the GS3 sensor arrangement. The manure samples

were manually packed under gravity into 1,240 cm³ polyvinyl chloride (PVC) rings of 20.32 cm (8 in.) diameter and 3.81 cm (1.5 in.) height. They were carefully prepared with no external compaction applied to maintain in-situ conditions as much as possible. For both the TDR probes and the GS3 sensors, positioning at the center of the rings while packing the manure samples ensured that the fringing fields associated with each measurement was contained within the manure sample volume (Robinson et al., 2003; Vaz et al., 2013). Each sample was left to dry at room temperature over a period of 30 days. For the TDR system, sample masses were continuously recorded with a high resolution balance (GX-6100, A&D Engineering Inc., San Jose, CA) to determine the water content on dry weight basis. For the GS3 sensor setup, the sample masses were continuously monitored using 10 kg pre-calibrated load cells (ESP-10, Transducer Techniques Inc., Temecula, CA) connected to the Campbell Scientific CR1000 data logger, which interfaced with a personal computer. Care was taken during packing to ensure that there was no air gap between the sensor needles and the manure samples. At the beginning and end of the experiment, the lengths, widths, and volumes of the manure and its subsequent shrunken state were estimated using the sand displacement method (Boelter, 1962). Ultimately, the equation used by Schaap et al. (1997) for the organic forest soils was fitted to the data measured by both TDR system and GS3 sensor to establish general calibration equations for manure.

The final θ_v and bulk densities were determined by drying the manure samples at 70 °C for 48 hours to dry while minimizing oxidation of organic material (Peters et al., 2003; Schaap et al., 1997). The oven-dry bulk density of the dairy manure samples was determined to be 0.15 ± 0.012 g cm⁻³. Hafez et al. (1974) reported air-dry bulk density of

dairy manure of 0.23 g cm^{-3} , somewhat greater than the oven-dried density measured in this study, which is not surprising given their air-dry weight likely had more residual water resulting in overestimation of the dry bulk density. The particle density of dairy feces was previously reported as 1.44 g cm^{-3} by Sobel (1966). Hafez et al. (1974) reported the particle density of dairy manure and beef cattle manure as 1.43 and 1.44 g cm^{-3} , respectively. Using the particle density of 1.44 g cm^{-3} , the solid phase volume of dairy manure samples can be estimated as approximately 0.104.

4.3.3 Manure Water Retention Curve:

The chilled mirror WP4-T dewpoint potentiometer with an accuracy of $\pm 0.1 \text{ MPa}$ from 0 to -10 MPa and $\pm 1\%$ from -10 to -300 MPa was used in this study to measure ψ_w in laboratory manure specimens. Prior to every measurement, the WP4-T was turned on for 30 minutes as a recommended warm-up period and calibrated with a verification standard, 0.5 mol kg^{-1} potassium chloride (KCl) salt solution, at $25 \text{ }^\circ\text{C}$. Two measurements were read to ensure that both readings were within the range of $-2.22 \pm 0.10 \text{ MPa}$ according to the recommended calibration and verification procedures (Decagon Device Inc., 2007).

Triplicate mixed cattle manure samples were measured to generate the water retention curve for as-excreted dairy cattle manure. In each trial, the suite of water potential measurements included six sub-samples prepared from mixed cattle manure samples. The manure sample were equilibrated at a constant room temperature ($\approx 22^\circ\text{C}$) in a sample holder at various potentials for different amounts of time by allowing the water to evaporate from as-excreted conditions until the samples were completely air-dry. The sample holder cup was 1.1-cm in height and 4-cm in diameter, being filled half-full

with the bottom of the cup entirely covered with the manure samples. The samples were weighed and then placed into the WP4-T and the water potential was measured and recorded. For each water potential reading, three replicates were recorded. The samples were then removed from the WP4-T sample chamber and immediately covered with the sample holder lid preventing evaporation of water. At the end of each trial, the samples were immediately oven dried (70 °C for 24 h) for determination of θ_v .

We paired ψ_m with the measured θ_v to obtain the water retention curve. A nonlinear regression algorithm (Marquardt, 1963) was performed to estimate the model parameters from the measurement data.

4.3.4 Estimated K_s and $K(\theta_v)$ of Dairy Manure using HYDRUS 1-D

The van Genuchten-Mualem model (Mualem, 1976; van Genuchten, 1980) was applied in the HYDRUS 1-D inverse solution simulations. The hydraulic properties, including θ_r , θ_s , α and n in the water retention function, obtained from the laboratory measurement, were used as the model input parameters, while K_s was assigned as the unknown parameter. Daily evaporation data and changes in volumetric water content, monitored from three evaporation experiments of dairy manure drying in a constant room temperature (≈ 22 °C), previously conducted to develop the GS3 sensor calibration equation, were used in establishment of the inverse solution simulations. The monitored daily evaporation rates (Figure 4-1) were used as time variable boundary conditions. The measured θ_v , obtained from the GS3 moisture sensors, were input into the simulation as the observed parameter to which the objective function in HYDRUS 1-D fits the unknown K_s and $K(\theta_v)$ in order to identify the optimal value of these unknowns.

4.3.5 Thermal Properties of Dairy Manure:

Three major thermal properties were investigated during the drying process of manure using PHPPs. The PHPP includes a central heater needle surrounded by an orthogonal arrangement of four thermistor needles (Figure 4-2). Based on the Gauss-Newton-Levenberg-Marquardt method, the thermal properties were determined using an analytical solution that simultaneously fits time series of temperature measurements from each of the four thermistor needles. Additional discussions on the PHPP and the inverse fitting method for determination of the thermal properties are given in Sakai et al.(2011), Yang and Jones (2009), and Yang et al. (2013).

The PHPPs simultaneously determined thermal properties of dairy cattle manure, namely, thermal conductivity (λ), thermal diffusivity (κ), and volumetric heat capacity (C) during the laboratory drying process. The PHPP consists of one 2.1-mm (OD) line-source heater needle and four 1.27-mm (OD) parallel thermistor needles with a physical center to center spacing of 6.5 mm (Figure 4-2). The two pairs of thermistor needles are orthogonally arranged equidistant from the heater needle. The precision and stability of the temperature measurements of the PHPPs are essential for determination of the thermal properties of the manure samples. To evaluate the precision of the thermistors used in the PHPPs, the PHPPs measured temperatures in an insulated container filled with saturated sand with 5-second interval reading for 10 minutes. The resulting temperatures were consistent, with less than 0.001°C fluctuation.

Dairy manure samples were prepared in triplicate for monitoring the thermal properties using the PHPPs. Each sample was prepared in similar procedures to those described in the TDR and GS3 sensor calibrations. The PHPP was inserted at the middle

height of the PVC ring, prior to filling the ring with the manure sample. A Decagon Devices GS3 water content sensor was buried in the sample at the same depth. After the PVC ring was fully filled with the manure sample, the sample then was left to dry in a greenhouse with temperature controls. Attention was given to packing the manure around the sensor to avoid air gaps between the PHPP needles and between the needles of the GS3 sensors. The PHPP and GS3 sensor were connected to and communicated with a data logger (Model CR1000, Campbell Scientific, Inc., Logan, UT) via SDI-12 communications. The PHPP includes an onboard microcontroller, which is programmed to control the heat source needle to generate a heat pulse of 8 seconds and the thermistor needles to measure temperature for a period of 60 seconds. Initial temperature was measured immediately prior to applying the heat input. The microcontroller processes onboard optimization of λ and κ values using the measurements of the temperature rise with additional computations performed on the data logger (Sakai et al., 2011; Yang and Jones, 2009; Yang et al., 2013).

4.3.6 Statistical Analyses:

The measured data presented in this study were statistically analyzed with the general statistical analysis module of the R statistical software package version 2.14.1 (R Development Core Team, 2011). For all analyses, a p-value of 0.05 or smaller was considered significant.

4.4 Results and Discussions

4.4.1 GS3 Sensor Volume of Influence:

Determination of zone or volume of influence for EM sensors (i.e., the volume generating most of the medium response) is essential to better understand the response of a medium to the sensor output. The approximate volume of influence for the GS3 sensor was determined according to the method described in Druyts et al. (2010) and Jones et al. (2005). In brief, the volume of influence for the GS3 sensor was estimated by observing K_a output from the sensor with a variety of probe orientations measured through a range of immersion depths in water i.e., in air, partially submerged in water, and completely submerged in water. Due to the strong contrast between the permittivity of water ($K_a \approx 80$) and air ($K_a \approx 1$), the layer of influence was estimated by initially placing the sensor in the air at a height above the water and gradually submerging the sensor into the water until K_a of 80 was reached at a specific depth of water. Ten independent replicate measurements were recorded for each depth and sensor position arrangement to determine the assay statistics.

The volume or zone of influence of the GS3 sensor was estimated in both axial (vertically along the sensor, y-axis in Figure 4-3) and radial (perpendicular to the sensor, x-axis and z-axis in Figure 4-3) components. In normal applications of soil moisture measurements, the axial sensibility establishes the sensor's depth resolution, and the radial sensitivity determines the susceptibility to lateral heterogeneities (Dean et al., 1987). The range and shape of the primary volume of influence predominantly depend on the sensor's physical geometry (Starr and Paltineanu, 2002). We found the axial zone of influence of the GS3 sensor to be 6.50 cm, originated at the inside face of the sensor, and

the radial zone of influence to be primarily within 6.30 cm, centered at the middle prong (Figure 4-3). The volume of influence was then approximated as 400 cm³, 33% greater than specified by the manufacturer. Apparent ranges of sensitivity of the dielectric permittivity (K_a) and EC determined with the sensor were similar, due to the linear relationship between these two parameters, programmed in the sensor microprocessor (Decagon Device Inc., 2012). The results suggest the significance of the proper sensor installation to ensure intimate contact between the dairy manure sample and sensor, and the importance in obtaining gravimetric samples within the sensor's zone of primary influence for the sensor calibrations. It is critical to calibrate the sensor in the same installation mode it is anticipated it will be used. For example, if the sensor will be inserted into the sample surface with the head left above the sample surface, the calibration must be performed similarly. On the other hand, if the sensors are to be buried completely in the sample, as in this study, the calibration should be performed similarly. The reason for this lies in the sensitivity of the GS3 to dielectric of the surrounding medium that extends above/behind the sensor head as seen in Figure 4-3.

4.4.2 Cattle Manure Dielectric - Moisture Content Relationships:

The GS3 sensors and TDRs were calibrated in dairy manure to establish a generic calibration equation identifying the correlation between K_a measured with the sensors and θ_v . All manure samples showed considerable shrinkage both in depth and diameter; however, no air gaps between the sensor needles and manure samples were found, confirming the validity of the measurements. Figure 4-4 presents all measurements performed by both GS3 sensors and TDRs, each with three replicate samples. Overall, the K_a outputs among three dairy manure samples for each measurement technique were

highly consistent. The deviation of the measurement between the GS3 sensor and TDR is anticipated owing to the different measurement frequencies (i.e., order of magnitude difference (Kelleners et al., 2005)) as illustrated in Figure 4-4. This deviation grows with increasing θ_v , which likely results from the high EC of the dairy manure (≈ 4.50 dS/m) which increases with θ_v . The TDR signal can become completely attenuated as the highly saline manure samples approach saturation (Jones et al., 2002; Mojid et al., 2003).

Table 4-1 lists the parameters fitted to the measurements and their estimation accuracy, based on the mathematical expression used by Schaap et al. (1997) for organic forest soils. In general, the fitting parameters in this study indicate reliable water content estimates with high coefficients of determination (R^2) values from both TDR and GS3 sensor measurements. It is worth noting that the calibration methods were performed in a constant room temperature ($\approx 22^\circ\text{C}$), whereas under field conditions diurnal fluctuations in temperature and associated changes in EC in addition to variable near-surface water content are common, as observed with many methods of measuring soil water (Jones et al., 2005; Or and Wraith, 1999; Starr and Paltineanu, 1998; Wraith and Or, 1999). Techniques for correcting EC and temperature sensitivity on capacitance measurements have been reported in several studies (Cobos and Campbell, 2007; Fares et al., 2009; Kelleners et al., 2004; Saito et al., 2013).

4.4.3 Dairy Manure Water Retention:

Figure 4-5(a) illustrates the water retention curve of dairy cattle manure measured with the WP4-T dew point potentiometer. The osmotic potential of the saturation extracts of 18 replicates samples estimated using Eq. (2), were $-1,380$ cm with a standard deviation of -54 cm, indicating low variability among sample replicates. The potential ψ_s

contributes substantially to ψ_w of the dairy manure samples; therefore, it was necessary to account for its contribution to the measured water potential and remove its effect, yielding only the matric potential used in developing the water retention curves. Due to the high porosity of dairy manure, θ_s of the manure samples was much greater than that of mineral soils, which is in agreement with that of other organic materials. Figure 4-5(b) shows the water retention curve of dairy manure in comparison with *Sphagnum* peat (high bog peat) and reed peat (fen peat) materials (Paivanen, 1973). The relationship between θ_v and ψ_m in organic matter depends on degree of decomposition and botanical composition of residues (Jan et al., 2002).

The accuracy of the water retention curve in the low matric potential range is limited due to the relatively high ψ_s of the manure samples near saturation together with diminishing measurement resolution of the WP4-T dewpoint potentiometer near saturation (i.e., 0.01MPa). Measurements near saturation that may be made by using other techniques can determine matric potential in this range (e.g., hanging water column, pressure plate, Tempe Cell, tensiometer). Estimated van Genuchten model parameters derived from the optimization algorithm compared with the previous studies that investigated those for peat soils are listed in Table 4-2. Schwarzel et al. (2006) applied inverse parameter estimations to determine the hydraulic properties of peat soils of humified organic peat soils on the surface layer (<15 cm) and Da Silva et al. (1993) reported the hydraulic properties of organic peat soils in drying process. The parameters reported in these two studies are nearly the same range of those for the dairy manure samples found in this study. However, Naasz et al. (2005) reported the hydraulic parameters θ_s , α , and n for drying organic peat soils in a different range. The parameters α

and n , which are different from other studies, likely resulted from different pedogenetic processes of the soil samples and parameter fitting criteria (Schwarzel et al., 2006).

Because the shape of the water retention curve is dependent on the medium structure, especially in the low matric potential range, it is interesting that the effect of the manure's surface crust formation and shrinkage can potentially change the water retention characteristic by reduction of the total porosity, particularly the volume of the large pores. Consequently, the manure θ_s and the initial decrease rate of water content are diminished. Some of the original large pores are forced into becoming intermediate-size pores due to the shrinkage, creating more intermediate-size pores than the initial condition. While the intermediate-size pores are anticipated to increase, the micro pores remain unaffected, making the water retention curve for manure's surface crust in the high matric potential range unchanged from the original shape. Further investigation is needed to better understand and characterize manure's surface crust and its dynamic properties.

4.4.4 K_s and $K(\theta_v)$ of Dairy Manure:

The inverse simulation with HYDRUS-1D provided estimates for K_s and $K(\theta_v)$ of dairy manure. The inverse solution yielded good agreement in θ_v when compared between the simulated and measured values as illustrated in Figure 4-6(a) and (b). Table 4-3 summarizes the estimation of dairy manure K_s using the HYDRUS-1D inverse solution simulation. Figure 4-6 (c) illustrates the relationship between θ_v and $K(\theta_v)$ for dairy manure, based on the van Genuchten-Mualem model (van Genuchten, 1980). The hydraulic conductivity function, derived by optimizing changes of θ_v from three dairy manure samples in the evaporation experiment, effectively characterized the

vertical transient water flow in dairy manure. The results support the validity of applying the Richards equation to characterize the unsaturated water flow in dairy manure, similar to organic forest (Kosugi et al., 2001) and organic peat soils (Da Silva et al., 1993; Naasz et al., 2005; Schwarzel et al., 2006). On the other hand, Ingram et al. (1974) and Rycroft et al. (1975a; 1975b) observed the “non-Darcian” behavior of organic peat soils, where Darcy’s law is not valid in organic peat soils with a high degree of decomposition in addition to issues of hydrophobicity, which complicate things further. The values of K_s for organic peat soils were reported over a wide range. Schwarzel et al. (2006) estimated K_s of organic peat soils in the surface layer to be $33.50 \text{ cm day}^{-1}$. Naasz et al. (2005) reported the value of K_s of drying organic peat as $3,326.4 \text{ cm day}^{-1}$. Nagare et al. (2013) measured K_s of organic peat in a laboratory using split-container and wax method and found K_s in a range between 2,100 and 31,400 cm day^{-1} .

It should be noted that the estimated K_s represents the “effective” saturated hydraulic conductivity of the dairy manure samples. This is complicated by the additional substances in the manure that increase liquid viscosity and form strong bonds upon drying. As-excreted dairy manure is prone to variable surface crust formation and therefore likely has a variation in K_s with drying. Similar to soil crusts, the crust layer of dairy manure contains higher bulk density and lower porosity than the underlying manure due to a higher shrinkage rate together with sodium and total salt contents of manure, which consequently may result in a surface saturated hydraulic conductivity several orders of magnitude less than in the underlying manure (Miller and Radcliffe, 1992). Another uncertainty that was not considered in the inverse solution simulation for the evaporation experiment is potential changes in pore space geometry due to clogging of

pores by gas bubbles and other by-products of organic matter decomposition through anaerobic microbiological processes in manure samples. Prediction of manure surface crust characteristic with associated changes in pore spaces from gas bubbles is difficult because of the random factors in formation and development processes. Further investigations are warranted to more accurately characterize manure surface crust and pore space dynamics in drying and wetting dairy manure.

4.4.5 Thermal Properties:

Figure 4-7(a) – (c) illustrates fitted values of λ and κ in addition to computed values of C as a function of θ_v . Table 4-4 shows the parametric expressions, fitted parameters, and R^2 for the relationships between the thermal properties and θ_v . Generally, λ and C decreased linearly with decreasing θ_v (Figure 4-7(a) and (b)), while κ decreased slowly at the beginning of the drying process, then decreased rapidly once θ_v was below $0.30 \text{ m}^3 \text{ m}^{-3}$ (Figure 4-7(c)).

The values of the dairy manure λ were found to be between 0.52 and $0.08 \text{ W m}^{-1} \text{ }^\circ\text{C}^{-1}$ from saturation to dry conditions, consistent with the values reported in previous studies (Table 4-5). The correlation between λ and θ_v , illustrated in Figure 4-7(a), supports the strong linear relationships of the two parameters, reported in previous studies (Ahn et al., 2009; Chandrakanthi et al., 2005; Nayyeri et al., 2009; Opoku et al., 2006). In addition to θ_v , Nayyeri et al. (2009) demonstrated the first order linear model of the temperature effect on thermal properties of dairy cattle manure.

The value of the dairy manure C at the saturation point was determined as approximately $3.95 \text{ MJ m}^{-3} \text{ }^\circ\text{C}^{-1}$, close to that of water ($4.18 \text{ MJ m}^{-3} \text{ }^\circ\text{C}^{-1}$). This is due to the high porosity of dairy manure (≈ 0.90). Similar to the relationship between λ and θ_v ,

there is a strong linear relationship between C and θ_v . The bulk volumetric heat capacity of manure was determined based on the measured λ and κ . The small change of κ during the entire manure drying process (approximately within $0.0003 \text{ cm}^2 \text{ s}^{-1}$) did not significantly modify the regression form between λ and θ_v . As a result, the regression form identifying the relation between C and θ_v was identical to the expression for λ and θ_v . These results were in agreement with previous thermal property determinations, indicating the linear regression between C and θ_v (Ahn et al., 2009; Nayyeri et al., 2009; Opoku et al., 2006; Yang et al., 2002).

While λ and θ_v are strongly linearly correlated, the relation between κ and θ_v was well approximated with the “plateau” curve expression as depicted in Figure 4-7(c). The parametric expressions, including parameters, are listed in Table 4-4. The change of κ during the manure drying process covers only a small range, approximately from 0.0013 (saturation) to $0.0010 \text{ cm}^2 \text{ s}^{-1}$ (dry). Perhaps it is because of this narrow range that previous studies have failed to identify a specific relationship between κ and θ_v , where these include ascending, descending, and mixed trends (Bristow, 1998; Iwabuchi et al., 1999; Labance et al., 2006; Opoku et al., 2006).

The accuracy of the PHPPs in estimating the thermal properties was assessed through a comparison of θ_v derived from Eq. (6) with θ_v measured by the GS3 sensors. The specific heat capacity of solid organic matter was taken as $1,925 \text{ J kg}^{-1} \text{ }^\circ\text{C}^{-1}$ (Hillel, 1998; Jury and Horton, 2004) and the dry bulk density was 0.15 g cm^{-3} (90% porosity). The regression relationship (Figure 4-8) suggests strong agreement between θ_v estimates derived from the GS3 sensors and those obtained with the PHPP method ($R^2 = 0.944$ and $RMSE = 0.0524 \text{ cm}^3 \text{ cm}^{-3}$). As illustrated in Figure 4-8, the regression equation indicates

a slight bias towards greater overestimation of θ_v by the PHPP method at lower water content. However, hypothesis tests show that the difference of θ_v obtained by both methods was found to be insignificant (p -value = 0.362). This well-correlated relationship verifies the accuracy of the thermal properties determined by the PHPPs and the dry bulk density of dairy manure presented in this study.

4.5 Summary and Conclusions

This study focused on the fundamental physical, hydraulic, and thermal properties of dairy manure that primarily affect the transport of liquid water and gas within the manure. Numerical modeling of transient water flow in cattle manure requires an accurate estimation of a number of physical and hydraulic parameters, including the water retention characteristic, K_s , and $K(\theta_v)$. Measurement techniques commonly applied in soil science were applied to determine physical properties of as-excreted dairy manure, including the empirical relationship between K_a and θ_v . The uncertainties of the measurements were anticipated from the shrinkage phenomenon during the drying process. The liquid water retention characteristic for cattle manure, determined based on volumetric measurements and the chilled-mirror dewpoint technique, was found to be similar to that of organic peat soils. Inverse analysis of $K(\theta_v)$, using the developed water retention characteristic and laboratory evaporation experiment, yielded reasonable results, demonstrating strong support for the hypothesis that the Richards equation can describe hydrodynamic processes taking place in dairy manure relevant to natural drying processes. The effects of surface crust formation and shrinkage, which are likely to occur variably upon drying, potentially modify the water retention and hydraulic conductivity functions due to high moisture content and high porosity of as-excreted manure. Further

work is needed to characterize the manure's surface crust formation to more completely understand key processes (e.g., gas emissions, nutrient leaching) impacting the environment and leading to a more sustainable system.

The thermal properties of λ , κ , and C were determined during the course of manure drying using PHPPs. Thermal properties of λ and C exhibited strong linear correlation with decreasing θ_v . Although κ also decreased with decreasing θ_v , it showed a more complex regression form. The accuracy and agreement of the thermal properties determined was assessed. The results suggested a reliable prediction of θ_v using the PHPPs, indicating well-estimated physical and thermal properties of dairy manure. The resulting thermal properties of dairy manure are likely to be used for development of heat transport models to identify the optimal conditions for manure composting processes as well as for prediction of manure water content and the movement of solutes and water from manure sources, in addition to microbial activity and gas generation. Overall, the results presented here provide a solid foundation upon which future research can build in better modeling and understanding dairy cow manure processes that impact the environment.

References

- Achkari-Begdouri A., Goodrich P.R. (1992). Bulk density and thermal properties of Moroccan dairy cattle manure. *Bioresource Technology* 40: 225-233. DOI: [http://dx.doi.org/10.1016/0960-8524\(92\)90147-P](http://dx.doi.org/10.1016/0960-8524(92)90147-P).
- Ahn H.K., Sauer T.J., Richard T.L., Glanville T.D. (2009). Determination of thermal properties of composting bulking materials. *Bioresource Technology* 100: 3974-3981. DOI: <http://dx.doi.org/10.1016/j.biortech.2008.11.056>.
- Assouline S. (2004). Rainfall-induced soil surface sealing. *Vadose Zone Journal* 3(2): 570-591. DOI: 10.2136/vzj2004.0570.

