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Developing and Applying Process-based Models for Estimating GHG and Air Emissions from California Dairies

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Developing and Applying Process-based Models for Estimating GHG and Air Emissions from California Dairies

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to

California Energy Commission

For

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Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million to conduct the most promising public interest energy research by partnering with Research, Development, and Demonstration (RD&D) organizations, including individuals, businesses, utilities, and public or private research institutions.

PIER funding efforts are focused on the following six RD&D program areas:

- Buildings End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research.

What follows is the final report for the Developing and Applying Process-based Models for Estimating GHG and Air Emissions from California Dairies, Contract #500-02-04, Work Authorization #MR-037 conducted by Applied Geosolutions, LLC, University of New Hampshire, University of California at Davis and University of California at Riverside. The report is entitled “Developing a Process-based Model for Estimating GHG from California Dairies”. This project contributes to