- Azevedo J. (1974). Farm animal manures: An overview of their role in the agricultural environment, University of California Agricultural Experiment Station, Berkeley, CA.
- Boelter D.H. (1962). A study of some physical properties of several peat materials and their relation to field water conditions in the peat bog, University of Minnesota, Minneapolis, MN.
- Boyd C.E. (1995). Bottom soils, sediment and pond aquaculture, Chapman & Hall, New York, NY.
- Boyd C.E. (2000). Water quality: An introduction, Kluwer Academic Publishers, Norwell, MA.
- Bristow K.L. (1998). Measurement of thermal properties and water content of unsaturated sandy soil using dual-probe heat-pulse probes. *Agricultural and Forest Meteorology* 89: 75-84. DOI: [http://dx.doi.org/10.1016/S0168-1923\(97\)00065-8](http://dx.doi.org/10.1016/S0168-1923(97)00065-8).
- Campbell G., Smith D., Teare B. (2007). Application of a dew point method to obtain the soil water characteristic. In *Experimental unsaturated soil mechanics*, Springer proceedings in physics 112. Springer, Heidelberg, Germany. pp. 71-77.
- Cater M., Parkin G., Culley J., Hao X., Ball B. (2007). Soil density and porosity, soil sampling and methods of analysis, Second Edition, CRC Press, Boca Raton, FL.
- Chandranthi M., Mehrotra A.K., Hettiaratchi J.P.A. (2005). Thermal conductivity of leaf compost used in biofilters: An experimental and theoretical investigation. *Environmental Pollution* 136: 167-174. DOI: <http://dx.doi.org/10.1016/j.envpol.2004.09.027>.
- Chen Y., Avnimelech Y. (1986). The role of organic matter in modern agriculture, Springer, New York, NY.
- Chen Y.R. (1983). Thermal properties of beef cattle manure. *Agricultural Wastes* 6: 13-29. DOI: [http://dx.doi.org/10.1016/0141-4607\(83\)90003-3](http://dx.doi.org/10.1016/0141-4607(83)90003-3).
- Chenu C., Roberson E.B. (1996). Diffusion of glucose in microbial extracellular polysaccharide as affected by water potential. *Soil Biology and Biochemistry* 28:877-884. DOI: [http://dx.doi.org/10.1016/0038-0717\(96\)00070-3](http://dx.doi.org/10.1016/0038-0717(96)00070-3).

- Chertkov V.Y. (2013). Shrinkage anisotropy characteristics from soil structure and initial sample/layer size. *Geoderma* 200–201: 1-8. DOI: <http://dx.doi.org/10.1016/j.geoderma.2013.02.009>.
- Christian T., Schneider R.J., Färber H.A., Skutlarek D., Meyer M.T., Goldbach H.E. (2003). Determination of antibiotic residues in manure, soil, and surface waters. *Acta Hydrochimica et Hydrobiologica* 31: 36-44. DOI: 10.1002/aheh.200390014.
- Cobos D., Campbell C. (2007). Correcting temperature sensitivity of ECH2O soil moisture sensors, Application note, Decagon Devices, Pullman, WA.
- Da Silva F.F., Wallach R., Chen Y. (1993). Hydraulic properties of sphagnum peat moss and tuff (scoria) and their potential effects on water availability. *Plant and Soil* 154: 119-126. DOI: 10.1007/bf00011080.
- Davis J.L., Chudobiak W.J. (1975). In situ meter for measuring relative permittivity of soils, GSC Paper 75–1A, Department of Energy, Mines, and Resources, Geological Survey of Canada, Ottawa, ON, Canada. pp. 75-79.
- Dean T.J., Bell J.P., Baty A.J.B. (1987). Soil moisture measurement by an improved capacitance technique, Part I. Sensor design and performance. *Journal of Hydrology* 93: 67-78. DOI: [http://dx.doi.org/10.1016/0022-1694\(87\)90194-6](http://dx.doi.org/10.1016/0022-1694(87)90194-6).
- Decagon Device Inc. (2007). WP4 dewpoint potentiometer for models WP4 and WP4-T operator's manual version 5, Decagon Device, Pullman, WA.
- Decagon Device Inc. (2012). GS3 water content, EC, and temperature sensors operator's manual version 1, Decagon Device, Pullman, WA.
- Del Grosso S.J., Parton W.J., Mosier A.R., Walsh M.K., Ojima D.S., Thornton P.E. (2006). DAYCENT national-scale simulations of nitrous oxide emissions from cropped soils in the United States. *Journal of Environmental Quality* 35: 1451-60. DOI: 10.2134/jeq2005.0160.
- Druyts P., Craeye C., Acheroy M. (2010). Volume of influence for magnetic soils and electromagnetic induction sensors. *Geoscience and Remote Sensing, IEEE Transactions on* 48: 3686-3697. DOI: 10.1109/tgrs.2010.2048573.
- Fares A., Safeeq M., Jenkins D.M. (2009). Adjusting temperature and salinity effects on single capacitance sensors. *Pedosphere* 19:588-596. DOI: [http://dx.doi.org/10.1016/S1002-0160\(09\)60153-3](http://dx.doi.org/10.1016/S1002-0160(09)60153-3).

- Gao J., Ren T., Gong Y. (2006). Correcting wall flow effect improves the heat-pulse technique for determining water flux in saturated soils. *Soil Science Society of America Journal* 70:711-717. DOI: 10.2136/sssaj2005.0174.
- Gee G.W., Campbell M.D., Campbell G.S., Campbell J.H. (1992). Rapid measurement of low soil water potentials using a water activity meter. *Soil Science Society of America Journal* 56: 1068-1070. DOI: 10.2136/sssaj1992.03615995005600040010x.
- Gerba C.P., Smith J.E. (2005). Sources of pathogenic microorganisms and their fate during land application of wastes. *Journal of Environmental Quality* 34: 42-48. DOI: 10.2134/jeq2005.0042.
- Grosso S.J.D., Parton W.J., Ojima D.S., Keough C.A., Riley T.H., Mosier A.R. (2008). DAYCENT simulated effects of land use and climate on county level N loss vectors in the USA, in: J. L. Hatfield and R. F. Follett (Eds.), *Nitrogen in the environment: sources, problems, and management*, Second edition, Academic Press/Elsevier, Amsterdam, Boston.
- Hafez A.A.R., Azevedo J., Rubin J., Stout P.R. (1974). Physical properties of farm animal manures. Bulletin 867, University of California Agricultural Experiment Station, Berkeley, CA.
- Ham J.M., Benson E.J. (2004). On the construction and calibration of dual-probe heat capacity sensors. *Soil Science Society of America Journal* 68: 1185-1190. DOI: 10.2136/sssaj2004.1185.
- Heitman J.L., Basinger J.M., Kluitenberg G.J., Ham J.M., Frank J.M., Barnes P.L. (2003). Field evaluation of the dual-probe heat-pulse method for measuring soil water content. *Vadose Zone Journal* 2: 552-560. DOI: 10.2136/vzj2003.5520.
- Hillel D. (1998). *Environmental soil physics*. Academic Press, San Diego, CA.
- Hopmans J.W., Simunek J., Romano N., Durner W. (2002). Inverse modeling of transient water flow. In: J. H. Dane and G. C. Topp, Editors, *Methods of soil analysis: Part 4, Physical methods*, Soil Science Society of America, Madison, WI. pp. 963-1008.
- Horn R., Smucker A. (2005). Structure formation and its consequences for gas and water transport in unsaturated arable and forest soils. *Soil and Tillage Research* 82: 5-14.

- Houkom R.L., Butchbaker A.F., Brusewitz G.H. (1974). Effect of moisture content on thermal diffusivity of beef manure. *TRANSACTIONS of the ASAE* 17: 973-977.
- Ingram H.A.P., Rycroft D.W., Williams D.J.A. (1974). Anomalous transmission of water through certain peats. *Journal of Hydrology* 22: 213-218. DOI: [http://dx.doi.org/10.1016/0022-1694\(74\)90076-6](http://dx.doi.org/10.1016/0022-1694(74)90076-6).
- Iwabuchi K., Kimura T., Otten L. (1999). Effect of volumetric water content on thermal properties of dairy cattle feces mixed with sawdust. *Bioresource Technology* 70: 293-297. DOI: [http://dx.doi.org/10.1016/S0960-8524\(99\)00038-3](http://dx.doi.org/10.1016/S0960-8524(99)00038-3).
- Jan S., Tomasz G., Tomasz B., Ryszard O. (2002). Water-related physical attributes of organic soils, organic soils and peat materials for sustainable agriculture, CRC Press, Boca Raton, FL.
- Jones S.B., Wraith J.M., Or D. (2002). Time domain reflectometry measurement principles and applications. *Hydrological Processes* 16: 141-153. DOI: 10.1002/hyp.513.
- Jones S.B., Blonquist J.M., Robinson D.A., Rasmussen V.P., Or D. (2005). Standardizing characterization of electromagnetic water content sensors. *Vadose Zone Journal* 4: 1048-1058. DOI: 10.2136/vzj2004.0140.
- Jury W.A., Horton R. (2004). *Soil physics*. John Wiley & Sons, Inc., Hoboken, NJ.
- Kamai T., Tuli A., Kluitenberg G.J., Hopmans J.W. (2008). Soil water flux density measurements near 1 cm d⁻¹ using an improved heat pulse probe design. *Water Resources Research* 44: W00D14. DOI: 10.1029/2008wr007036.
- Kelleners T.J., Robinson D.A., Shouse P.J., Ayars J.E., Skaggs T.H. (2005). Frequency dependence of the complex permittivity and its impact on dielectric sensor calibration in soils. *Soil Science Society of America Journal* 69: 67-76.
- Kelleners T.J., Soppe R.W.O., Robinson D.A., Schaap M.G., Ayars J.E., Skaggs T.H. (2004). Calibration of capacitance probe sensors using electric circuit theory. *Soil Science Society of America Journal* 68: 430-439. DOI: 10.2136/sssaj2004.4300.
- Klop G., Velthof G.L., van Groenigen J.W. (2012). Application technique affects the potential of mineral concentrates from livestock manure to replace inorganic nitrogen fertilizer. *Soil Use and Management* 28: 468-477. DOI: 10.1111/j.1475-2743.2012.00434.x.

- Knight J.H., Kluitenberg G.J., Kamai T., Hopmans J.W. (2012). Semianalytical solution for dual-probe heat-pulse applications that accounts for probe radius and heat capacity. *Vadose Zone Journal* 11(2). DOI: 10.2136/vzj2011.0112.
- Kosugi K., Mori K., Yasuda H. (2001). An inverse modeling approach for the characterization of unsaturated water flow in an organic forest floor. *Journal of Hydrology* 246: 96-108. DOI: [http://dx.doi.org/10.1016/S0022-1694\(01\)00366-3](http://dx.doi.org/10.1016/S0022-1694(01)00366-3).
- Labance S.E., Heinemann P.H., Graves R.E., Beyer D.M. (2006). Evaluation of the effects of forced aeration during phase 1 mushroom substrate preparation: Part 1. Model development. *Transactions of the ASAE* 49: 167-174.
- Liang C., Das K.C., McClendon R.W. (2003). The influence of temperature and moisture contents regimes on the aerobic microbial activity of a biosolids composting blend. *Bioresource Technology* 86: 131-137. DOI: [http://dx.doi.org/10.1016/S0960-8524\(02\)00153-0](http://dx.doi.org/10.1016/S0960-8524(02)00153-0).
- Liu J., Xu X.-h., Li H.-t., Xu Y. (2011). Effect of microbiological inocula on chemical and physical properties and microbial community of cow manure compost. *Biomass and Bioenergy* 35: 3433-3439. DOI: <http://dx.doi.org/10.1016/j.biombioe.2011.03.042>.
- Longhurst B., Houlbrooke D., Orchiston T., Muirhead R. (2012). Characterizing dairy manures and slurries, In: L. D. Currie and C. L. Christensen, Editors, *Advanced nutrient management: Gains from the past - goals for the future*. Occasional Report No. 25. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand.
- Malicki M.A., Plagge R., Roth C.H. (1996). Improving the calibration of dielectric TDR soil moisture determination taking into account the solid soil. *European Journal of Soil Science* 47: 357-366. DOI: 10.1111/j.1365-2389.1996.tb01409.x.
- Marquardt D.W. (1963). An algorithm for least-squares estimation of nonlinear parameters. *Journal of the Society for Industrial and Applied Mathematics* 11: 431-441. DOI: 10.2307/2098941.
- Miller F.C. (1992). Composting as a process based on the control of ecologically selective factors. In: J. F. Blaine Metting, Editor, *Soil microbial ecology: Applications in agricultural and environmental management*, Marcel Dekker, Inc., New York, NY. pp. 515-544.

- Miller W.P., Radcliffe D.E. (1992). Soil crusting in the southeastern United States. In: M. E. Sumner and B. A. Stewart, Editors, *Soil crusting: Chemical and physical processes*, Lewis Publishers, Boca Raton, FL. pp. 233-266.
- Mojid M.A., Wyseure G.C.L., Rose D.A. (2003). Electrical conductivity problems associated with time-domain reflectometry (TDR) measurement in geotechnical engineering. *Geotechnical & Geological Engineering* 21: 243-258. DOI: 10.1023/a:1024910309208.
- Mualem Y. (1976). A new model for predicting the hydraulic conductivity of unsaturated porous media. *Water Resources Research* 12: 513-522. DOI: 10.1029/WR012i003p00513.
- Naasz R., Michel J.C., Charpentier S. (2005). Measuring hysteretic hydraulic properties of peat and pine bark using a transient method. *Soil Science Society of America Journal* 69: 13-22. DOI: 10.2136/sssaj2005.0013.
- Nagare R., Schincariol R., Mohammed A., Quinton W., Hayashi M. (2013). Measuring saturated hydraulic conductivity and anisotropy of peat by a modified split-container method. *Hydrogeology Journal* 21: 515-520. DOI: 10.1007/s10040-012-0930-7.
- Nayyeri M.A., Kianmehr M.H., Arabhosseini A., Hassan-Beygi S.R. (2009). Thermal properties of dairy cattle manure. *International Agrophysics* 23: 359-366.
- Nennich T.D., Harrison J.H., VanWieringen L.M., Meyer D., Heinrichs A.J., Weiss W.P., St-Pierre N.R., Kincaid R.L., Davidson D.L., Block E. (2005). Prediction of manure and nutrient excretion from dairy cattle. *Journal of Dairy Science* 88: 3721-3733. DOI: [http://dx.doi.org/10.3168/jds.S0022-0302\(05\)73058-7](http://dx.doi.org/10.3168/jds.S0022-0302(05)73058-7).
- Oleson K.W., Niu G.Y., Yang Z.L., Lawrence D.M., Thornton P.E., Lawrence P.J., Stöckli R., Dickinson R.E., Bonan G.B., Levis S., Dai A., Qian T. (2008). Improvements to the community land model and their impact on the hydrological cycle. *Journal of Geophysical Research: Biogeosciences* 113: G01021. DOI: 10.1029/2007JG000563.
- Opoku A., Tabil L.G., Crerar B., Shaw M.D. (2006). Thermal conductivity and thermal diffusivity of timothy hay. *Canadian Biosystems Engineering* 48:3.
- Or D. (1996.) Wetting-induced soil structural changes: The theory of liquid phase sintering. *Water Resources Research* 32: 3041-3049. DOI: 10.1029/96wr02279.

- Or D., Wraith J.M. (1999). Temperature effects on soil bulk dielectric permittivity measured by time domain reflectometry: A physical model. *Water Resources Research* 35: 371-383. DOI: 10.1029/1998wr900008.
- Or D., Phutane S., Dechesne A. (2007). Extracellular polymeric substances affecting pore-scale hydrologic conditions for bacterial activity in unsaturated soils. *Vadose Zone Journal* 6: 298-305. DOI: 10.2136/vzj2006.0080.
- Or D., Jones S.B., VanShaar J.R., Humphries S., Koberstein L. (2004). WinTDR soil analysis software. Soil Physics Group, Utah State University, Logan, UT.
- Paivanen J. (1973). Hydraulic conductivity and water retention in peat soils. *Acta Forestalia Fennica* 129: 1-70.
- Parton W.J., Hartman M., Ojima D., Schimel D. (1998). DAYCENT and its land surface submodel: description and testing. *Global and Planetary Change* 19:35-48.
- Peters J., Combs S.M., Hoskins B., Jarman J., Watson M.E., Wolf A.M., Wolf N. (2003). Recommended methods of manure analysis (A3769). Cooperative Extension Publishing Operations, Madison, WI.
- R Development Core Team. (2011). R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna, Austria.
- Ritter A., Hupet F., Munoz-Carpena R., Lambot S., Vanclooster M. (2003). Using inverse methods for estimating soil hydraulic properties from field data as an alternative to direct methods. *Agricultural Water Management* 59: 77-96. DOI: [http://dx.doi.org/10.1016/S0378-3774\(02\)00160-9](http://dx.doi.org/10.1016/S0378-3774(02)00160-9).
- Robinson D.A., Jones S.B., Wraith J.M., Or D., Friedman S.P. (2003). A review of advances in dielectric and electrical conductivity measurement in soils using time domain reflectometry. *Vadose Zone Journal* 2: 444-475. DOI: 10.2136/vzj2003.4440.
- Ruan H., Ahuja L.R., Green T.R., Benjamin J.G. (2001). Residue cover and surface-sealing effects on infiltration. *Soil Science Society of America Journal* 65: 853-861. DOI: 10.2136/sssaj2001.653853x.
- Rycroft D.W., Williams D.J.A., Ingram H.A.P. (1975a). The transmission of water through peat: I. Review. *Journal of Ecology* 63: 535-556. DOI: 10.2307/2258734.

- Rycroft D.W., Williams D.J.A., Ingram H.A.P. (1975b) The transmission of water through peat: II. Field experiments. *Journal of Ecology* 63: 557-568. DOI: 10.2307/2258735.
- Sailor D., Hutchinson D., Bokovoy L. (2008). Thermal property measurements for ecoroof soils common in the western US. *Energy and Buildings* 40: 1246-1251.
- Saito T., Fujimaki H., Yasuda H., Inosako K., Inoue M. (2013). Calibration of temperature effect on dielectric probes using time series field data. *Vadose Zone Journal* 12(2). DOI: 10.2136/vzj2012.0184.
- Sakai M., Jones S.B., Tuller M. (2011). Numerical evaluation of subsurface soil water evaporation derived from sensible heat balance. *Water Resources Research* 47: W02547. DOI: 10.1029/2010WR009866.
- Scanlon B.R., Andraski B.J., Bilskie J. (2002). Miscellaneous methods for measuring matric or water potential. In: *Methods of soil analysis: Part 4 Physical methods*. Soil Science Society of America, Madison, WI. p. 643–670. DOI: 10.2136/sssabookser5.4.c23.
- Schaap M.G., Leij F.J. (2000). Improved prediction of unsaturated hydraulic conductivity with the Mualem-Van Genuchten model. *Soil Science Society of America Journal* 64: 843-851. DOI: 10.2136/sssaj2000.643843x.
- Schaap M.G., de Lange L., Heimovaara T.J. (1997). TDR calibration of organic forest floor media. *Soil Technology* 11: 205-217. DOI: [http://dx.doi.org/10.1016/S0933-3630\(96\)00128-6](http://dx.doi.org/10.1016/S0933-3630(96)00128-6).
- Schröder J.J., De Visser W., Assinck F.B.T., Velthof G.L., Van Geel W., Van Dijk W. (2013). Nitrogen fertilizer replacement value of the liquid fraction of separated livestock slurries applied to potatoes and silage maize. *Communications in Soil Science and Plant Analysis* 45: 73-85. DOI: 10.1080/00103624.2013.848881.
- Schwarzal K., Simunek J., Stoffregen H., Wessolek G., van Genuchten M.T. (2006). Estimation of the unsaturated hydraulic conductivity of peat soils: Laboratory versus field data. *Vadose Zone Journal* 5: 628-640. DOI: 10.2136/vzj2005.0061.
- Scott H.D. (2000) *Soil physics: Agricultural and environmental applications*. Iowa State University Press, Ames, IA.
- Sharpley A., Meisinger J., Breeuwsma A., Sims J., Daniel T., Schepers J. (1998). Impacts of animal manure management on ground and surface water quality. In: *Animal*

waste utilization: Effective use of manure as a soil resource. CRC Press, Boca Raton, FL. pp. 173-242.

- Si B.C., Kachanoski R.G. (2000). Estimating soil hydraulic properties during constant flux infiltration inverse procedures. *Soil Science Society of America Journal* 64: 439-449. DOI: 10.2136/sssaj2000.642439x.
- Simunek J., Jacques D., Genuchten M.T.v., Mallants D. (2006). Multicomponent geochemical transport modeling using Hydrus-1D and HP1. *Journal of the American Water Resources Association* 42: 1537–1547.
- Simunek J., van Genuchten M.T., Wendroth O. (1998). Parameter estimation analysis of the evaporation method for determining soil hydraulic properties. *Soil Science Society of America Journal* 62: 894-905. DOI: 10.2136/sssaj1998.03615995006200040007x.
- Simunek J., van Genuchten M.T., Sejna M. (2008). Development and applications of the HYDRUS and STANMOD software packages and related codes. *Vadose Zone Journal* 7: 587-600. DOI: 10.2136/vzj2007.0077.
- Simunek J., Sejna M., Saito H., Sakai M., Genuchten M.T.v. (2009). The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media version 4.08. Department of Environmental Sciences, University of California Riverside, Riverside, CA.
- Sobel A.T. (1966). Physical properties of animal manures associated with handling, National Symposium on Animal Waste Management. ASAE, St. Joseph, MI.
- Spellman F.R., Whiting N.E. (2007). Environmental management of concentrated animal feeding operations (CAFOs). CRC Press, Boca Raton, FL.
- Starr J.L., Paltineanu I.C. (1998). Soil water dynamics using multisensor capacitance probes in nontraffic interrows of corn. *Soil Science Society of America Journal* 62: 114-122. DOI: 10.2136/sssaj1998.03615995006200010015x.
- Starr J.L., Paltineanu I.C. (2002). Capacitance devices. In: J. H. Dane and G. C. Topp ,Editors, *Methods of soil analysis: Part 4, Physical methods*, Soil Science Society of America, Madison, WI. pp. 463-474.
- Sutherland I. (2001). Exopolysaccharides in biofilms, flocs and related structures. *Water Science & Technology* 43: 77-86.

- Topp G.C., Davis J.L., Annan A.P. (1980). Electromagnetic determination of soil water content: Measurements in coaxial transmission lines. *Water Resources Research* 16: 574-582. DOI: 10.1029/WR016i003p00574.
- Toride N., Chen D. (2011). Fate and transport of nitrogen and organic matter in soils based on a coupled nitrogen-carbon cycling model using the HP1 program, ASA CSSA SSSA International Annual Meetings October 16 – 19, 2011, San Antonio, TX.
- Touma J., Raclot D., Al-Ali Y., Zante P., Hamrouni H., Dridi B. (2011). In situ determination of the soil surface crust hydraulic resistance. *Journal of Hydrology* 403: 253-260. DOI: <http://dx.doi.org/10.1016/j.jhydrol.2011.04.004>.
- United States Department of State (2010). U.S. climate action report 2010, Global Publishing Services, Washington, DC.
- United States Salinity Laboratory Staff (1954). Diagnosis and improvement of saline and alkali soils. USDA agriculture handbook 60. US Government Print Office, Washington, DC.
- van Genuchten M.T. (1980). A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Journal of the Soil Science Society of America* 44: 892-898.
- Vaz C.M.P., Jones S.B., Meding M., Tuller M. (2013). Evaluation of standard calibration functions for eight electromagnetic soil moisture sensors. *Vadose Zone Journal* 12. DOI: [doi:10.2136/vzj2012.0160](https://doi.org/10.2136/vzj2012.0160).
- Wraith J.M., Or D. (1999). Temperature effects on soil bulk dielectric permittivity measured by time domain reflectometry: Experimental evidence and hypothesis development. *Water Resources Research* 35: 361-369. DOI: 10.1029/1998wr900006.
- Yang C., Jones S.B. (2009). INV-WATFLX, a code for simultaneous estimation of soil properties and planar vector water flux from fully or partly functioning needles of a penta-needle heat-pulse probe. *Computers & Geosciences* 35: 2250-2258. DOI: <http://dx.doi.org/10.1016/j.cageo.2009.04.005>.
- Yang C., Sakai M., Jones S.B. (2013). Inverse method for simultaneous determination of soil water flux density and thermal properties with a penta-needle heat pulse probe. *Water Resources Research* 49: 1-14. DOI: 10.1002/wrcr.20459.

- Yang W., Sokhansanj S., Tang J., Winter P. (2002). Determination of thermal conductivity, specific heat and thermal diffusivity of storage seeds. *Biosystems engineering* 82: 169-176.
- Young M.H., Campbell G.S., Yin J. (2008). Correcting dual-probe heat-pulse readings for changes in ambient temperature. *Vadose Zone Journal* 7: 22-30. DOI: 10.2136/vzj2007.0015.

Table 4-1. Parametric expression and accuracy of the parameters fitted to the measured data to determine the relationship between dielectric permittivity (K_a) and volumetric water content (θ_v)

Measurement Technique	Coefficients $\theta_v = (A\sqrt{K_a} - B)^C$			n	RMSE ($\text{cm}^3 \text{cm}^{-3}$)	R^2
	A	B	C			
GS3 - Dairy manure	0.136	0.150	1.061	2579	0.0125	0.982
TDR - Dairy manure	0.121	0.130	0.990	135	0.0120	0.987
GS3 (Decagon Device Inc., 2012) - Non-mineral soils†	0.118	0.117	1.000	-	-	-
TDR (Schaap et al., 1997) - Organic forest soils	0.133	0.146	0.885	505	-	0.963

† potting soils, perlite, and peat moss at salinities ranging from 0 to greater than 4 dS/m.

Table 4-2. Model parameters obtained from fitting the van Genuchten parametric expression to the measurement data compared with the previous studies that investigated those for peat soils

Authors	Medium	van Genuchten model parameters					
		θ_r ($\text{cm}^3 \text{ cm}^{-3}$)	θ_s ($\text{cm}^3 \text{ cm}^{-3}$)	α (cm^{-1})	n	m^\dagger	R^2
This study‡	Cattle Manure	0.0869	0.895	0.027	1.391	0.281	0.997
Schwarzel et al. (2006)	Peat	0	0.880	0.026	1.190	0.160	0.98
Naasz et al.(2005)	Peat	0.3390	0.875	0.0068	10.30	0.180	0.99
Da Silva et al. (1993)	Peat	0	0.901	0.0264	1.390	0.281	0.99

† $m = 1 - 1/n$, except the study by Naasz et al.(2005) that m was fitted to the measurement data as a model parameter

‡ Number of replicates = 3 with the total number of measurements (N) = 210

Table 4-3. Statistical summary of non-linear regression analysis from estimation of the saturated hydraulic conductivity (K_s) with the HYDRUS-1D inverse solution simulation

Parameter	Value (cm day ⁻¹)
K_s	190
Number of observed θ_v (N)	90
Standard error coefficient (SE)	56.88
Lower 95% confidence limit	81.173
Upper 95% confidence limit	307.20

Table 4-4. Parametric expressions and parameters describing the thermal conductivity (λ), thermal diffusivity (κ), and volumetric heat capacity (C) as a function of the volumetric water content (θ_v).

Thermal property	Unit	Expression	Parameter			R^2
			a	b	c	
λ	$\text{W m}^{-1} \text{ }^\circ\text{C}^{-1}$	$\lambda = a \cdot \theta_v + b$	0.5427	0.0509	-	0.991
κ	$\text{cm}^2 \text{ s}^{-1}$	$\kappa = \frac{a \cdot \theta_v}{b + \theta_v} + c$	0.0012	0.0276	0.00014	0.957
C	$\text{MJ m}^{-3} \text{ }^\circ\text{C}^{-1}$	$C = a \cdot \theta_v + b$	3.8772	0.5671	-	0.990

Table 4-5. Summary of thermal properties of dairy and beef cattle manure reported in previous studies.

Medium type	Thermal properties			Observation ranges	Authors
	λ [W m ⁻¹ °C ⁻¹]	κ [cm ² s ⁻¹]	C [MJ m ⁻³ °C ⁻¹]		
Beef cattle manure	0.22 – 0.03	0.00150 – 0.00142	–	Wet weight basis between 100% and 0%	Houkom et al.(1974)
Beef cattle manure	0.63±0.059 – 0.064±0.003	1.515 – 0.849	–	TS† between 2.8% and 95% at 20 °C	Chen (1983)
Dairy manure	0.64 – 0.54	–	–	TS between 0% and 8%	Achkari-Begdouri and Goodrich (1992)
Mixture of fresh dairy feces and cedar sawdust	0.202 – 0.05	0.00155‡	–	θ_v between 0.44 and 0	Iwabuchi et al.(1999)
Dairy manure	0.55 – 0.08	0.001125 – 0.001250	–	Wet weight basis 80% and 20% at 40 °C	Nayyeri et al. (2009)
Beef manure compost	0.39 – 0.05	0.0010 – 0.0008	3.82 – 0.59	From saturation to dry conditions	Ahn et al. (2009)

† TS = Percentage of total solid (wet weight basis)

‡ Mean value, reported as independent of θ_v

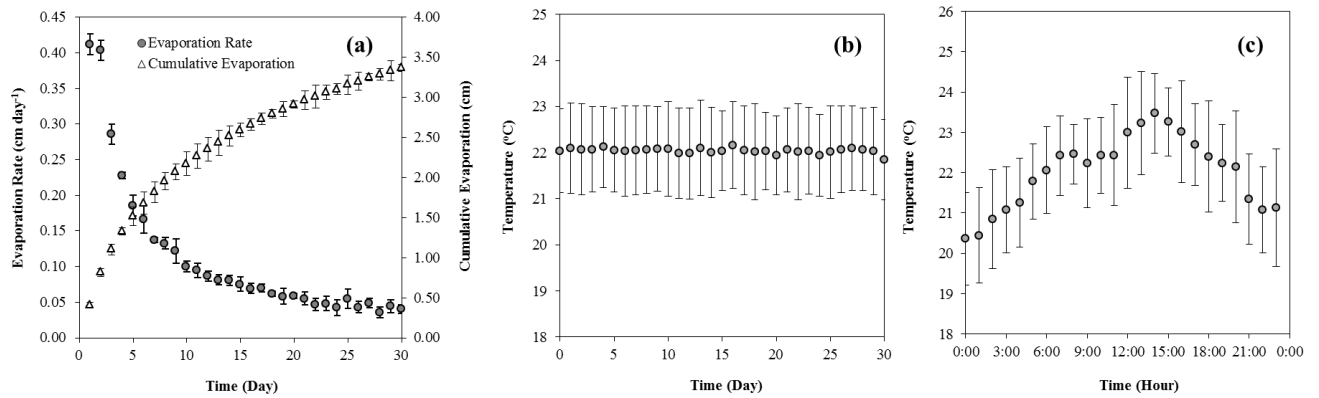


Figure 4-1. (a) Mean daily evaporation rate (left axis) and cumulative evaporation (right axis) monitored during the evaporation experiments of three dairy manure samples at room temperatures. (b) Daily average of hourly room temperatures. (c) 30-day average of room temperatures recorded on the hour. All error bars denote plus and minus one standard deviation from triplicate sample measurements.

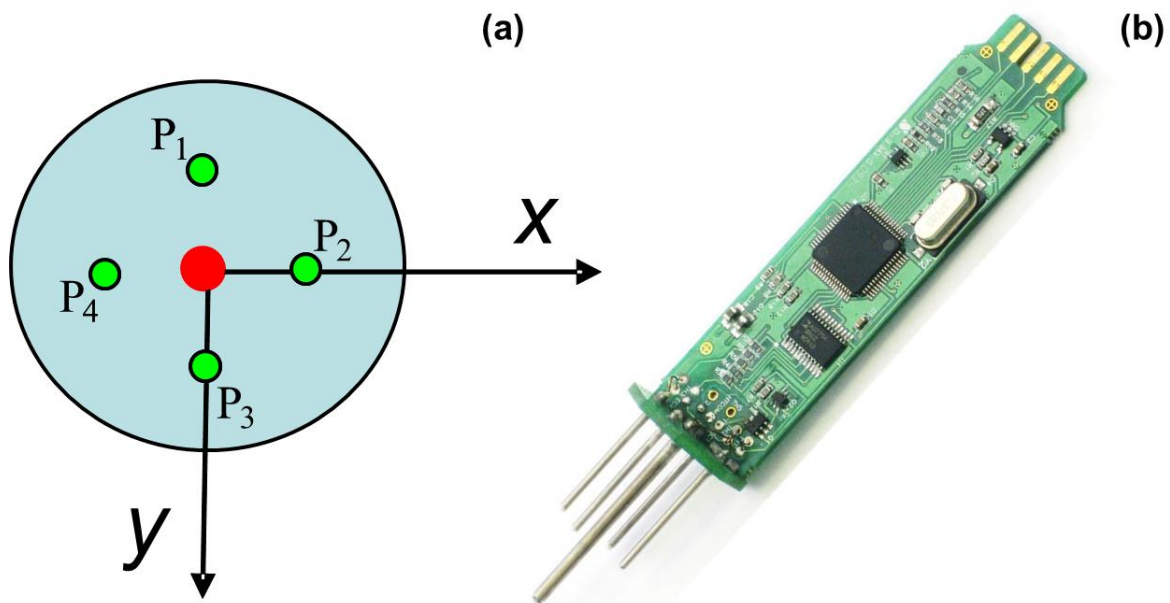


Figure 4-2. (a) End view of the penta-needle heat pulse probe (PHPP) depicting the location of the heater needle and four thermistors (P₁, P₂, P₃, and P₄). (b) The actual PHPP used for determination of the thermal properties of the dairy manure samples. Prior to the measurements, the electrical components were coated with water resistant epoxy resin.

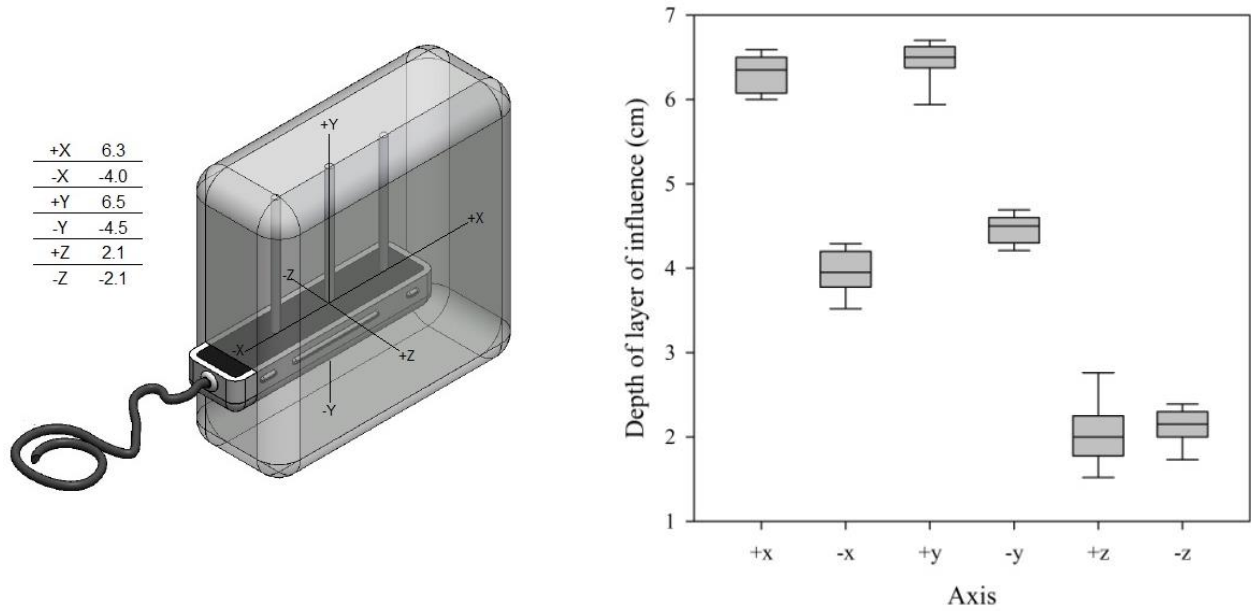


Figure 4-3. The GS3 sensor and its estimated zone of influence. The dimensions shown on the left are the mean values (in centimeter) from ten replicated independent measurements. The variations of the measurements from ten replicate measurements are shown on the right.

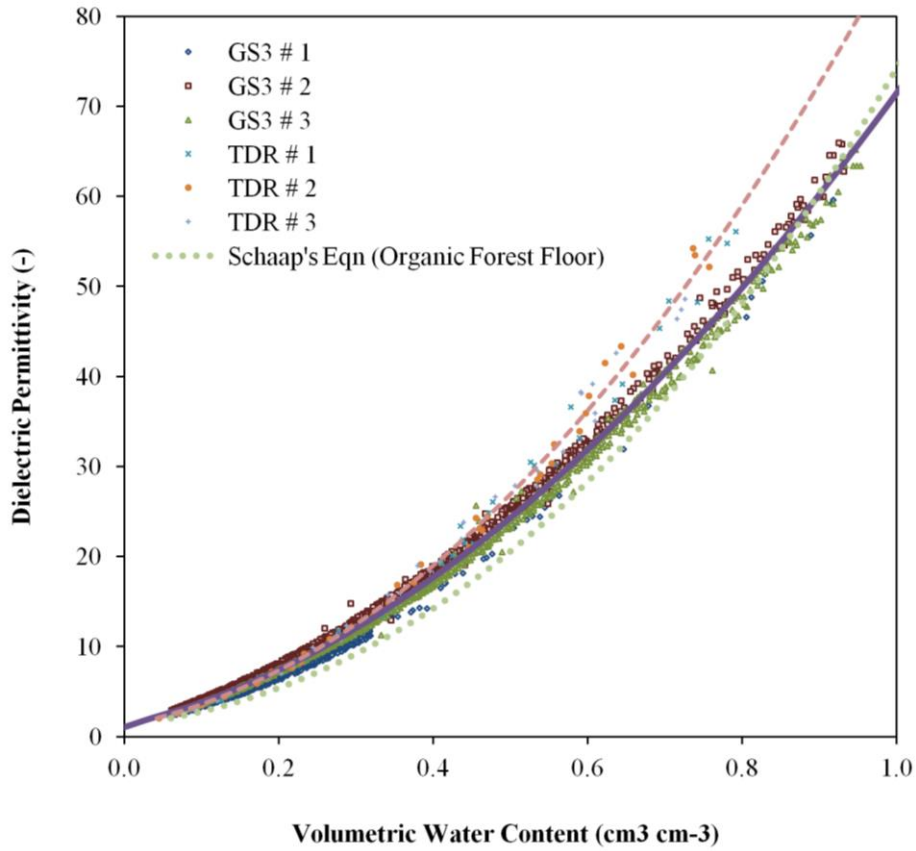


Figure 4-4. Measured water contents (θ_v) versus dielectric permittivity (K_d) determined with GS3 sensors (fitted to solid line) and TDR probes (fitted to dashed line). The Schaap et al. (1996) curve for TDR-measured organic forest soils is also shown for reference.

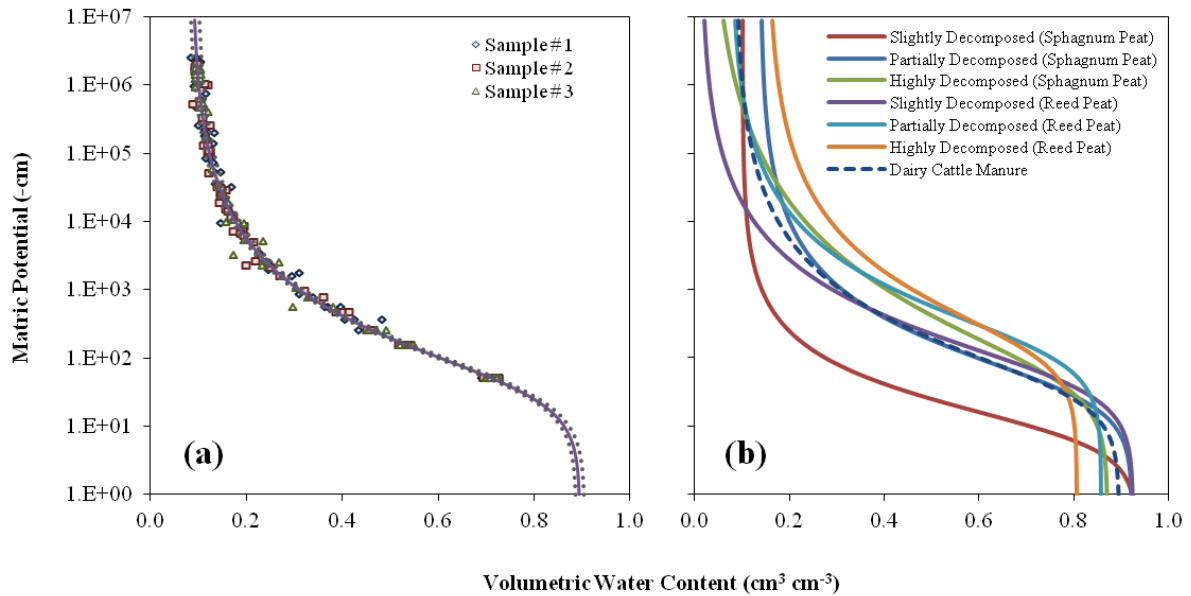


Figure 4-5. (a) Measured water retention curve of as-excreted cow manure determined by the WP4-T dewpoint potentiometer. The solid line illustrates the van Genuchten hydraulic model with the fitted parameters. The dashed lines show 95% confidence interval of the curve fitting. (b) Water retention curve of dairy manure (dashed line) in comparison with *Sphagnum* and reed peats in different degrees of decomposition (Paivanen, 1973).

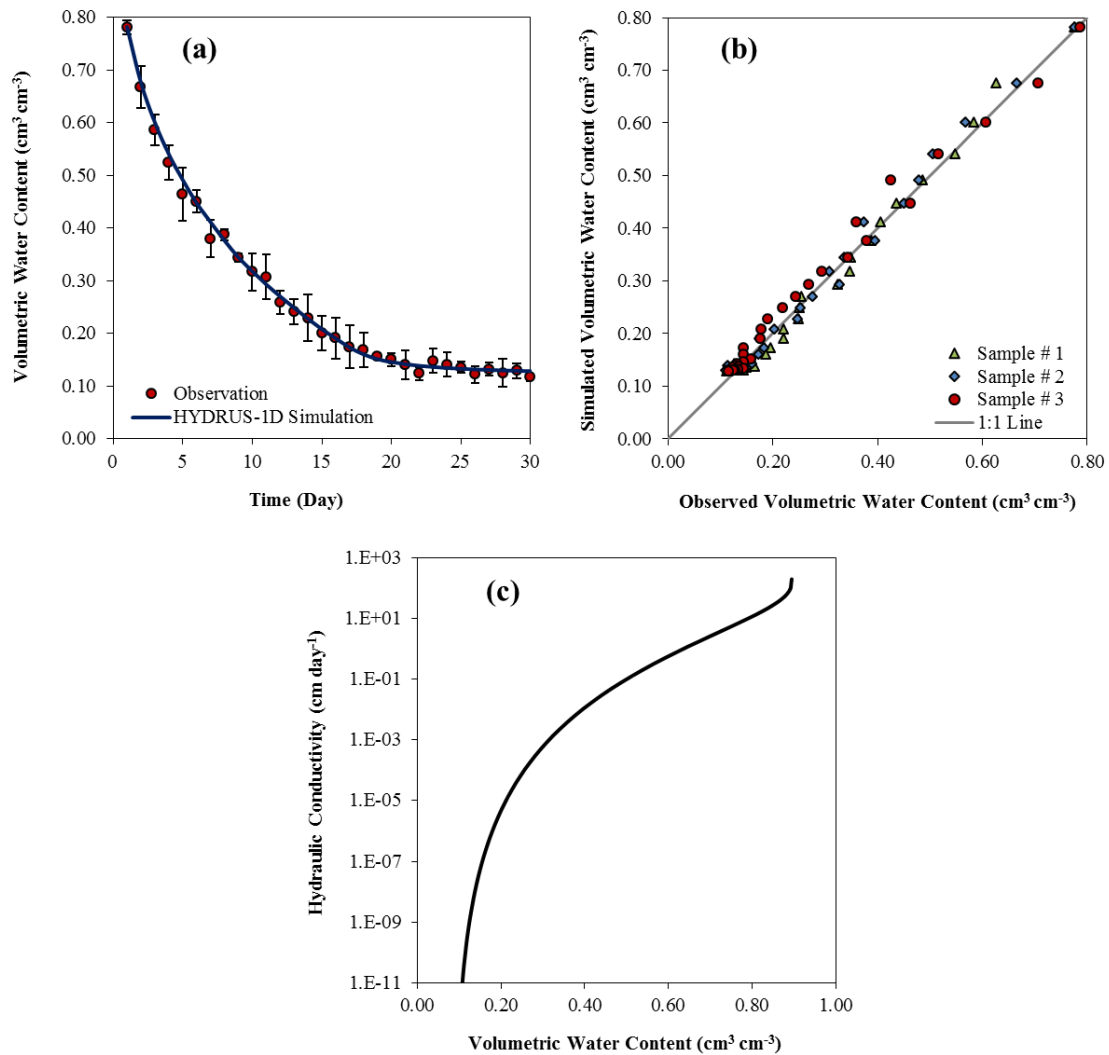


Figure 4-6. (a) Simulated θ_v fitted to the measurements during the evaporation experiments. The error bars denote plus and minus one standard deviation. (b) Comparison between the measured and simulated θ_v . The $RMSE$ and R^2 value of the model simulation relative to the measured θ_v is $0.020 \text{ cm}^3 \text{ cm}^{-3}$ and 0.9884 , respectively (c) Unsaturated hydraulic conductivity for dairy manure as a function of θ_v , based on the van Genuchten-Mualem model.

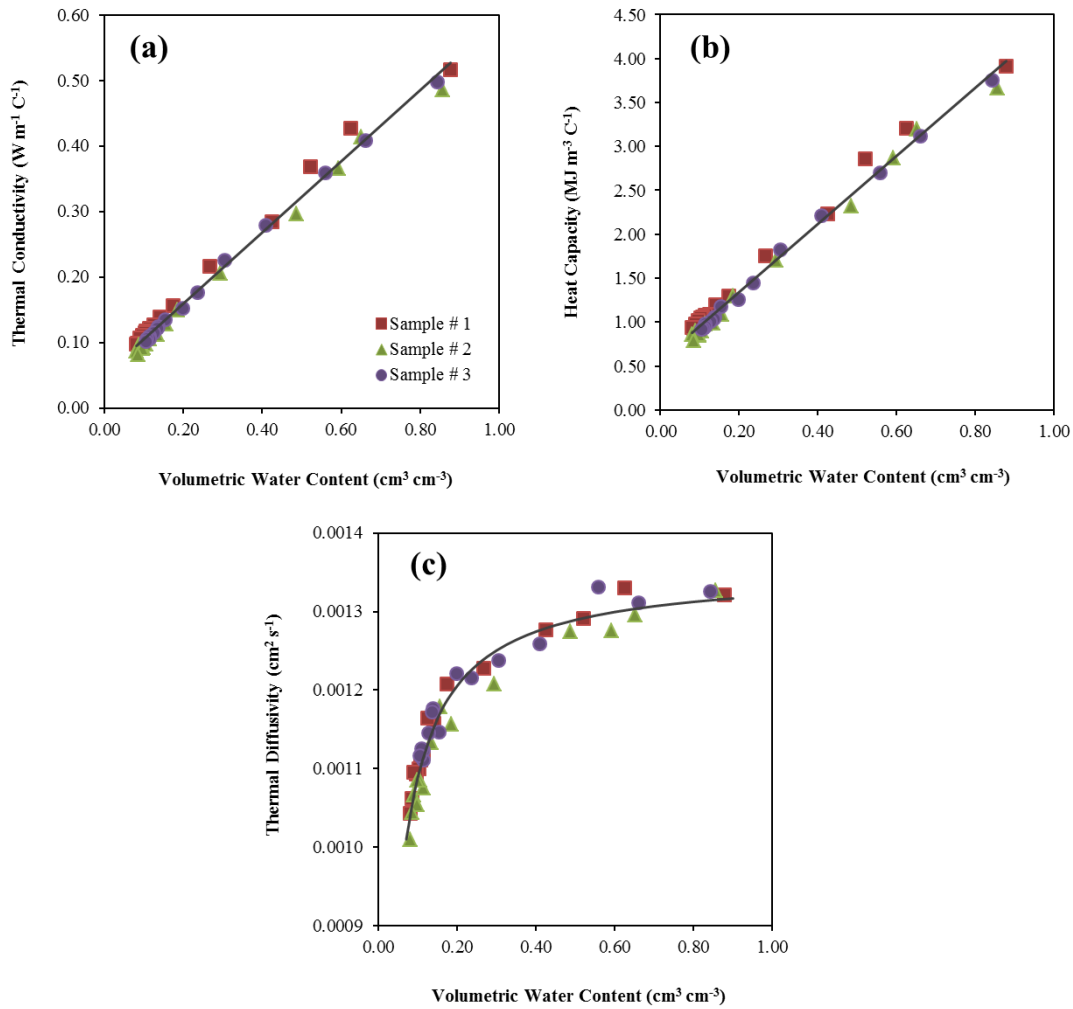


Figure 4-7. Changes in (a) thermal conductivity (λ), (b) bulk volumetric heat capacity (C), and (c) thermal diffusivity (κ) with θ_v of dairy manure samples. The solid lines show the parametric expressions with the parameters indicated in Table 4-4.

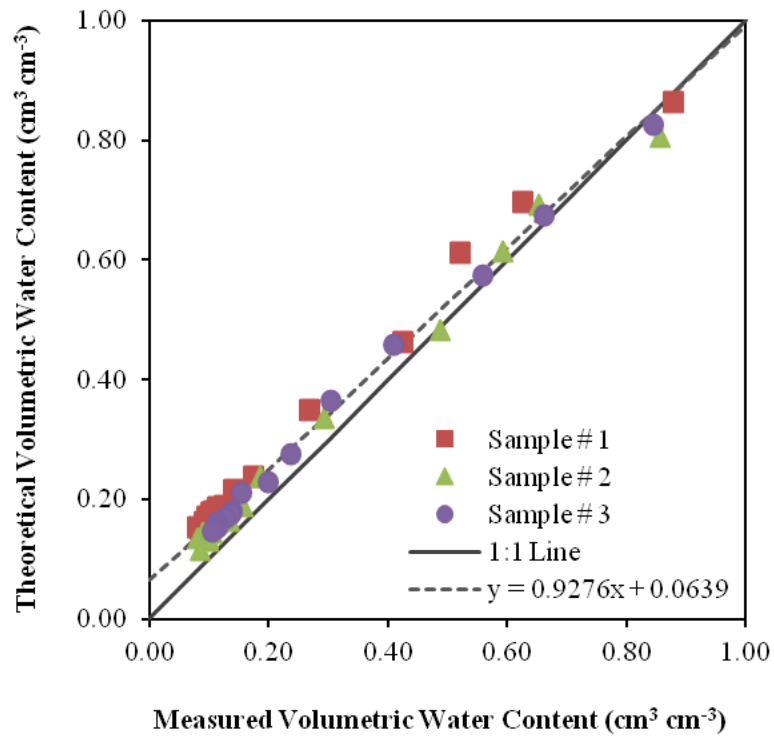


Figure 4-8. Theoretical θ_v estimated from the heat capacity (C_m) using the PHPPs compared with θ_v measured with the GS3 sensors.

CHAPTER 5
CARBON DIOXIDE, METHANE, AND AMMONIA EMISSIONS FROM
SURFACE APPLICATION OF CATTLE MANURE

Abstract: Gaseous emissions from surface application with manure source materials (i.e., manure, compost) are part of the major contribution of greenhouse gas (GHG) and air pollution emissions in agricultural production. Carbon dioxide (CO₂), methane (CH₄), and ammonia (NH₃) emissions were estimated and characterized using the automated surface chamber measurement method during the ambient drying process of manure and compost for 15 days after surface application. The measurements included four treatments; beef manure, dairy manure, beef compost, and dairy compost. The estimated CO₂, CH₄, and NH₃ emissions from the surface application with dairy manure (452.4 ± 35.4 g m⁻², 1.2 ± 0.1 g m⁻², and 1,786.0 ± 206.7 g m⁻², respectively) were the highest among other treatments. The emissions of CO₂, CH₄, and NH₃ from the surface application with beef compost treatment (210.5 ± 14.4 g m⁻², 0.2 ± 0.02 g m⁻², and 0.07 ± 0.01 g m⁻², respectively) were the lowest. Linear correlations with the strong coefficients of determination (R^2) were reported between the CO₂ and CH₄ emissions and temperature. Weak linear correlations ($R^2 = 0.39$ for beef and dairy manure treatments and 0.24 for beef and dairy compost treatments) were observed between the NH₃ emissions and temperature. Daily CO₂ and CH₄ emissions and average daily volumetric water content were well correlated and described by an exponential function. The solubility of NH₃ most likely affected the accuracy of the NH₃ emission measurements in the study. An empirical model, based on the Arrhenius equation, was verified with the emission measurement data confirming strong dependency of CO₂ and CH₄ emissions on

temperature and moisture content of the soil surface applied with manure source materials.

5.1 Introduction

Cattle manure is widely applied to land in agricultural production by land surface spreading or surface application as the nutrient and organic matter content of manure is beneficial for plant growth, long-term fertility, and soil structure in agronomic systems (Klop et al., 2012; Schröder et al., 2013). Livestock manure is responsible for approximately 7.5% of methane (CH₄) in the US (United States Department of State, 2010). Carbon dioxide (CO₂) is considered as a primary loss of carbon via gaseous emissions due to organic matter decomposition and soil respiration (Hao et al., 2004). In addition to contribution to the greenhouse effect, rates of CO₂ emission indicate biological activity and the rate at which the decomposition processes are occurring. Manure spread on the surface and not worked into the soil may lose most of the volatile nitrogen compounds as ammonia (NH₃) gas to the atmosphere. This lost nitrogen is not available for plant growth, and has been identified as a possible air quality contaminant contributing to acid rain. Ammonia emitted to the atmosphere, is primarily converted to ammonium sulfate (NH₄)₂SO₄ and ammonium nitrate (NH₄)NO₃ aerosols, which contribute to formation of particulate matter with an aerodynamic diameter less than 2.5 μm or PM_{2.5}.

Several methods and techniques have been developed to estimate and characterize gaseous emissions from agricultural soils, manure, and other porous media generated by animal feeding operations (AFOs). Hu et al. (2014) provided a comprehensive review on the techniques commonly used to measure on-farm emissions from livestock systems.

One of the techniques most widely used for estimating gas emissions from agricultural and AFOs are chamber methods. The chamber method is more useful for treatment comparison and more suitable for mitigation studies (Rochette and Eriksen-Hamel, 2008). The major disadvantage of chamber methods are the artificial, constrained environment created by the chamber, which can alter the surrounding environmental conditions for natural gas production (Parkin et al., 2012; Rochette and Eriksen-Hamel, 2008).

There are limited on-farm emissions data, particularly from surface applications. Most of the studies reported gaseous emissions from open lots, manure stockpiles, wastewater ponds, and composting areas (Borhan et al., 2011; Ding et al., 2016a; Ding et al., 2016b; Hao et al., 2004; Khan et al., 1997; Leytem et al., 2011; Leytem et al., 2013; Misselbrook et al., 2001; Mukhtar et al., 2008; Pereira et al., 2012; Pereira et al., 2011). In addition, the reported emissions data are found to be varied due to differences in measurement technique, farm operation, measurement location, manure management practice, and cattle diet. Diurnal and seasonal variations also play important roles in gaseous emissions.

Temperature and moisture content were repeatedly reported as the major factors that impact microbial activity and gas diffusion processes driving emissions from farmyard manure and manure compost (Dewes, 1996; González-Avalos and Ruiz-Suárez, 2001; Hu et al., 2018; Mazzetto et al., 2014). The objectives of this study were to estimate and describe CO₂, CH₄, and NH₃ emissions from surface application with beef manure, dairy manure, beef compost, and dairy compost by using an automated surface

chamber measurement method and to assess impacts of diurnal temperature and soil surface moisture content on the emissions.

5.2 Materials and Methods

5.2.1 Manure Samples and Field Setup

Four cattle manure treatments, including i) dairy manure, ii) beef manure, iii) dairy compost, and iv) beef compost, were used as targeted sources of gaseous emissions. The dairy and beef manure samples were collected from Utah State University's Caine Dairy Farm (Central Coordinates: 41° 39' 22" N; 111° 53' 57" W) and Animal Science Farm (Central Coordinates: 41° 40' 6" N; 111° 53' 17" W) in Wellsville, UT, respectively. Both dairy and beef manures were collected from the manure storage area, where manures were openly piled up. Solid manure with bedding materials (i.e., straw) scraped and collected from the confinement facilities was directly transferred to the storage area prior to land application or transporting to off-site manure management facilities. There were approximately 100 cattle fed in the beef cattle facilities (open feedlots) within the Animal Science Farm. Similar to the Caine Dairy Farm operation, solid manure, collected for removal from the feedlots by scraping using tractor-mounted blades, was moved daily by tractors to stockpiles in the manure storage area. Manure compost samples were obtained from, 1) local dairy compost produced from fresh dairy manure mixed with straw from the Caine Dairy Farm utilizing the turned windrow method (USDA, 2010) and 2) local commercial beef compost (Miller Companies LC, Hyrum, UT) produced from steer manure mixed with straw.

Gas emission measurements from these samples were made in a field at the Greenville Research Farm in North Logan, UT (Central Coordinates: 41° 45' 57" N;

111° 48' 43" W). The elevation is about 1,355 m (4,445 ft.). A meteorological station was located within Greenville Research Farm, approximately 480 feet to the northeast of the measurement field, which recorded air temperature, barometric pressure, solar radiation, precipitation, wind speed and direction during the experimental period. The background soil was a highly calcareous Millville silt loam. The field was cleared and irrigated to field capacity (i.e., volumetric water content at approximately $0.24 \text{ cm}^3 \text{ cm}^{-3}$) prior to the commencement of measurements. Twelve 1.70 m by 1.20 m plots were prepared for the four manure types, each with three replicate samples to determine the assay statistics. The location of each manure type (Figure 5-1) was statistically independent (i.e., assigned randomly), using a true random number generator (Eddelbuettel, 2006). The application rates for dairy and beef manure were 12 kg m^{-2} or 55 tons per acre (Midwest Plan Service, 1985) and those for dairy and beef compost were approximately 6 kg m^{-2} or 27.5 tons per acre as directed by the compost producers.

5.2.2 Field Measurements

Gas emission measurements of CO_2 , CH_4 , and NH_3 from each treatment were monitored continuously between August 9 and August 27, 2013. A multiplexing system based on the closed dynamic chamber principle was integrated with a Fourier Transformed Infrared (FTIR) gas spectroscopy analyzer (DX-4030, Gaset Technologies Oy, Helsinki, Finland). The system was capable of monitoring concentrations of 15 pre-programmed gases simultaneously (Sutitaranontr et al., 2012; Sutitaranontr et al., 2013). The theoretical detection limits of the gases of concern in this study were 10 ppm CO_2 , 0.11 ppm CH_4 , and 0.13 ppm NH_3 , respectively. Nitrous oxide (N_2O) was initially one of the target gas emissions in this study. However, N_2O concentration data did not generate

detectable slopes in the measurements due to a substantial number of concentrations below the detection limit of 0.02 ppm N₂O. Therefore, N₂O emission data are not presented in this study.

The cross-interference effects (i.e., cross-sensitivity to gases other than the target gas of interest) were automatically compensated for by the FTIR gas analyzer during automated calculation of the gas concentrations. A zero-concentration calibration was performed daily using 99.999% nitrogen gas (N₂) with an approximate flow rate of 1.8 L min⁻¹ to improve accuracy of very low concentration readings. During the measurement, the air sample from the measurement chamber was continuously drawn into the gas analyzer with an approximate flow rate of 2.0 L min⁻¹ by an external diaphragm pump (model D737-23-01, Parker-Hannifin Corp., Mooresville, NC). The air sample was filtered through a PTFE 2- μ m membrane (part 450-25-3, Savillex Corp., Eden Prairie, MN) to prevent solid particles from accumulating in the sample cell in the gas analysis unit, which would deteriorate measurement quality. PTFE tubing (6-mm OD) was used for the gas sampling lines in the closed-loop system.

The program control allowed each chamber 5 minutes of time, 3 minutes where the chamber was closed over the sample and measuring, and 2 minutes to allow the chamber to move into and out of position and for the system to be thoroughly flushed out prior to the next measurement. A 10-cm long 6-mm OD PTFE tubing was utilized as a vent tube to permit pressure equilibration between the closed surface cover and its surroundings (Hutchinson and Mosier, 1981; Hutchinson and Livingston, 2001). There were, however, anticipated increases in the chamber air temperatures relative to ambient as the presence of the chambers induced steady, less turbulent wind flows over the

surfaces in comparison to ambient conditions, which may have altered the surface energy balance. Temperatures inside and outside the chamber during the measurements were monitored with thermistor temperature sensors (ST-100, Apogee Instruments, Inc., Logan, UT) to investigate the significance of the difference in the temperatures inside and outside the chambers. In addition, relative humidity (RH) inside the chamber was monitored with a humidity sensor (HIH-4021-001; Honeywell, Minneapolis, MN). A small fan (Top Motor DF122510BL, Dynatron Corp., Union City, CA) was housed in the chamber to mix air in the chamber headspace. Hutchinson and Livingston (2001) and Christiansen et al. (2011) reported gaseous fluxes could be significantly underestimated, if the chamber headspace was not constantly mixed during a chamber enclosure as the mixing homogenized the gas concentration inside the chamber. However, the turbulence caused by the mixing fan may alter the wind profile at the emitting surface, disturbing the gas exchange between emitting surface and atmosphere, and may result in an overestimation of gaseous flux.

In this study, the water or moisture content of the surface soil is described in terms of volumetric water content (θ_v), which for dielectric sensor-based measurements is inherently given by the sensor output. Due to a strong correlation between the dielectric permittivity (K_a) and θ_v , sensors are able to estimate θ_v by measuring the apparent K_a (Davis and Chudobiak, 1975). A commercial capacitance-based dielectric sensor (GS3, Decagon Device Inc., Pullman, WA) was utilized for monitoring the water contents in each sample during the experiment. The output range of K_a was from 1 (air) to 80 (water). The calibration equation provided by the sensor manufacturer for estimation of θ_v is given as:

$$\theta_v = \left(A\sqrt{K_a} - B \right)^C \quad (1)$$

where $A = 0.118$, $B = 0.117$, and $C = 1.000$. The sensor accuracy was stated as better than $\pm 5\%$ volumetric water content at salinities below 4 dS/m.

In addition to K_a , the output from the GS3 sensor included the sample temperature and electrical conductivity (EC). The EC measurement was calibrated from the sensor manufacturer to be accurate within $\pm 10\%$ from 0 to 10 dS/m.

5.2.3 Gas Flux Emission Calculations

The surface chamber techniques employ the rate of gas concentration increase with time within the measurement chamber to determine the rate at which each target gas diffuses from the manure into the ambient air. The equation used for the calculation of gaseous flux with correction for temperature and pressure is given as:

$$F = \frac{V \cdot P \cdot T_s \cdot M_w}{A \cdot P_s \cdot (273.15 + T) \cdot (2.24 \cdot 10^{-2})} \cdot \frac{\partial C}{\partial t} \quad (2)$$

where F is the gaseous flux [$\mu\text{g m}^{-2} \text{s}^{-1}$], V is the total system volume including the chamber headspace [m^3], P is the ambient pressure [kPa], T_s is the standard temperature [273.15 K], M_w is the molecular weight of a gas [g mol^{-1}], A is the surface area of the chamber over the emission source [m^2], P_s is the standard pressure [101.33 kPa], T is the temperature ($^{\circ}\text{C}$), $2.24 \cdot 10^{-2}$ is the molar volume of a gas at STP [$\text{m}^3 \text{mol}^{-1}$], and $\partial C/\partial t$ is the gradient of gas concentration changing over time derived from linear regression [ppm s^{-1} or $\mu\text{m}^3 \text{m}^{-3} \text{s}^{-1}$]. The gas concentration gradients with insignificant correlation (i.e., R^2 is less than 0.80) were removed from the data set presented in this study.

5.2.4 Statistical Analyses

Continuous hourly emission data were examined to characterize natural flux variations. The measurement data presented in this study were statistically analyzed with the general statistical analysis module of the R statistical software package version 2.14.1.

5.3 Results and Discussion

5.3.1 Environmental Conditions

Background air temperature (T), relative humidity (RH), wind speed, and solar radiation during field measurements are shown in Table 5-1. Figure 5-2 shows the hourly air T , RH variation, and wind rose. No precipitation was recorded during measurements. The average high and low air temperature was 30.6 and 14.6 °C, respectively. The prevailing wind blew from the northeast and east directions with an average wind speed of 1.94 m s⁻¹. This represents the typical weather in August for the region.

5.3.2 Gas Emissions from the Surface Application

The emissions of CO₂ from the surface application are presented in Figure 5-3. There was a strong diurnal trend in emissions of CO₂ from the surface application with lower emissions during late evening, at night, and early morning and then increasing throughout the day, with maximum rates in the mid to late afternoon. This strong diurnal pattern of CO₂ emissions was found to be associated with temperature (Ding et al., 2016b; Flessa et al., 2002; Hu et al., 2018; Leytem et al., 2011; Leytem et al., 2013). The CO₂ emissions gradually decreased over the measurement period of 15 days to what are typical of background emissions due to soil respiration. Generally, the CO₂ emissions

from the surface application with dairy manure were slightly higher than those with beef manure as shown in Figure 5-3(a) and Figure 5-3(b). The CO₂ emissions from the surface application with the manure sources were approximately two fold higher than those with the compost. The estimated average CO₂, CH₄, and NH₃ emissions from all treatments are summarized in Table 5-2.

Figure 5-3(b) and 5-3(d) show the daily and cumulative CO₂ emissions during the 15-day measurement period. After the surface application, the daily emissions of CO₂ gradually decreased until they ceased. The estimated CO₂ emissions from the beef and dairy manure surface application were slightly higher than the average CO₂ emissions from ground level brick-paved open feedlot emissions ($15.6 \pm 7.4 \text{ g m}^{-2} \text{ d}^{-1}$) reported by Ding et al. (2016b) employing closed chamber measurements. This is most likely due to the contribution of CO₂ from background soil respiration. Pereira et al. (2011) also reported gaseous emissions can be affected by the floor type. Emissions of CO₂, CH₄, and NH₃ were reported to be significantly greater from the solid floor relative to the slatted floor. Similar to manure sources, CO₂ emissions from composts were observed with the strong diurnal trend accompanied by a lower magnitude and shorter emissions duration. Pattey et al. (2005) reported similar trends in CO₂ emissions from beef and dairy composts. The decrease in CO₂ emissions over time indicate biological activity and the rate at which the microbe-based decomposition processes are occurring.

The emissions of CH₄ from the surface application (Figure 5-4) also show a clear diurnal variation and were closely correlated with CO₂ emissions, similar to the study by Amon et al. (2001). Previous studies (Leytem et al., 2011; Leytem et al., 2013) showed little CH₄ generation from fresh manure. The dairy manure surface application generated

the highest CH₄ emissions; while, those with beef compost were lowest with approximately 83 percent lower emissions than dairy manure. Ding et al. (2016b) and Borhan et al. (2011) reported CH₄ emissions from the ground level of an open feedlot of $51.8 \pm 24.1 \text{ mg m}^{-2} \text{ d}^{-1}$ and $9.6 \text{ mg m}^{-2} \text{ d}^{-1}$, respectively. CH₄ emissions from feed yards were reported within a range of between $4.9 \text{ mg m}^{-2} \text{ d}^{-1}$ and $16.71 \text{ mg m}^{-2} \text{ d}^{-1}$ by Misselbrook et al. (2001). The estimated CH₄ emissions reported in the literature are in the same range as those found in this study.

Figure 5-5 shows the surface application emissions of NH₃. Similar to the CO₂ and CH₄ emissions, the dairy manure surface application generated the highest NH₃ emissions, while the NH₃ emissions from the beef compost surface application were the lowest among four treatments. However, the NH₃ emissions were found to decrease faster than the CO₂ and CH₄ emissions, which could be caused by the solubility and adhesive characteristics of the NH₃ molecule. Stickiness of NH₃ molecules to the tubing wall accumulated over time during the measurements was speculated to be the primary cause for the rapid decrease of NH₃ emissions. A considerable uncertainty of NH₃ emission measurements due to the sticky nature of the NH₃ molecules were reported in several previous studies (Osada et al., 2011; Yokelson et al., 2003; Zhu et al., 2012). The measurement issues, especially for low NH₃ concentration levels, included slower response time and higher detection limits.

Pereira et al. (2011) reported the cumulative emissions of NH₃ within a range of between 2.14 g m^{-2} and 5.23 g m^{-2} during the first 72 hours following excreta deposition on concrete floors, which are lower than those observed in this study. Variations in CO₂, CH₄, and NH₃ emissions could be due to differences in diet such as forage type, forage

quality, and dry matter intake (DMI), measurement systems, measurement times and locations, ground types, seasons, and manure management systems (Leytem et al., 2011; Leytem et al., 2013; Pereira et al., 2011).

5.3.3 Surface Soil Moisture Content

Figure 5-6 shows changes in the volumetric water contents (θ_v) in soil surfaces for each treatment during the measurements. The initial θ_v for dairy manure treatment (approximately 33%) was the highest among all treatments. The saturated water content (θ_s) of as-excreted cow manure was reported in a range between $85 \text{ m}^3 \text{ m}^{-3}$ and $90 \text{ m}^3 \text{ m}^{-3}$ (Sutitarnnontr et al., 2014). After 15 days of drying, θ_v decreased approximately from $0.30 \text{ m}^3 \text{ m}^{-3}$ to $0.10 \text{ m}^3 \text{ m}^{-3}$. The variations of the measurements are most likely due to the temperature influence on the soil moisture sensors (Jones et al., 2005; Mead et al., 1996; Or and Wraith, 1999; Paltineanu and Starr, 1997; Starr and Paltineanu, 1998; Wraith and Or, 1999). Techniques for correcting temperature sensitivity on capacitance measurements have been reported in several studies (Campbell, 2001; Chanzy et al., 2012; Cobos and Campbell, 2007; Kelleners et al., 2004; Robinson et al., 1998).

Table 5-3 lists the parameters fitted to our measurements and their estimation accuracy, based on the quadratic function given as

$$\theta_v = At^2 + Bt + C \quad (3)$$

where θ_v is the volumetric water content [$\text{m}^3 \text{ m}^{-3}$], t is time after application [hr], and A , B , and C are quadratic coefficients.

In general, our fitting parameters indicate reliable water content estimates based on the time after application with high R^2 values in all treatments. Drying rates of soil surface (Figure 5-7) could be estimated from the derivative of Equation (3), written,

$$\frac{\partial \theta_v}{\partial t} = 2At + B \quad (4)$$

where $\partial \theta_v / \partial t$ is the drying rate [$\text{m}^3 \text{ m}^{-3} \text{ hr}^{-1}$], $2A$ and B are linear equation coefficients.

Table 5-4 lists the linear equations and their coefficients representing the drying rates of surface soils.

5.3.4 Impact of Temperature on CO₂, CH₄, and NH₃ Emissions

Temperature is one key parameter that explains variations in trace gas emissions from soils (Oertel et al., 2016). The percentages of hourly CO₂, CH₄, and NH₃ emissions and temperatures were used to assess the impacts of diurnal temperature. Figure 5-8 illustrates linear correlations between the percentages of hourly CO₂, CH₄, and NH₃ emissions and temperatures. CO₂ and CH₄ emissions shown in Figures 5-8(a) through 5-8(d) were found to have strong correlation with the diurnal temperature. NH₃ emissions depicted in Figures 5-8(e) and 5-8(f) indicate weak linear correlation with the diurnal temperature, which most likely could be caused by the solubility and sticky nature of NH₃ molecules.

Table 5-5 reports the linear coefficients and their coefficients of determination (R^2). Hu et al. (2018) demonstrated effects of temperature and moisture on CO₂ and CH₄ emissions from drying dairy cow manure based on the Arrhenius equation. Methane emissions from the surface applications of manure shown in Figure 5-8(c) show the strongest linear correlation, while NH₃ emissions from the surface applications of compost depicted in Figure 5-8(f) show the weakest linear correlation with the temperature. Ding et al. (2016a) investigated effects of temperatures on CO₂ and CH₄ emissions from the scale model of open dairy feedlots and found CO₂ and CH₄ emissions

highly dependent on air temperature, which is in agreement with other studies (Husted, 1994; Pereira et al., 2012; Pereira et al., 2011).

5.3.5 Impact of Water Content on CO₂, CH₄, and NH₃ emissions

Water content is the most important soil parameter for soil gas emissions as it controls microbial activity and all related processes (Oertel et al., 2016). Daily CO₂, CH₄, and NH₃ emissions and average daily water content (θ_{vd}) were used in assessing the impacts of water contents on the emission. The daily emissions and θ_{vd} were selected to eliminate the diurnal variability of instantaneous emissions and are therefore more generalizable. The relationships between daily CO₂ and CH₄ emissions and θ_{vd} (Figure 5-9) were found to fit well with the exponential function given as

$$F_d = A \cdot e^{B(\theta_{vd})} + C \quad (5)$$

where F_d is the daily emissions [$\text{g m}^{-2} \text{d}^{-1}$], θ_{vd} is the average daily volumetric water content [$\text{m}^3 \text{m}^{-3}$], and A , B , and C are exponential function coefficients.

Table 5-6 lists the parameters of the exponential function fitted to the measurements and their estimation accuracy. Figures 5-9(a) and 5-9(b) suggest that CO₂ emissions due to the background soil respiration can be estimated to be $10 \text{ g m}^{-2} \text{d}^{-1}$. Hu et al. (2018) reported the parabolic relationship between the moisture content and gas emission fluxes from drying dairy cow manure. The peak emissions were observed after approximately 5 days of drying. This delayed peak emission most likely resulted from the initial near saturated condition (low gas transport) followed by crust formation on the manure surface in the first few days suppressing gaseous emissions.

5.3.6 Impacts of Temperature and Water Content on CO₂, CH₄, and NH₃ Emissions

Effects of temperature and moisture content on gaseous emissions were well described by Hu et al. (2018). The combined temperature and moisture content dependent gas emission relationship, which was derived from the Arrhenius equation, may be expressed as

$$F = A \cdot e^{\left[-\frac{B \cdot \theta_v^2 + C \cdot \theta_v + D}{R \cdot (273.15 + T)} \right]} \quad (6)$$

where F is the gaseous emissions [$\text{g m}^{-2} \text{d}^{-1}$], θ_v is the volumetric water content [$\text{m}^3 \text{m}^{-3}$], R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is the temperature in Celcius degrees, A , B , C , and D are model fitting parameters. Figures 5-10, 5-11, and 5-12 depict CO₂, CH₄, and NH₃ emissions, respectively, as a function of time and temperature. Table 5-7 lists the model parameters fitted to the emission measurements and their estimation accuracy.

Overall the empirical model confirmed the strong-dependency of gaseous emissions on temperature and moisture content, particularly for CO₂ and CH₄ emissions. Lower correlations were noted for NH₃ emissions most likely due to the solubility and stikiness of NH₃ molecules reflecting a considerable uncertainty.

5.4. Summary and Conclusions

The new protocol, based on hourly, gradient-based and automated surface chamber measurements, was developed for assessment of regulated pollutant and greenhouse gas emissions from agricultural and natural systems. The new system was tested to investigate CO₂, CH₄, and NH₃ emissions from cattle manure surface applications, including beef manure, dairy manure, beef compost, and dairy compost. The estimated CO₂, CH₄, and NH₃ emissions from the surface application with dairy manure ($452.4 \pm$

35.4 g m⁻², 1.2 ± 0.1 g m⁻², and 1,786.0 ± 206.7 g m⁻², respectively) were the highest among other treatments. The emissions of CO₂, CH₄, and NH₃ from the surface application with beef compost treatment (210.5 ± 14.4 g m⁻², 0.2 ± 0.02 g m⁻², and 0.07 ± 0.01 g m⁻², respectively) were the lowest. Emissions of CO₂ and CH₄ were highly dependent on the air temperature. Linear correlations with strong *R*², particularly for CH₄ emissions, were observed between the percentages of hourly CO₂ and CH₄ emissions and temperature. Daily CO₂, CH₄, and NH₃ emissions were well correlated with average daily θ_v and well described using an exponential function.

Further assessments are warranted to understand the magnitude and variation of emissions due to seasonal cycles. A more accurate model, which takes into account physical, chemical, and biological factors, is necessary to estimate and describe regulated pollutant and greenhouse gas emissions.

References

- Amon B., Amon T., Boxberger J., Alt C. (2001). Emissions of NH₃, N₂O and CH₄ from dairy cows housed in a farmyard manure tying stall (housing, manure storage, manure spreading). *Nutrient Cycling in Agroecosystems* 60: 103-113. DOI: 10.1023/a:1012649028772.
- Borhan M.S., Capareda S., Mukhtar S., Faulkner W.B., McGee R., Parnell C.B. (2011). Determining seasonal greenhouse gas emissions from ground-level area sources in a dairy operation in central Texas. *Journal of the Air & Waste Management Association* 61: 786-795. DOI: 10.3155/1047-3289.61.7.786.
- Campbell C.S. (2001). Response of ECH₂O soil moisture sensor to temperature variation. Decagon Devices Inc., Pullman, WA.
- Chanzy A., Gaudu J. C., Marloie O. (2012). Correcting the temperature influence on soil capacitance sensors using diurnal temperature and water content cycles. *Sensors* 12: 9773-9790. DOI: 10.3390/s120709773.

- Christiansen J.R., Korhonen J.F.J., Juszczak R., Giebels M., Pihlatie M. (2011). Assessing the effects of chamber placement, manual sampling and headspace mixing on CH₄ fluxes in a laboratory experiment. *Plant and Soil* 343: 171-185. DOI: 10.1007/s11104-010-0701-y.
- Cobos D., Campbell C. (2007). Correcting temperature sensitivity of ECH₂O soil moisture sensors. Decagon Devices Inc., Pullman, WA.
- Davis J.L., Chudobiak W.J. (1975). In situ meter for measuring relative permittivity of soils, Department of Energy, Mines, and Resources, Geological Survey of Canada, Ottawa, ON, Canada. pp. 75-79.
- Dewes T. (1996). Effect of pH, temperature, amount of litter and storage density on ammonia emissions from stable manure. *The Journal of Agricultural Science* 127: 501-509. DOI: Doi: 10.1017/s0021859600078722.
- Ding L., Cao W., Shi Z., Li B., Wang C., Zhang G., Kristensen S. (2016a). Carbon dioxide and methane emissions from the scale model of open dairy lots. *Journal of the Air & Waste Management Association* 66: 715-725. DOI: 10.1080/10962247.2016.1173605.
- Ding L., Lu Q., Xie L., Liu J., Cao W., Shi Z., Li B., Wang C., Zhang G., Ren S. (2016b). Greenhouse gas emissions from dairy open lot and manure stockpile in northern China: A case study. *Journal of the Air & Waste Management Association* 66: 267-279. DOI: 10.1080/10962247.2015.1124058.
- Eddelbuettel D. (2006). random: An R package for true random numbers.
- Flessa H., Potthoff M., Loftfield N. (2002). Greenhouse estimates of CO₂ and N₂O emissions following surface application of grass mulch: importance of indigenous microflora of mulch. *Soil Biology and Biochemistry* 34: 875-879. DOI: [https://doi.org/10.1016/S0038-0717\(02\)00028-7](https://doi.org/10.1016/S0038-0717(02)00028-7).
- González-Avalos E., Ruiz-Suárez L.G. (2001). Methane emission factors from cattle manure in Mexico. *Bioresource Technology* 80: 63-71. DOI: [https://doi.org/10.1016/S0960-8524\(01\)00052-9](https://doi.org/10.1016/S0960-8524(01)00052-9).
- Hao X., Chang C., Larney F.J. (2004). Carbon, nitrogen balances and greenhouse gas emission during cattle feedlot manure composting. *Journal of Environmental Quality* 33: 37-44. DOI: 10.2134/jeq2004.3700.

- Hu E., Sutitarnnontr P., Tuller M., Jones S.B. (2018). Modeling temperature and moisture dependent emissions of carbon dioxide and methane from drying dairy cow manure. *Frontiers of Agricultural Science and Engineering* 5: 280.
- Hu E., Babcock E.L., Bialkowski S.E., Jones S.B., Tuller M. (2014). Methods and techniques for measuring gas emissions from agricultural and animal feeding operations. *Critical Reviews in Analytical Chemistry* 44: 200-219. DOI: 10.1080/10408347.2013.843055.
- Husted S. (1994). Seasonal variation in methane emission from stored slurry and solid manures. *Journal of Environmental Quality* 23: 585-592. DOI: 10.2134/jeq1994.00472425002300030026x.
- Hutchinson G.L., Mosier A.R. (1981). Improved Soil cover method for field measurement of nitrous oxide fluxes. *Soil Science Society of America Journal* 45: 311-316. DOI: 10.2136/sssaj1981.03615995004500020017x.
- Hutchinson G.L., Livingston G.P. (2001). Vents and seals in non-steady-state chambers used for measuring gas exchange between soil and the atmosphere. *European Journal of Soil Science* 52: 675-682. DOI: 10.1046/j.1365-2389.2001.00415.x.
- Jones S.B., Blonquist J.M., Robinson D.A., Rasmussen V.P., Or D. (2005). Standardizing characterization of electromagnetic water content sensors. *Vadose Zone Journal* 4: 1048-1058. DOI: 10.2136/vzj2004.0140.
- Kelleners T.J., Soppe R.W.O., Robinson D.A., Schaap M.G., Ayars J.E., Skaggs T.H. (2004). Calibration of capacitance probe sensors using electric circuit theory. *Soil Science Society of America Journal*. 68: 430-439. DOI: 10.2136/sssaj2004.4300.
- Khan R.Z., Muller C., Sommer S.G. (1997). Micrometeorological mass balance technique for measuring CH₄ emission from stored cattle slurry. *Biology and Fertility of Soils* 24: 442-444. DOI: 10.1007/s003740050270.
- Klop G., Velthof G.L., van Groenigen J.W. (2012). Application technique affects the potential of mineral concentrates from livestock manure to replace inorganic nitrogen fertilizer. *Soil Use and Management* 28: 468-477. DOI: 10.1111/j.1475-2743.2012.00434.x.
- Leytem A.B., Dungan R.S., Bjorneberg D.L., Koehn A.C. (2011). Emissions of ammonia, methane, carbon dioxide, and nitrous oxide from dairy cattle housing

- and manure management systems. *Journal of Environmental Quality* 40: 1383-1394. DOI: 10.2134/jeq2009.0515.
- Leytem A.B., Dungan R.S., Bjorneberg D.L., Koehn A.C. (2013). Greenhouse gas and ammonia emissions from an open-freestall dairy in southern Idaho. *Journal of Environmental Quality* 42: 10-20. DOI: 10.2134/jeq2012.0106.
- Mazzetto A.M., Barneze A.S., Feigl B.J., Van Groenigen J.W., Oenema O., Cerri C.C. (2014). Temperature and moisture affect methane and nitrous oxide emission from bovine manure patches in tropical conditions. *Soil Biology and Biochemistry* 76: 242-248. DOI: <https://doi.org/10.1016/j.soilbio.2014.05.026>.
- Mead R.M., Soppe R.W.O., Ayars J.E. (1996) Capacitance probe observations of daily soil moisture fluctuations, Evapotranspiration and Irrigation Scheduling, ASAE, St. Joseph, MI, San Antonio, TX. pp. 916-923.
- Midwest Plan Service (1985). Livestock waste facilities handbook. MWPS-18. University of Missouri Extension, Columbia, MO.
- Misselbrook T.H., Webb J., Chadwick D.R., Ellis S., Pain B.F. (2001). Gaseous emissions from outdoor concrete yards used by livestock. *Atmospheric Environment* 35: 5331-5338. DOI: [http://dx.doi.org/10.1016/S1352-2310\(01\)00289-8](http://dx.doi.org/10.1016/S1352-2310(01)00289-8).
- Mukhtar S., Mutlu A., Capareda S.C., Parnell C.B. (2008). Seasonal and spatial variations of ammonia emissions from an open-lot dairy operation. *Journal of the Air & Waste Management Association* 58: 369-376. DOI: 10.3155/1047-3289.58.3.369.
- Oertel C., Matschullat J., Zurba K., Zimmermann F., Erasmi S. (2016). Greenhouse gas emissions from soils - A review. *Chemie der Erde - Geochemistry* 76: 327-352. DOI: <https://doi.org/10.1016/j.chemer.2016.04.002>.
- Or D., Wraith J.M. (1999). Temperature effects on soil bulk dielectric permittivity measured by time domain reflectometry: A physical model. *Water Resources Research* 35: 371-383. DOI: 10.1029/1998wr900008.
- Osada, K., Ueda, S., Egashira, T., Takami, A., Kaneyasu, N. (2011). Measurements of gaseous NH₃ and particulate NH₄⁺ in the atmosphere by fluorescent detection after continuous air-water droplet sampling. *Aerosol Air Quality Research*, 11: 170-178. DOI: 10.4209/aaqr.2010.11.0101.

- Paltineanu I.C., Starr J.L. (1997). Real-time soil water dynamics using multisensor capacitance probes: Laboratory calibration. *Soil Science Society of America Journal* 61: 1576-1585. DOI: 10.2136/sssaj1997.03615995006100060006x.
- Parkin T.B., Venterea R.T., Hargreaves S.K. (2012). Calculating the detection limits of chamber-based soil greenhouse gas flux measurements. *Journal of Environmental Quality* 41: 705-715. DOI: 10.2134/jeq2011.0394.
- Pattey E., Trzcinski M.K., Desjardins R.L. (2005). Quantifying the reduction of greenhouse gas emissions as a result of composting dairy and beef cattle manure. *Nutrient Cycling in Agroecosystems* 72: 173-187. DOI: 10.1007/s10705-005-1268-5.
- Pereira J., Misselbrook T.H., Chadwick D.R., Coutinho J., Trindade H. (2012). Effects of temperature and dairy cattle excreta characteristics on potential ammonia and greenhouse gas emissions from housing: A laboratory study. *Biosystems engineering* 112:138-150. DOI: <https://doi.org/10.1016/j.biosystemseng.2012.03.011>.
- Pereira J., Figueiro D., Misselbrook T.H., Chadwick D.R., Coutinho J., Trindade H. (2011). Ammonia and greenhouse gas emissions from slatted and solid floors in dairy cattle houses: A scale model study. *Biosystems engineering* 109: 148-157. DOI: <https://doi.org/10.1016/j.biosystemseng.2011.02.011>.
- Robinson D.A., Gardner C.M.K., Evans J., Cooper J.D., Hodnett M.G., Bell J.P. (1998). The dielectric calibration of capacitance probes for soil hydrology using an oscillation frequency response model. *Hydrology and Earth System Sciences* 2: 111-120. DOI: 10.5194/hess-2-111-1998.
- Rochette P., Eriksen-Hamel N.S. (2008). Chamber measurements of soil nitrous oxide flux: Are absolute values reliable? *Soil Science Society of America Journal* 72: 331-342. DOI: 10.2136/sssaj2007.0215.
- Schröder J.J., De Visser W., Assinck F.B.T., Velthof G.L., Van Geel W., Van Dijk W. (2013). Nitrogen fertilizer replacement value of the liquid fraction of separated livestock slurries applied to potatoes and silage maize. *Communications in Soil Science and Plant Analysis* 45: 73-85. DOI: 10.1080/00103624.2013.848881.
- Starr J.L., Paltineanu I.C. (1998). Soil water dynamics using multi-sensor capacitance probes in non-traffic interrows of corn. *Soil Science Society of America Journal* 62: 114-122. DOI: 10.2136/sssaj1998.03615995006200010015x.

- Sutitaranontr P., Hu E., Tuller M., Jones S.B. (2014). Physical and Thermal Characteristics of Dairy Cattle Manure. *Journal of Environmental Quality* 43: 2115-2129. DOI: 10.2134/jeq2014.05.0212.
- Sutitaranontr, P., Miller, R., Bialkowski, S., Tuller, M., & Jones, S. B. (2012). A multiplexing system for monitoring greenhouse and regulated gas emissions from manure sources using a portable FTIR gas analyzer. In *ASABE Annual International Meeting 2012, ASABE 2012 (Vol. 4, pp. 2782-2788)*. American Society of Agricultural and Biological Engineers, St. Joseph, MI.
- Sutitaranontr, P., Hu, E., Miller, R., Tuller, M., & Jones, S. B. (2013). Measurement accuracy of a multiplexed portable FTIR - Surface chamber system for estimating gas emissions. In *ASABE Annual International Meeting 2013, ASABE 2013 (Vol. 6, pp. 4634-4645)*. American Society of Agricultural and Biological Engineers, St. Joseph, MI.
- United States Department of State (2017). *U.S. climate action report 2017*, Global Publishing Services, Washington, DC.
- USDA (2010). *Composting, Chapter 2 - Part 637 Environmental Engineering, National Engineering Handbook*.
- Wraith J.M., Or D. (1999). Temperature effects on soil bulk dielectric permittivity measured by time domain reflectometry: Experimental evidence and hypothesis development. *Water Resources Research* 35: 361-369. DOI: 10.1029/1998wr900006.
- Yokelson, R. J., Christian, T. J., Bertschi, I. T., & Hao, W. M. (2003). Evaluation of adsorption effects on measurements of ammonia, acetic acid, and methanol. *Journal of Geophysical Research: Atmospheres*, 108(D20): 4649. DOI: 10.1029/2003JD003549.
- Zhu, Z., Xin, H., Li, H., & Dong, H. (2012). Assessment of tubing type on ammonia gas adsorption. *Applied Engineering in Agriculture*, 28(2), 265-269. DOI: 10.13031/2013.41343.

Table 5-1. Air temperature (T), relative humidity (RH), wind speed, and solar radiation during field measurements.

Parameter	$T(^{\circ}C)$	RH (%)	Wind Speed ($m\ s^{-1}$)	Solar Radiation ($W\ m^{-2}$)
Mean \pm SD	23.33 ± 7.04	39.44 ± 21.30	3.14 ± 1.80	277.62 ± 329.32
Range	8.9 ~ 35.0	6.0 ~ 93.0	0.0 ~ 10.29	0.6 ~ 936.76
CV [†]	30.18%	54.01%	57.19%	118.62%

[†] CV = coefficient of variation, $CV = (SD/Mean) \times 100\%$

Table 5-2. Estimated CO₂, CH₄, and NH₃ emissions from each treatment (Mean ± SD)

Treatment	CO ₂ †		CH ₄		NH ₃	
	g m ⁻² ‡	g m ⁻² d ⁻¹	g m ⁻² ‡	mg m ⁻² d ⁻¹	g m ⁻² ‡	mg m ⁻² d ⁻¹
Beef Manure	368.0 ± 28.0	24.5 ± 1.9	1.1 ± 0.1	70.7 ± 6.7	10.86 ± 1.6	724.0 ± 106.7
Dairy Manure	452.4 ± 35.4	30.2 ± 2.4	1.2 ± 0.1	78.0 ± 5.3	26.79 ± 3.1	1,786.0 ± 206.7
Beef Compost	210.5 ± 14.4	14.0 ± 1.0	0.2 ± 0.02	13.3 ± 1.3	0.07 ± 0.01	4.7 ± 0.7
Dairy Compost	243.1 ± 15.3	16.2 ± 1.0	0.3 ± 0.03	20.0 ± 2.0	0.14 ± 0.03	9.3 ± 2.0
Other Studies						
Ding et al. (2016b) §	-	15.6 ± 7.4	-	51.8 ± 24.1	-	-
Borhan et al. (2011) ¶	-	-	-	9.6	-	-
Misselbrook et al. (2001) ††	-	-	-	4.9 - 16.71	-	6,720
Pereira et al. (2011) ‡‡	-	-	0.14 - 0.40	-	2.14 - 5.23	-

† Including CO₂ from soil respiration

‡ Total emissions during field measurements (15 days)

§ Using closed chamber to measure emissions from the ground level of bricked-paved open lots at a commercial dairy farm

¶ Using closed chamber to measure emissions in a free-stall dairy operation in central Texas

†† Using the equilibrium concentration technique in measurements of NH₃ emission and closed chambers for CH₄ emissions from outdoor concrete yards used by dairy cows

‡‡ Using two chamber scale models in measurements of gas emissions for the first 72 hours after excreta application

Table 5-3. Parametric expression and accuracy of the parameters fitted to the measured water content to determine the relationship between volumetric water content (θ_v) and time (t) in hour †

Treatment	Coefficients $\theta_v = At^2 + Bt + C$			RMSE ($\text{cm}^3 \text{cm}^{-3}$)	R^2
	A [$\times 10^{-6}$]	B [$\times 10^{-4}$]	C [$\times 10^{-1}$]		
Beef manure	1.083	-9.225	2.916	0.012	0.955
Beef compost	0.983	-8.285	2.908	0.013	0.942
Dairy compost	1.167	-9.255	2.800	0.011	0.950
Dairy manure	1.511	-12.386	3.202	0.012	0.960

† N of each treatment = 1,080

Table 5-4. Coefficients of parametric expression for drying rate of soil surface ($\partial\theta_v / \partial t$).

Treatment	Coefficients $\partial\theta_v / \partial t = 2At + B$	
	$2A [x 10^{-6}]$	$B [x 10^{-4}]$
Beef manure	2.166	-9.225
Beef compost	1.966	-8.285
Dairy compost	2.334	-9.255
Dairy manure	3.022	-12.386
Mean	2.372	-9.780

Table 5-5. Coefficients of the linear function $F_s = A \cdot T + B$ demonstrating correlation between percentage of hourly emissions (F_s) and temperature (T) shown in Figure 5-8.

Treatment	CO ₂			CH ₄			NH ₃		
	A	B	R ²	A	B	R ²	A	B	R ²
Beef and dairy manure	0.12	1.29	0.74	0.37	-4.34	0.87	0.42	-5.09	0.39
Beef and dairy compost	0.05	3.11	0.56	0.31	-3.54	0.63	0.58	-6.18	0.24

Table 5-6. Coefficients of the exponential function $F_d = A \cdot e^{B(\theta_{vd})} + C$ for the relation between daily emissions (F_d) and average daily water content (θ_{vd}) shown in Figure 5-9.

Treatment	CO ₂				CH ₄				NH ₃			
	A	B	C	R ²	A	B	C	R ²	A	B	C	R ²
Beef manure	2.02	11.56	6.73	0.96	$3.66 \cdot 10^{-3}$	14.82	0.0	0.95	$3.49 \cdot 10^{-3}$	24.05	0.0	0.72
Dairy manure									$3.85 \cdot 10^{-3}$	26.67	0.0	0.89
Beef compost	0.87	5.02	6.04	0.93	$1.72 \cdot 10^{-5}$	30	0.0	0.93	$1.76 \cdot 10^{-5}$	29.57	0.0	0.92
Dairy compost					$4.38 \cdot 10^{-4}$	19.8	0.0	0.94	$1.66 \cdot 10^{-5}$	30.95	0.0	0.82

Table 5-7. Parameters of the empirical model expressed as $F = A \cdot e^{\left[\frac{-B \cdot \theta_v^2 + C \cdot \theta_v + D}{R \cdot (273.15 + T)} \right]}$ for the relation between emissions (F), water content (θ_v), and temperature (T) as depicted in Figures 5-10, 5-11, and 5-12.

Treatment	CO ₂						CH ₄					
	A	B	C	D	R ²	MSE	A	B	C	D	R ²	MSE
Beef manure	4.8 · 10 ³	-8.1 · 10 ⁴	1.3 · 10 ⁴	1.7 · 10 ⁴	0.88	1.57	3.1 · 10 ¹⁴	1.2 · 10 ⁵	-9.4 · 10 ⁴	1.0 · 10 ⁵	0.89	0.02
Dairy manure	5.6 · 10 ⁵	-2.3 · 10 ⁴	-1.0 · 10 ⁴	3.1 · 10 ⁴	0.88	2.34	2.9 · 10 ¹⁵	1.8 · 10 ⁵	-1.3 · 10 ⁵	1.0 · 10 ⁵	0.89	0.02
Beef compost	43.9	-7.5 · 10 ⁴	2.2 · 10 ⁴	4.8 · 10 ³	0.74	0.49	1.7 · 10 ⁷	-7.3 · 10 ⁴	-5.3 · 10 ⁴	6.9 · 10 ⁴	0.79	0.01
Dairy compost	167.0	-7.3 · 10 ⁴	1.8 · 10 ⁴	8.3 · 10 ³	0.79	0.65	3.5 · 10 ¹⁰	1.3 · 10 ⁵	-1.1 · 10 ⁵	8.6 · 10 ⁴	0.90	0.01

Treatment	NH ₃					
	A	B	C	D	R ²	MSE
Beef manure	6.9 · 10 ¹²	-5.6 · 10 ⁵	1.9 · 10 ⁵	6.4 · 10 ⁴	0.56	1.45
Dairy manure	5.0 · 10 ¹⁸	-2.4 · 10 ⁵	9.8 · 10 ⁴	9.9 · 10 ⁴	0.30	3.43
Beef compost	8.1 · 10 ⁻¹	-6.6 · 10 ⁵	1.9 · 10 ⁵	5.1 · 10 ³	0.30	0.02
Dairy compost	4.9 · 10 ⁶	2.1 · 10 ⁵	-2.3 · 10 ⁵	9.4 · 10 ⁴	0.52	0.02

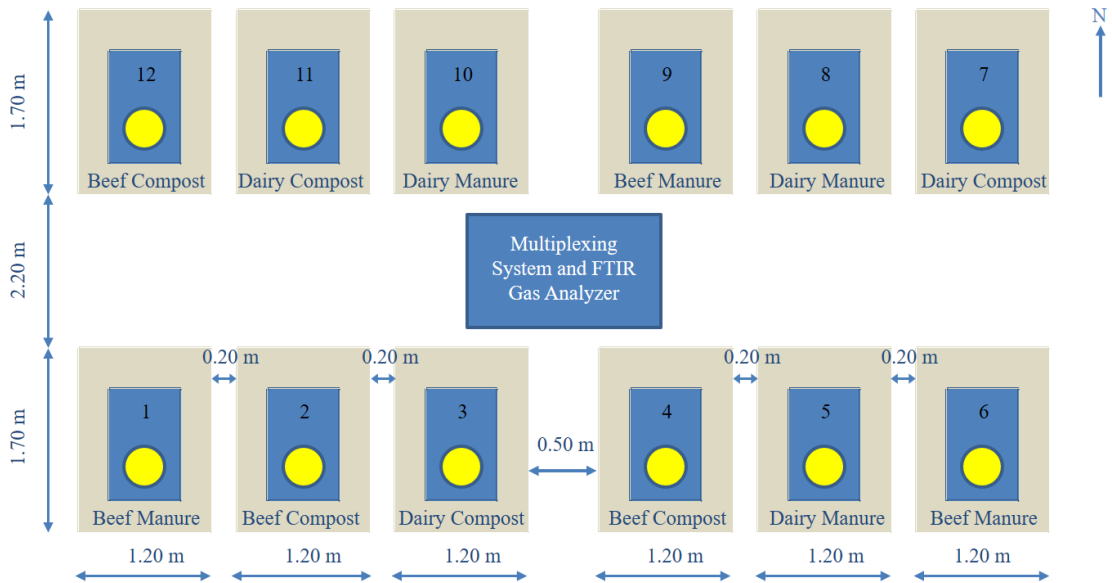


Figure 5-1: Experimental design illustrating four manure treatments with three replicates each (Not to scale).

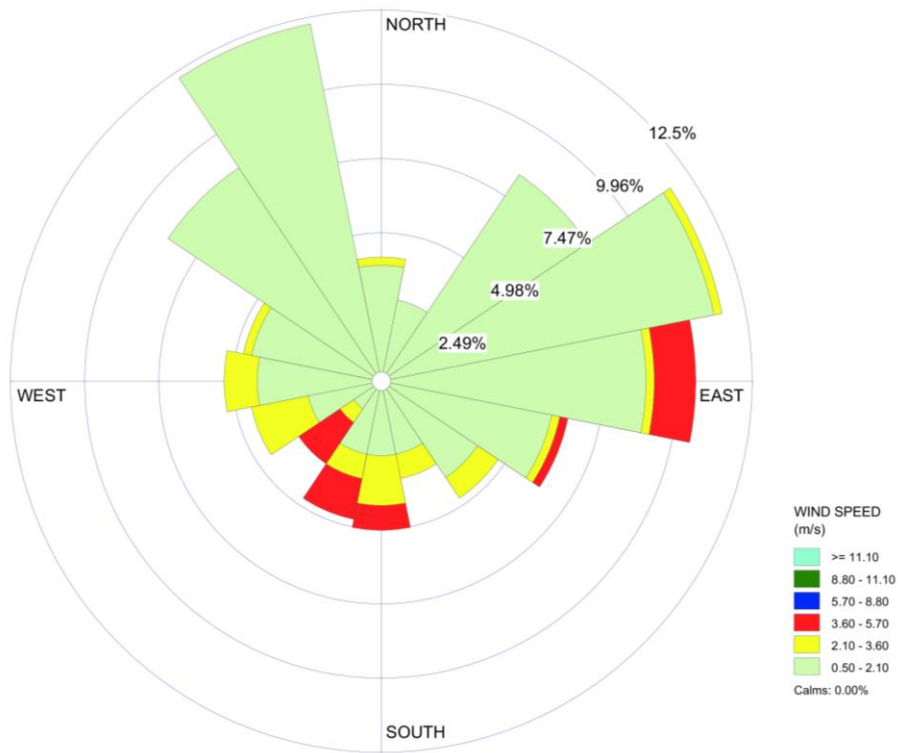
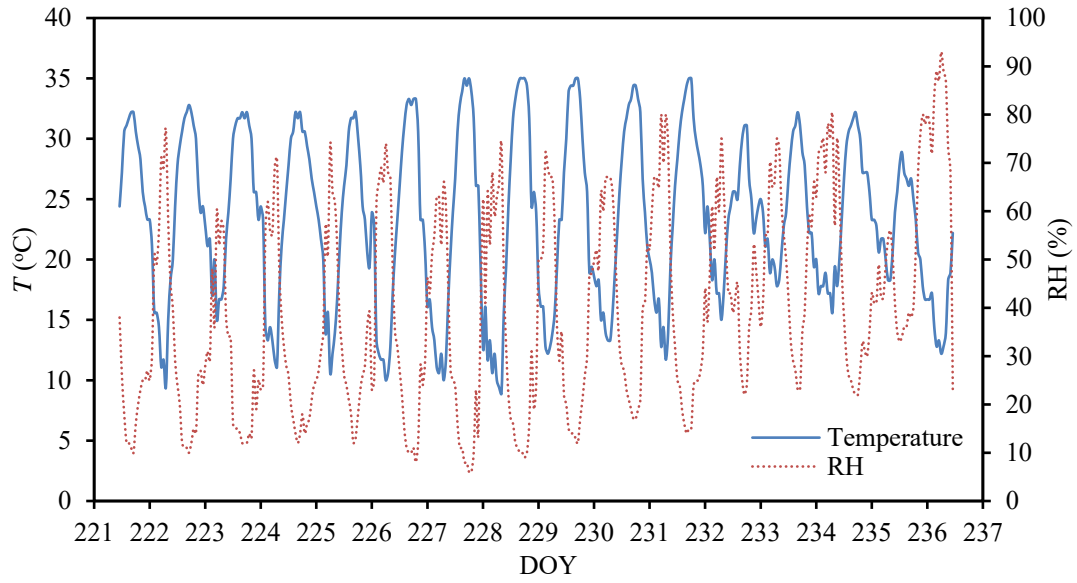


Figure 5-2: Background temperature, relative humidity (RH), wind speed, and wind direction during measurements.

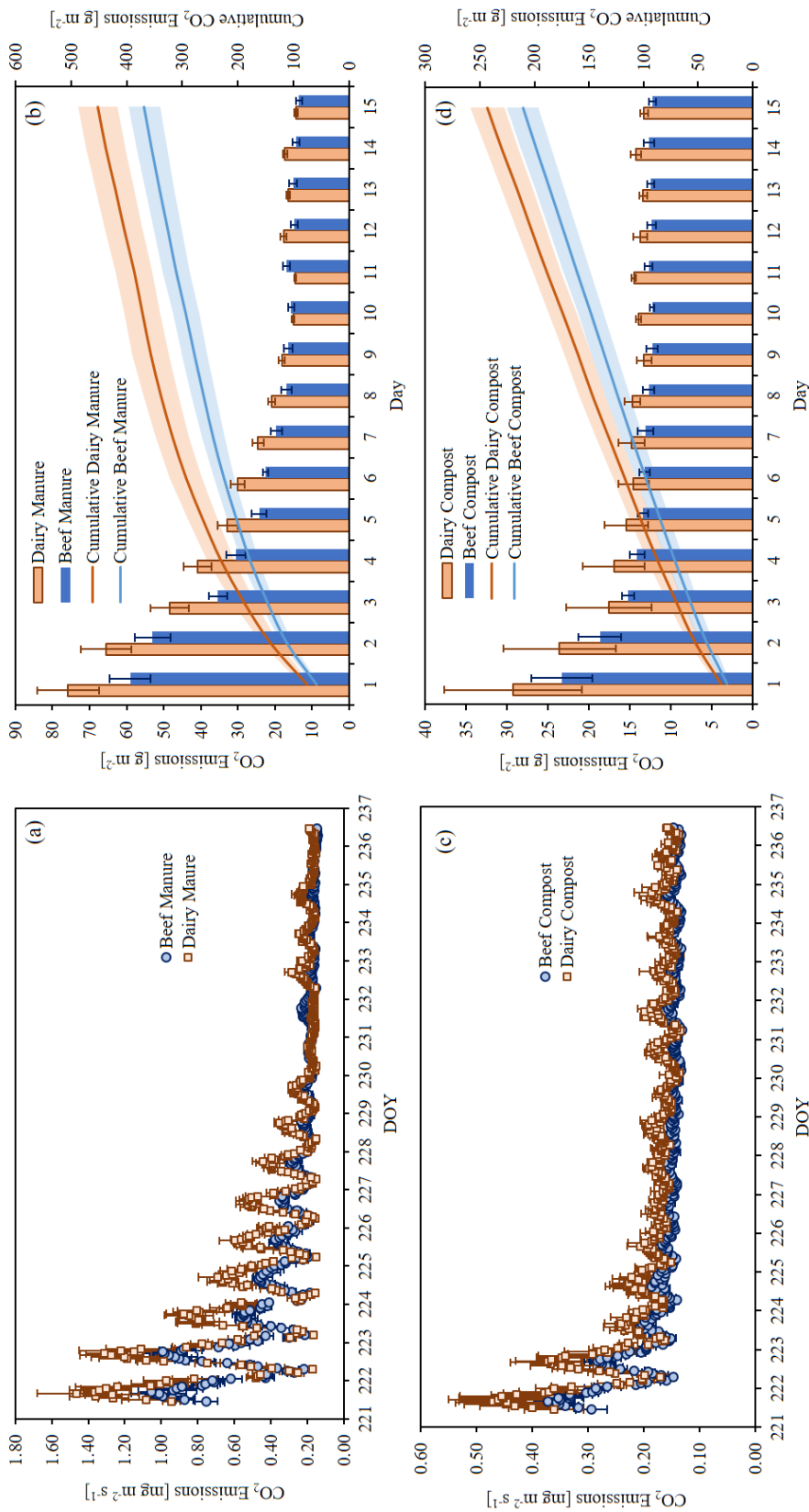


Figure 5-3: (a) CO₂ emissions from the surface application with beef and dairy manure (b) Cumulative emission of CO₂ from beef manure and dairy manure (c) CO₂ emissions from the surface application with beef and dairy compost, and (d) Cumulative emission of CO₂ from beef manure and dairy compost.

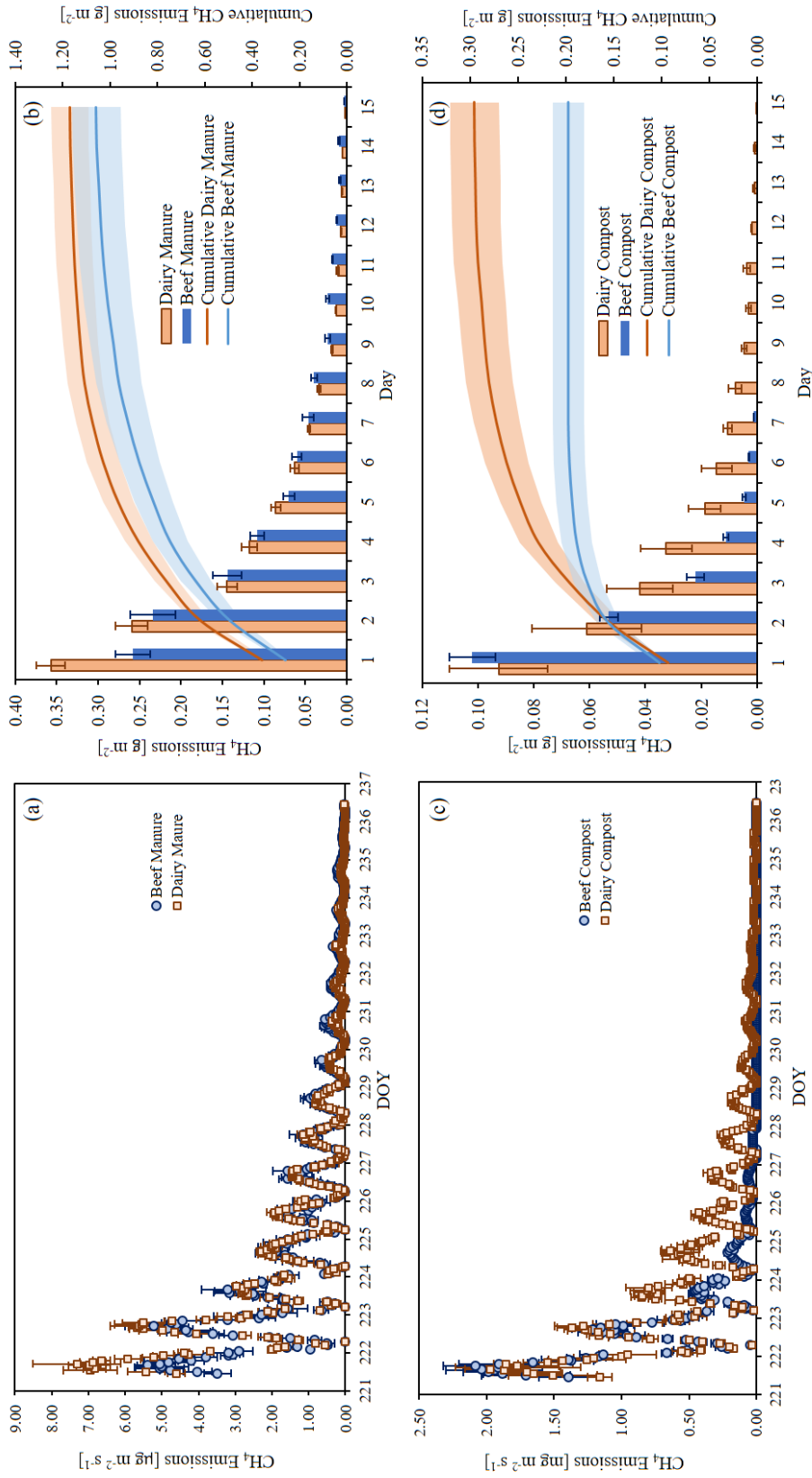


Figure 5-4: (a) CH₄ emissions from the surface application with beef and dairy manure (b) Cumulative emission of CH₄ from beef manure and dairy manure (c) CH₄ emissions from the surface application with beef and dairy compost, and (d) Cumulative emission of CH₄ from beef manure and dairy compost.

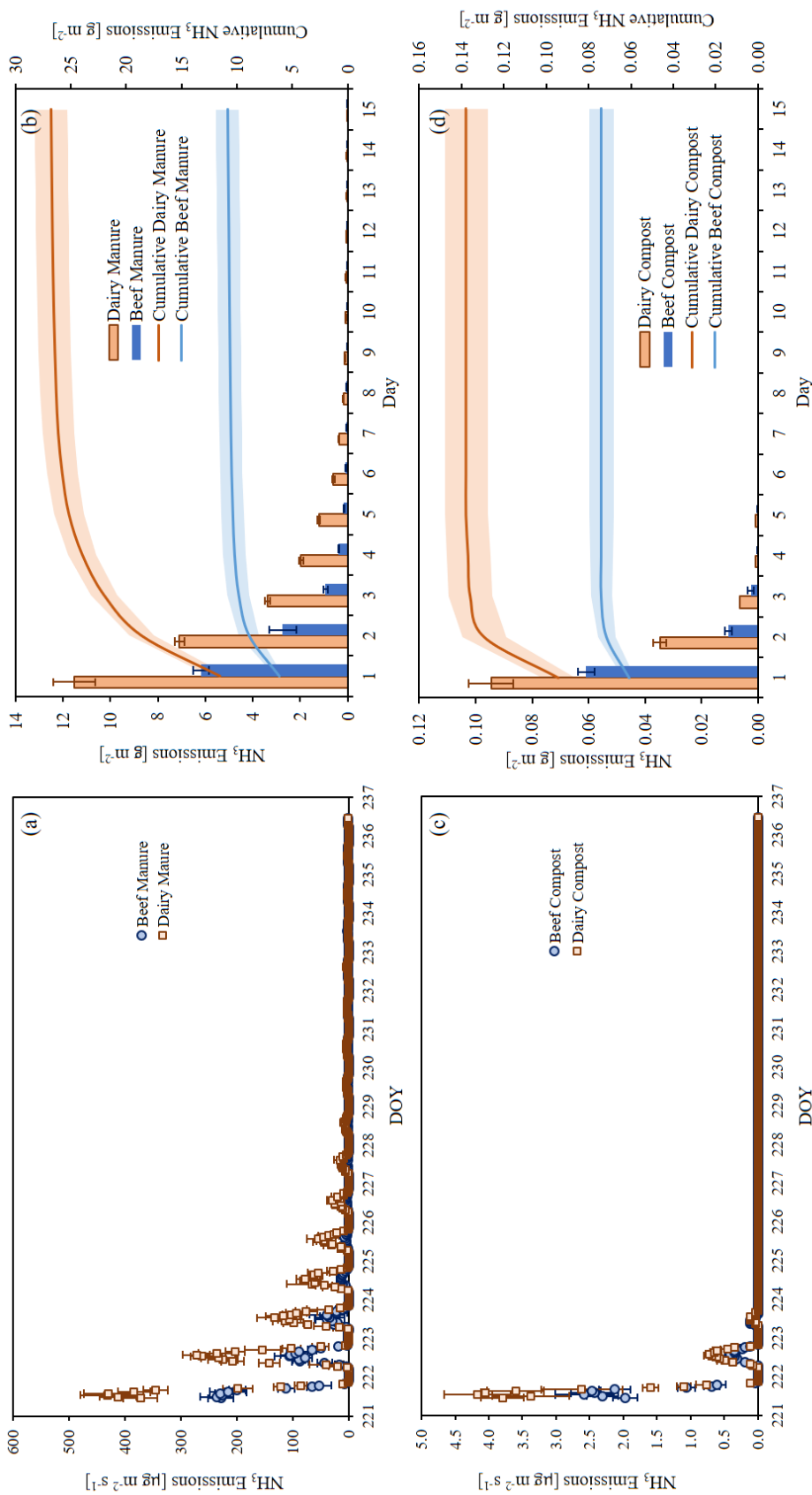


Figure 5-5: (a) NH_3 emissions from the surface application with beef and dairy manure (b) Cumulative emission of NH_3 from beef manure and dairy manure (c) NH_3 emissions from the surface application with beef and dairy compost, and (d) Cumulative emission of NH_3 from beef manure and dairy compost.

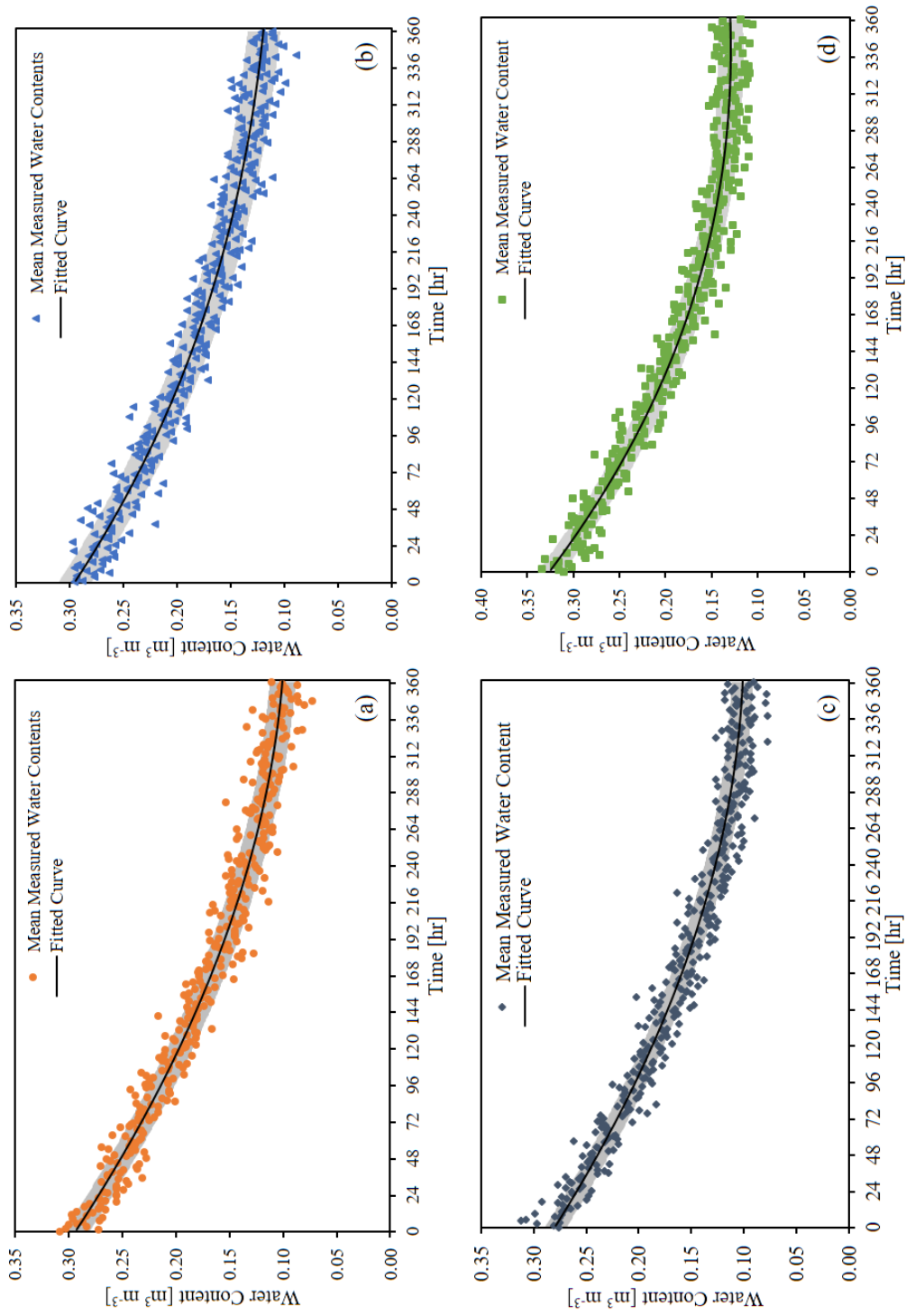


Figure 5-6: Measured water content vs. time since application for (a) Beef manure, (b) Beef compost, (c) Dairy compost, and (d) Dairy manure. The black solid lines are fitted curves with the shaded 95% confidence intervals of the curve fitting.

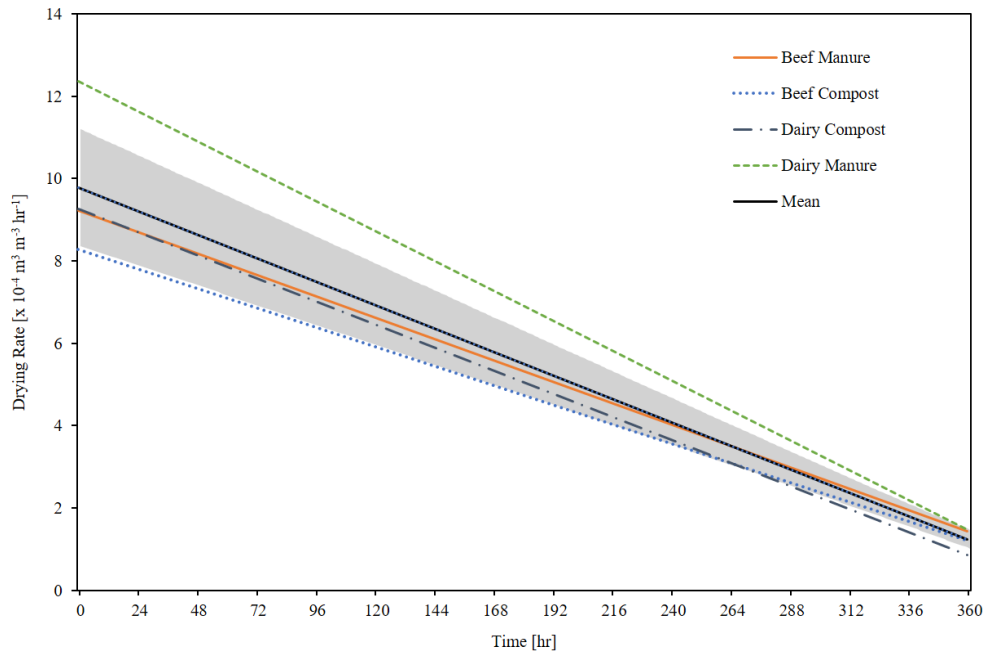


Figure 5-7: Drying rates of soil surface vs. time for beef manure, beef compost, dairy compost, and dairy manure applications. The black solid line represents the mean from all treatments with shaded standard deviation.

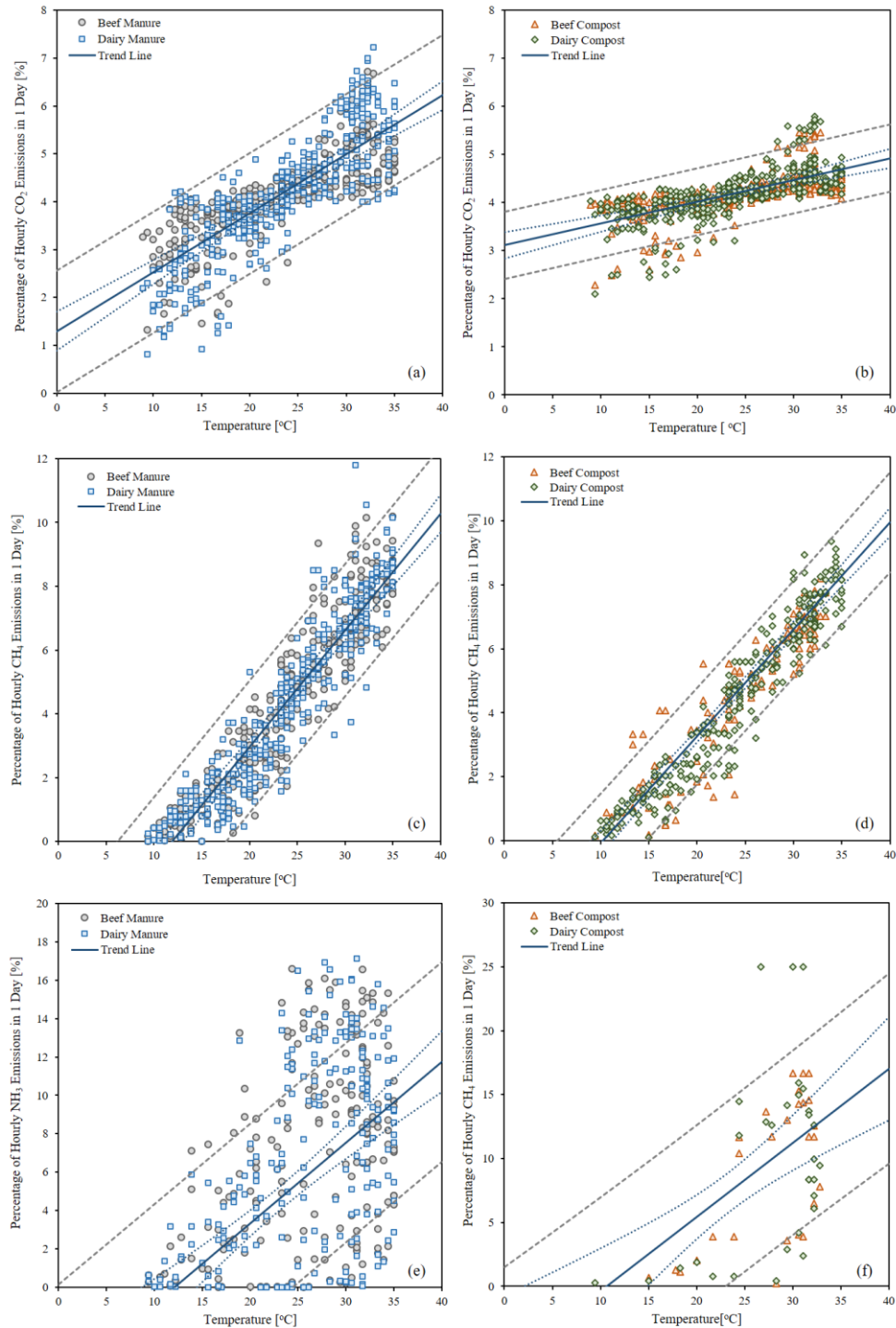


Figure 5-8: (a), (c), and (e) Percentage of hourly CO₂, CH₄, and NH₃ emissions vs. temperature from the surface application with beef and dairy manure. (b), (d), and (f) Percentage of hourly CO₂, CH₄, and NH₃ emissions vs. temperature from the surface application with beef and dairy compost. All figures show 95% confidence interval and 95% prediction interval from the trend line.

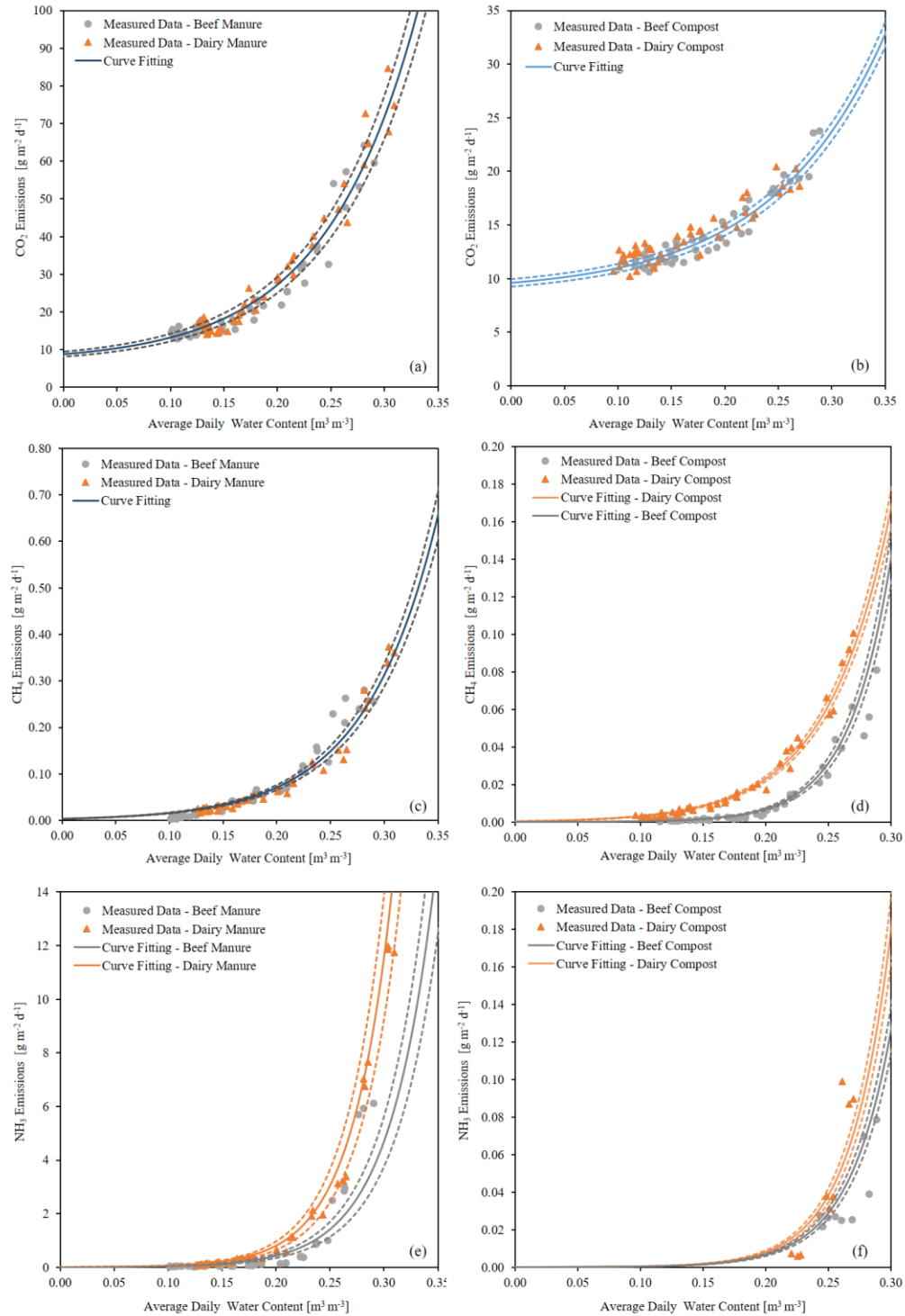


Figure 5-9: (a), (c), and (e) Daily CO₂, CH₄, and NH₃ emissions from the surface application with beef and dairy manure vs. average daily water content. (b), (d), and (f) Daily CO₂, CH₄, and NH₃ emissions from the surface application with beef and dairy compost vs. average daily water content. The solid line is the fitted curve with the exponential function. The dashed lines show 95% confidence interval of the curve fitting.

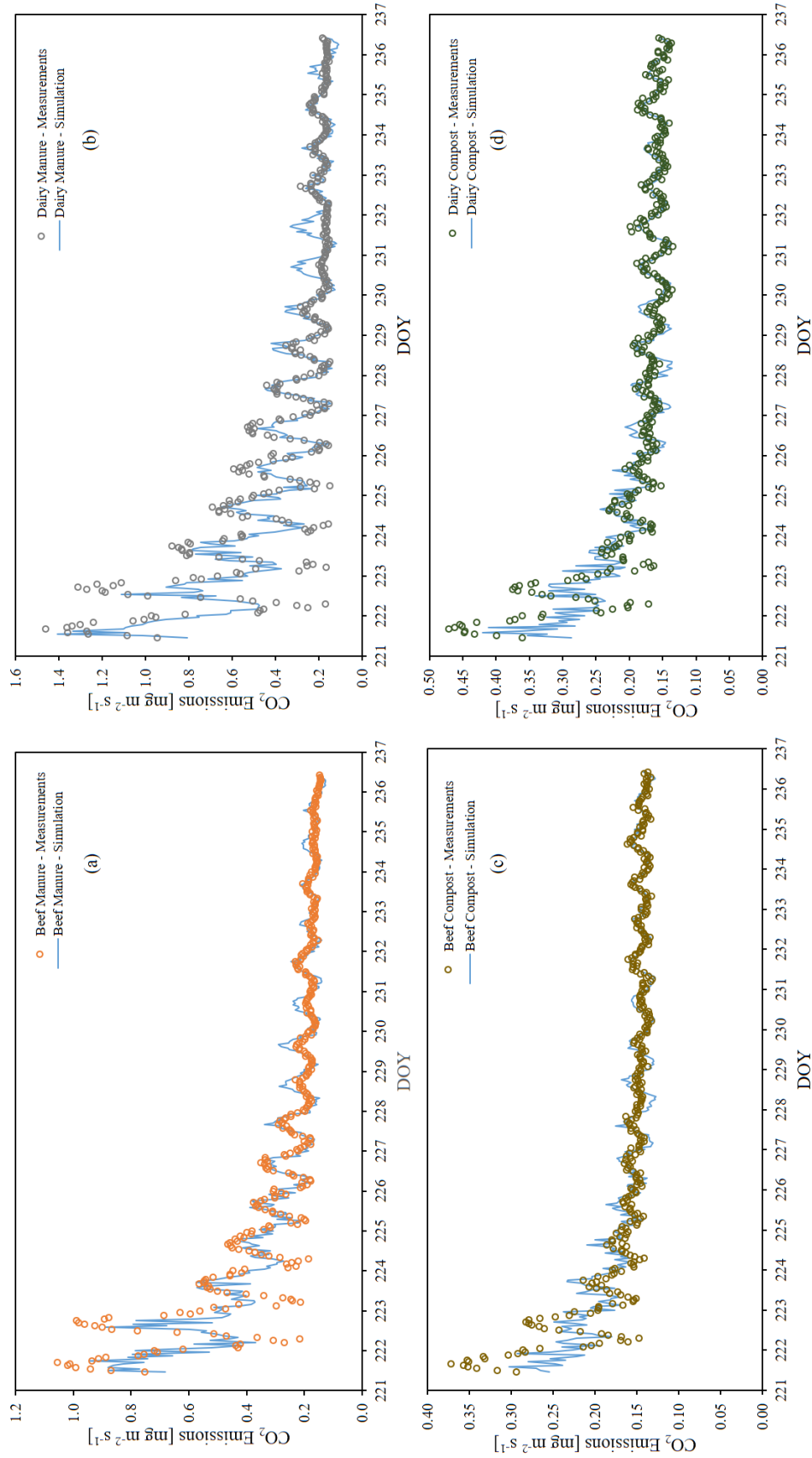


Figure 5-10: Mean measured CO₂ emissions vs. simulations for (a) Beef manure, (b) Dairy manure, (c) Beef compost, and (d) Dairy compost.

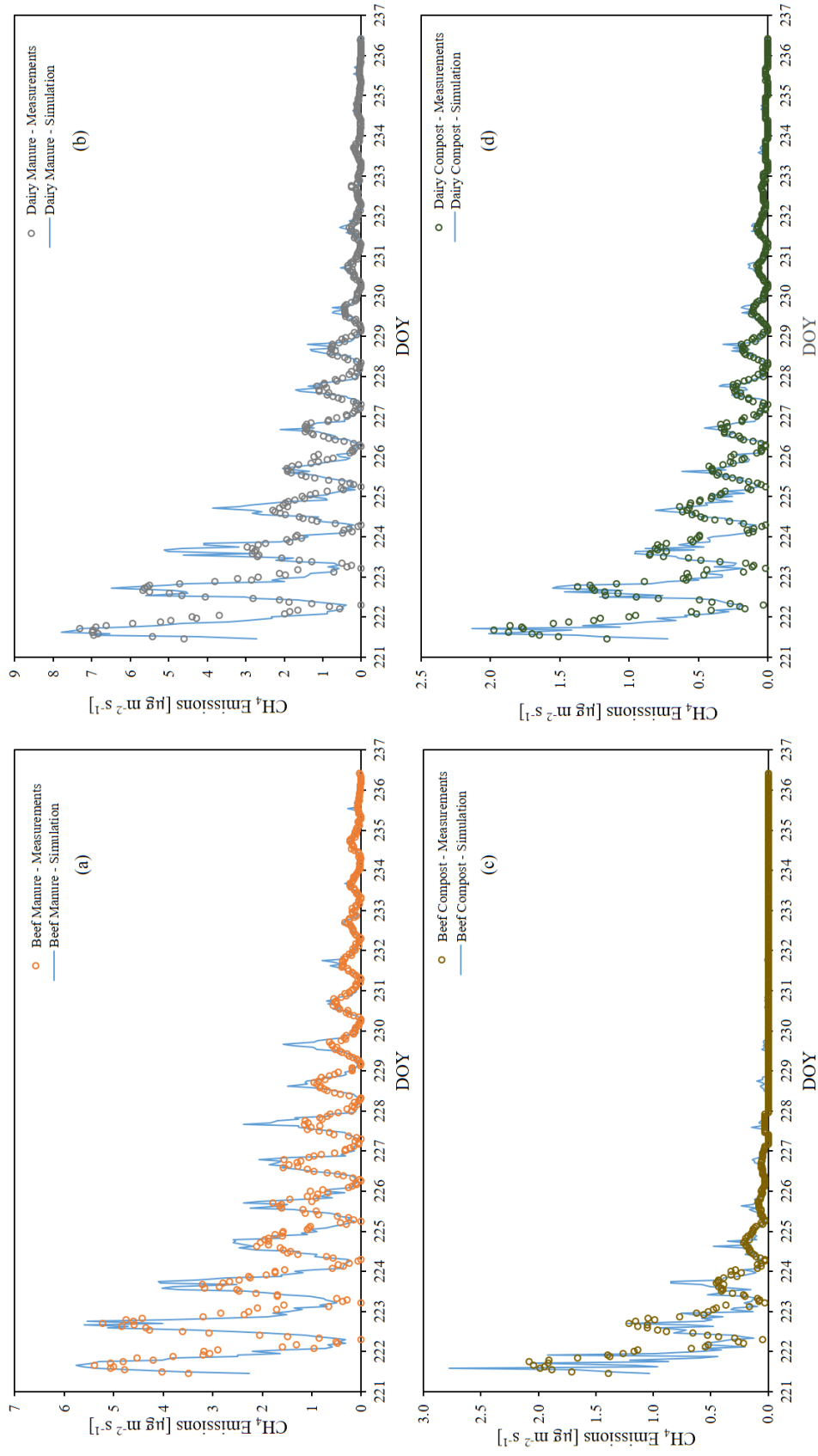


Figure 5-11: Mean measured CH_4 emissions vs. simulations for (a) Beef manure, (b) Dairy manure, (c) Beef compost, and (d) Dairy compost.

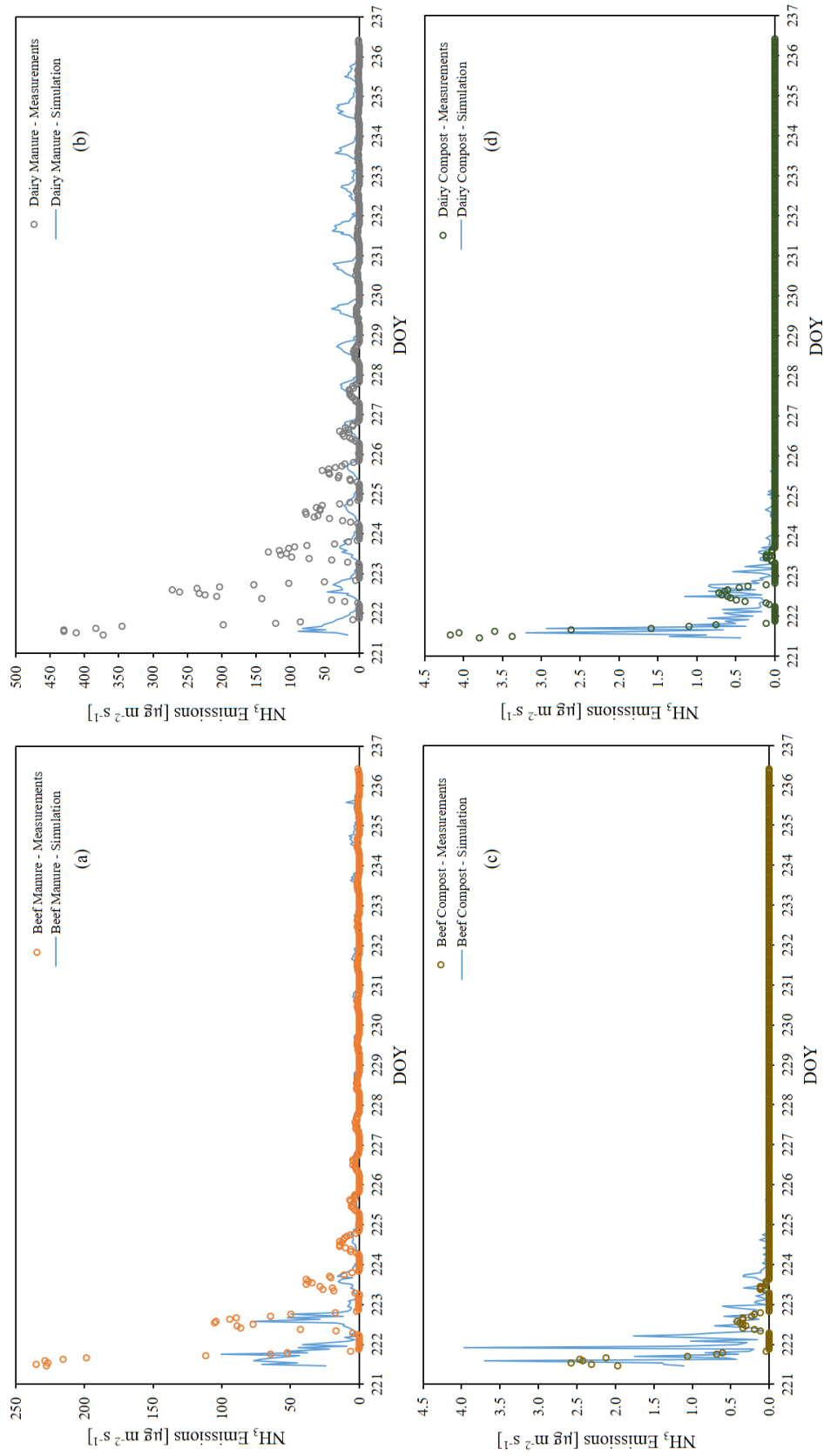


Figure 5-12: Mean measured NH_3 emissions vs. simulations for (a) Beef manure, (b) Dairy manure, (c) Beef compost, and (d) Dairy compost.

CHAPTER 6

SUMMARY AND CONCLUSIONS

The research presented in this dissertation was to develop an automated multi-gas emission measurement system, based on the multiplexed portable FTIR-surface chamber network for continuous measurements and monitoring of target gas emissions. Chamber-based techniques have been widely used for area flux estimates at small-scales, when micrometeorological techniques are inappropriate. The surface chamber techniques effectively isolate sample sources from external environmental conditions (e.g., wind speed and wind direction). The measurements are not strongly dependent on the weather conditions; therefore, they can be directly comparable from day-to-day and site-to-site or for treatment comparison. The framework in development of an automated multi-gas emission measurement system, based on the multiplexed portable FTIR-surface chamber network, is introduced in Chapter 2.

Chapter 3 presents the evaluation of the precision and accuracy of the surface chamber system in controlled laboratory conditions. Comparisons of methane emission measurements were used to evaluate the measurement accuracy of the system with statistical one-way ANOVA tests with a level of significance of 0.05. Analyses revealed that there were no significant differences across the twelve chambers with resulting p-values of 0.54, 0.58, and 0.80 in three different experiments. The system accuracy was observed as relative percentage differences between the mean of the methane fluxes determined by the system and the fluxes estimated using the gradient-based technique. Overall, the measurement biases were less than 1%.

The fundamental physical, hydraulic, and thermal properties of dairy manure that primarily affect the transport of liquid water and gas within the manure are discussed in Chapter 4. Numerical modeling of transient water flow in cattle manure requires an accurate estimation of a number of physical and hydraulic parameters, including the water retention characteristic, saturated hydraulic conductivity (K_s), and unsaturated hydraulic conductivity function ($K(\theta_v)$). Measurement techniques commonly applied in soil science were applied to determine physical properties of as-excreted dairy manure, including the empirical relationship between manure dielectric permittivity (K_d) and volumetric water content (θ_v). The uncertainties of the measurements were anticipated from the shrinkage phenomenon during the drying process. The liquid water retention characteristic for cattle manure, determined based on volumetric measurements and the chilled-mirror dewpoint technique, was found to be similar to that of organic peat soils. Inverse analysis of $K(\theta_v)$, using the developed water retention characteristic and laboratory evaporation experiment, yielded reasonable results, showing strong support for the hypothesis that the Richards equation can describe hydrodynamic processes taking place in dairy manure relevant to natural drying processes. The effects of surface crust formation and shrinkage, which are likely to occur variably upon drying, potentially modify the water retention and hydraulic conductivity functions due to high moisture content and high porosity of as-excreted manure.

The physical and hydraulic properties of cattle manure are key requirements in the model development to accurately describe manure leachate transport mechanisms and response from point- to field- and feedlot-scales. From a physical perspective, manure is a heterogeneous, polyphasic, disperse porous medium generally consisting of solid,

liquid, and gaseous phases. The solid fraction primarily consists of fibrous organic material, which may include hay, grain, and silage, creating a complex manure matrix. The liquid phase is mostly water, commonly containing dissolved solutes and organic matter. The gas fraction occupies the empty pores or void space. The manure matrix determines the geometric characteristics of the empty pores that play an important role in the transport of the water and gases.

The thermal properties of thermal conductivity (λ), thermal diffusivity (κ), and bulk volumetric heat capacity (C) were determined during the course of manure drying, using three penta-needle heat pulse probes (PHPPs). Thermal properties of λ and C exhibited strong linear correlation with decreasing θ_v . Although κ also decreased with decreasing θ_v , it showed a more complex regression form. The accuracy and agreement of the thermal properties determined was assessed. The results suggested a reliable prediction of θ_v using the PHPPs, indicating well-characterized physical and thermal properties of dairy manure.

By characterizing physical, hydraulic, and thermal properties of dairy manure using well established analytical models, advanced modeling of greenhouse gas emissions, in addition to water, solute and colloid transport processes can be simulated using analytical and advanced numerical modeling. The resulting thermal properties of dairy manure reported in this chapter are likely to be used for development of heat transport models to identify the optimal conditions for manure composting processes as well as for prediction of manure water content and the movement of solutes and water from manure sources in addition to microbial activity and gas generation. Overall, the results presented in Chapter 4 provide a solid foundation upon which future research can

build in better modeling and understanding dairy cow manure processes that impact the environment.

Finally, the developed multi-gas emission measurement system was tested to determine and monitor CO₂, CH₄ and NH₃ emissions from cattle manure surface applications, including beef manure, dairy manure, beef compost, and dairy compost from field plots at Greenville Research Farm. The estimated CO₂, CH₄, and NH₃ emissions from the surface application with dairy manure ($452.4 \pm 35.4 \text{ g m}^{-2}$, $1.2 \pm 0.1 \text{ g m}^{-2}$, and $1,786.0 \pm 206.7 \text{ g m}^{-2}$, respectively) were the highest among other treatments. The emissions of CO₂, CH₄, and NH₃ from the surface application with beef compost treatment ($210.5 \pm 14.4 \text{ g m}^{-2}$, $0.2 \pm 0.02 \text{ g m}^{-2}$, and $0.07 \pm 0.01 \text{ g m}^{-2}$, respectively) were the lowest. CO₂ and CH₄ emissions presented in this study were found to be highly dependent on the air temperature and moisture content agreeing with previous studies. Linear correlations with strong coefficient of determination (R^2), particularly for CH₄ emissions, were observed between the percentages of hourly CO₂ and CH₄ emissions and temperature. Daily CO₂ and CH₄ emissions were found to be well correlated with average daily θ_v and well described using an exponential function. An empirical model, based on the Arrhenius equation, was verified with the emission measurement data confirming strong dependency of CO₂ and CH₄ emissions on temperature and moisture content of the soil surface applied with manure source materials. The solubility of NH₃ most likely affected the accuracy of the NH₃ emission measurements in the study.

CHAPTER 7

RECOMMENDATIONS

This dissertation demonstrates the development of the gas emission measurement system and quantification of gas emissions from surface application with different manure types using the measurement system. The results of the current research show the performance of the measurement system and correlations between gas emissions and the air temperature and surface soil moisture content. While the goals of the research were achieved, a number of issues exist which warrant further investigation and extend beyond the scope of this dissertation.

The design of the measurement chamber could be improved to minimize the artificial, constrained environment created by the chamber, which can alter the boundary conditions (i.e., inhibition) for natural gas emissions. The inside and outside conditions including the concentration gradients driving diffusion, barometric pressure, temperature and moisture of the surface soil inside and outside the chamber must be as identical as possible to provide accurate measurements. It is important to consider the effect of the presence of the chamber on gaseous concentration gradients within the measurement environment, leading to errors in gaseous flux estimates. The measurement times should be limited to three minutes in order to maintain chamber gas concentration changes as small as possible, and minimize this effect. Additionally, the measurement chamber should be designed and developed to equalize pressure in the chamber with atmospheric pressure, particularly in windy conditions. The location and position of the chamber during the measurement are other factors to be considered for further investigation as

they could alter the moisture of the surface soil and temperature inside the chamber from the surrounding area.

Physical, hydraulic, and thermal properties of cattle manure reported in Chapter 4 represent a novel and unique contribution for advancing prediction and modeling capabilities of gas emissions from manure sources, while the uncertainties of the results can be due to the complexity of shrinkage, surface crust formation, and shrinkage cracks. The effects of surface crust formation and shrinkage, which are likely to occur variably upon drying, potentially modify the water retention and hydraulic conductivity functions due to high moisture content and high porosity of as-excreted manure. Further work is needed to characterize the manure's surface crust formation to more completely understand key processes (e.g., gas emissions, nutrient leaching) impacting the environment and leading to a more sustainable system. The magnitude and variation of gaseous emissions due to seasonal cycles should also be further investigated for complete mitigation strategies. A more accurate model, which takes into account physical, chemical, and biological factors, is necessary to estimate and describe gas emissions.

The measurement system presented in this work, based on the multiplexed portable FTIR-surface chamber network, is particularly well suited for fully automated continuous monitoring necessary for in-situ assessment of long-term gas emissions from manure sources. The multiplexing system, which facilitates automation of multiple chambers and management of chamber air flow, can be employed to assess the temporal and spatial variability of emissions from different manure sources or farming practices. The measurement technique will be advantageous for treatment comparison and mitigation strategies, which tend to be comparative in nature. Application of the

developed measurement system can also be extended for other agricultural management or natural ecosystems.

APPENDICES

APPENDIX A
COPYRIGHTS AND PERMISSIONS

Request for Permission to Reprint

Glenn Laing <laing@asabe.org>

Thu, Jul 11, 2019 at 7:31 AM

To: Pakorn Sutitarnnontr <pakorn@aggiemail.usu.edu>

Hi Pakorn,

We hereby grant non-exclusive permission for you to include the two papers that you identify below in your PhD dissertation for the Department of Biological Engineering at Utah State University. Please indicate in your dissertation that these two papers have been reprinted with permission of ASABE.

I hope this answers your question, and best wishes for your doctorate,

Glenn

Glenn Laing
Technical Publications Editor
ASABE
2950 Niles Road
St. Joseph, MI 49085
269-932-7014

From: Pakorn Sutitaranontr [mailto:pakorn@aggiemail.usu.edu]
Sent: Thursday, July 11, 2019 5:24 AM
To: Glenn Laing <laing@asabe.org>
Subject: Request for Permission to Reprint

American Society of Agricultural and Biological Engineers (ASABE)
2950 Niles Road
St. Joseph, MI 49085

July 11, 2019

To Whom It May Concern,

I am in the process of preparing my Ph.D. dissertation in the Biological Engineering Department at Utah State University. I am writing you this message to request your permission to reprint and include two of my published papers in the ASABE Technical Library in my dissertation. I will include acknowledge and appropriate citations in these works in the appendix of my dissertation. These two papers are:

1. *Sutitaranontr, P., R. Miller, et al. (2012). A Multiplexing System for Monitoring Greenhouse and Regulated Gas Emissions from Manure Sources using a Portable FTIR Gas Analyzer. 2012 Dallas, Texas, July 29 - August 1, 2012. St. Joseph, MI, ASABE (Paper No. 121337982. doi: 10.13031/2013.41858).*
2. *Sutitaranontr, P., E. Hu, et al. (2013). Measurement Accuracy of a Multiplexed Portable FTIR – Surface Chamber System for Estimating Gas Emissions. 2013 Kansas City, Missouri, July 21 - July 24, 2013. St. Joseph, MI, ASABE (Paper No. 131620669. doi:http://dx.doi.org/10.13031/aim.20131620669).*

Would you please indicate your approval by sending me an official permission/release letter?

Sincerely,

Pakorn Sutitaranontr



Confirmation Number: 11803407
Order Date: 03/31/2019

Customer Information

Customer: Pakorn Sutitarnnontr
Account Number: 3001429334
Organization: Pakorn Sutitarnnontr
Email: pakorn@aggiemail.usu.edu
Phone: +1 (239) 898-0831
Payment Method: Invoice

This is not an invoice

Order Details

Journal of environmental quality

Billing Status:
N/A

Order detail ID: 71865374

ISSN: 0047-2425

Publication Type: Journal

Volume:

Issue:

Start page:

Publisher: PUBLISHED COOPERATIVELY BY
 AMERICAN SOCIETY OF AGR
Author/Editor: SOIL SCIENCE SOCIETY OF AMERICA ;
 CROP SCIENCE SOCIETY OF AMERICA
 ; AMERICAN SOCIETY OF AGRONOMY

Permission Status: **Granted**

Permission type: Republish or display content
Type of use: Thesis/Dissertation

Order License Id: 4559561302010

Requestor type: Author of requested content

Format: Print, Electronic

Portion: chapter/article

The requesting person/organization: Pakorn Sutitarnnontr

Title or numeric reference of the portion(s): Chapter 4

Title of the article or chapter the portion is from: Physical and Thermal Characteristics of Dairy Cattle Manure

Editor of portion(s): N/A

Author of portion(s): Pakorn Sutitarnnontr

Volume of serial or monograph: 43

Page range of portion:

Publication date of portion: November 10, 2014

Rights for: Main product

Duration of use: Life of current edition

Creation of copies for the disabled: no

With minor editing privileges: no

For distribution to: Worldwide

In the following language(s): Original language of publication

With incidental promotional use: no

Lifetime unit quantity of new product: Up to 499

Title: DETERMINATION OF GAS EMISSION CHARACTERISTICS FROM ANIMAL WASTES USING A MULTIPLEXED PORTABLE FTIR-SURFACE CHAMBER SYSTEM

Institution name: Utah State University

Expected presentation date: Jul 2019

Note: This item was invoiced separately through our **RightsLink service**. [More info](#)

\$ 0.00

Total order items: 1

Order Total: \$0.00

APPENDIX B

PERMISSION FROM AUTHORS TO REPRINT PUBLISHED MATERIALS

Request for Coauthors' Approval

Tuller, Markus - (mtuller) <mtuller@cals.arizona.edu>
To: Pakorn Sutitarnnontr <pakorn@aggiemail.usu.edu>

Sat, Jul 13, 2019 at 6:52 PM

Hi Pakorn,

No problem. You have my approval.

Good luck with the completion of your dissertation.

Markus

Markus Tuller
Professor of Soil & Environmental Physics
Department of Soil, Water & Environmental Science
The University of Arizona
Shantz Bldg. 38, Room 526
Tucson, AZ 85721
Phone: (520) 621-7225
Fax: (520) 621-1647
Email: mtuller@cals.arizona.edu
Web: <http://ag.arizona.edu/swes/soilphysics/>

On Jul 13, 2019, at 3:42 PM, Pakorn Sutitaranontr <pakorn@aggiemail.usu.edu> wrote:

Pakorn Sutitaranontr
Utah State University
Department of Biological Engineering
4 Old Main Hill
Logan, UT 84322-4105

July 13, 2019

Dr. Markus Tuller
Professor of Soil and Environmental Physics
University of Arizona
526 Shantz Building
Tucson, AZ 85721

Dear Dr. Tuller,

I am in the process of preparing my dissertation in the Department of Biological Engineering at Utah State University. I hope to complete in August, 2019.

I am requesting your permissions to include the papers we co-authored in 2012, 2013, and 2014 shown below as Chapters 2, 3, and 4, respectively in my dissertation. I will include acknowledgements and appropriate citations in this work and copyright and reprint rights in a special appendix.

1. *Sutitaranontr, P., R. Miller, et al. (2012). A Multiplexing System for Monitoring Greenhouse and Regulated Gas Emissions from Manure Sources using a Portable FTIR Gas Analyzer. 2012 Dallas, Texas, July 29 - August 1, 2012. St. Joseph, MI, ASABE.*
2. *Sutitaranontr, P., E. Hu, et al. (2013). Measurement Accuracy of a Multiplexed Portable FTIR – Surface Chamber System for Estimating Gas Emissions. 2013 Kansas City, Missouri, July 21 - July 24, 2013. St. Joseph, MI, ASABE.*

3. *Sutitarnnontr P., Hu E., Tuller M., Jones S.B. (2014) Physical and Thermal Characteristics of Dairy Cattle Manure. J. Environ. Qual. 43:2115-2129. DOI: 10.2134/jeq2014.05.0212.*

Would you please indicate your approval of this request by replying this message?

Thank you for all your support and cooperation.

Sincerely,

Pakorn Sutitarnnontr

Request for Coauthors' Approval

胡恩柱 <huez@smm.neu.edu.cn>

Sun, Jul 14, 2019 at 8:41 PM

To: Pakorn Sutitarnnontr <pakorn@aggiemail.usu.edu>

Hi Pakorn,

Yes, I do agree. Please use these materials in your dissertation as you want.

Best regards,

Enzhu

Enzhu Hu

Ph.D. Associate Professor

Institute of Resources and Environmental Sciences

Northeastern University

Phone: +86 – 159 4003 8853

On Jul 13, 2019, at 6:42 PM, Pakorn Sutitaranontr <pakorn@aggiemail.usu.edu> wrote:

Pakorn Sutitaranontr
Utah State University
Department of Biological Engineering
4 Old Main Hill
Logan, UT 84322-4105

July 13, 2019

Dr. Enzhu Hu
Institute of Resources and Environmental Sciences
School of Metallurgy, Northeastern University
Shenyang 110819, China

Dear Dr. Hu,

I am in the process of preparing my dissertation in the Department of Biological Engineering at Utah State University. I hope to complete in August, 2019.

I am requesting your permissions to include the papers we co-authored in 2013 and 2014 shown below as Chapters 3 and 4, respectively in my dissertation. I will include acknowledgements and appropriate citations in this work and copyright and reprint rights in a special appendix.

1. *Sutitaranontr, P., E. Hu, et al. (2013). Measurement Accuracy of a Multiplexed Portable FTIR - Surface Chamber System for Estimating Gas Emissions. 2013 Kansas City, Missouri, July 21 - July 24, 2013. St. Joseph, MI, ASABE.*

2. *Sutitaranontr P., Hu E., Tuller M., Jones S.B. (2014) Physical and Thermal Characteristics of Dairy Cattle Manure. J. Environ. Qual. 43:2115-2129. DOI: 10.2134/jeq2014.05.0212.*

Would you please indicate your approval of this request by replying this message?

Thank you for all your support and cooperation.

Sincerely,

Pakorn Sutitaranontr

Pakorn Sutitaranontr - Curriculum Vitae

Environmental Soil Physics Group

Utah State University

Logan, UT 84322-4820

pakorn@aggiemail.usu.edu

EDUCATION	Utah State University Ph.D. Candidate, Biological Engineering	Logan, UT, USA
	Carnegie Mellon University M.S., Computer–Aided Engineering	Pittsburgh, PA, USA
	Chulalongkorn University B. Eng., Environmental Engineering	Bangkok, Thailand

PUBLICATIONS:

E. Hu, *Sutitaranontr*, P., M. Tuller, and S.B. Jones. 2018. Modeling Temperature and Moisture Dependent Emissions of Carbon Dioxide and Methane from Drying Dairy Cow Manure. *Frontiers of Agricultural Science & Engineering*, 5(2): 280-286.

P. Sutitaranontr, E. Hu, M. Tuller, and S.B. Jones. 2014. Physical and Thermal Characteristics of Dairy Cattle Manure. *Journal of Environmental Quality*, 43(6), 2115-2129.

P. Sutitaranontr, E. Hu, R. Miller, M. Tuller, and S.B. Jones. 2013. Measurement Accuracy of a Multiplexed Portable FTIR - Surface Chamber System for Estimating Gas Emissions. ASABE Paper No. 13-1620669. St. Joseph, Mich.: ASABE.

P. Sutitaranontr, R. Miller, S. Bialkowski, M. Tuller, and S.B. Jones. 2012. A Multiplexing System for Monitoring Greenhouse and Regulated Gas Emissions from Manure Sources using a Portable FTIR Gas Analyzer. ASABE Paper No. 12-1337982. St. Joseph, Mich.: ASABE.

ACADEMIC RESEARCHS / PRESENTATIONS

P. Sutitaranontr, R. Miller, M. Tuller, and S.B. Jones. 2014. Simulation of Greenhouse Gas Emissions after Land Application of Cattle Manure. 2014 ASA, CSSA, and SSSA International Annual Meeting, Long Beach, CA, November 2 – 5, 2014.

P. Sutitarnontr, M. Tuller, R. Miller, and S.B. Jones. 2014. Cumulative Evaporation from Manure Surface Application Using a Closed Dynamic Chamber Technique. 2014 Spring Runoff Conference, Eccles Conference Center, Utah State University, Logan, UT, April 1 – 2, 2014.

P. Sutitarnontr, E. Hu, M. Tuller, and S.B. Jones. 2013. Determination of Physical and Hydraulic Properties of Cattle Manure Using Soil Analysis Techniques. 2013 ASA, CSSA, and SSSA International Annual Meeting, Tampa, FL, November 3 – 6, 2013.

E. Hu, *P. Sutitarnontr*, M. Tuller, and S.B. Jones. 2013. Emissions of CO₂, CH₄, and NH₃ from Dairy Cow Feces and Manure. 2013 ASA, CSSA, and SSSA International Annual Meeting, Tampa, FL, November 3 – 6, 2013.

P. Sutitarnontr, E. Hu, M. Tuller, R. Miller, and S.B. Jones. 2013. Effectiveness of Manure Incorporation in Reducing Gas Emissions. 2013 Spring Runoff Conference “Water, People and Sustainability: Integrating Physical, Social and Ecological Dimensions”, Eccles Conference Center, Utah State University, Logan, UT, April 9 – 10, 2013.

E. Hu, *P. Sutitarnontr*, M. Tuller, R. Miller, and S.B. Jones. 2013. Emissions of Carbon Dioxide, Methane and Ammonia from Fresh Dairy and Beef Manure. 2013 Spring Runoff Conference “Water, People and Sustainability: Integrating Physical, Social and Ecological Dimensions”, Eccles Conference Center, Utah State University, Logan, UT, April 9 – 10, 2013.

P. Sutitarnontr, E. Hu, R. Miller, M. Tuller, and S.B. Jones. 2013. Drying and Rewetting Effects on Gas Emissions from Dairy Manure in Semi-arid Regions. 2013 Livestock and Poultry Environmental Learning Center National Conference “Waste to Worth: Spreading Science and Solutions”, Denver, CO, April 1 – 5, 2013.

P. Sutitarnontr, M. Tuller, R. Miller, and S.B. Jones. 2012. Monitoring Temporal Variations in Greenhouse and Regulated Gas Emissions from Cow Manure in Relation to Moisture Content and Temperature. 2012 ASA, CSSA, and SSSA Annual Meeting, Cincinnati, OH, Oct 21 – 24, 2012.

P. Sutitarnontr, M. Tuller, R. Miller, and S.B. Jones. 2012. Temporal Variations in Greenhouse Gas Emissions from Dairy Cow Manure. 2012 Spring Runoff Conference, Eccles Conference Center, Utah State University, Logan, UT, April 3 – 4, 2012.

P. Sutitarnontr, M. Tuller and S.B. Jones. 2011. Metal oxide gas sensors for monitoring regulated and greenhouse gas fluxes from manure sources. ASA, CSSA, and SSSA International Annual Meetings, San Antonio, TX, October 16 – 19, 2011.

P. Sutitarnontr, M. Tuller and S.B. Jones. 2011. An Automated Multi-gas Sensor System for Long-term Monitoring of Regulated and Greenhouse Gas Fluxes from Animal Feeding Operations. 2011 Annual Spring Runoff Conference, Utah State University, Eccles Conference Center, Logan, UT, March 29 – 30, 2011.

AWARDS AND ACTIVITIES:

- 2013 Western SARE Graduate Student Project Grant
- 2012 RGS Graduate Student Travel Award
- Outstanding Student Poster Presentation, 2012 Spring Runoff Conference
- Member of American Society of Agricultural and Biological Engineers (ASABE)
- Member of American Society of Agronomy (ASA), Crop Science Society of America (CSSA), and Soil Science Society of America (SSSA)
- Member of American Society of Civil Engineers (ASCE)
- Carnegie Institute of Technology Scholarship 2000 -2001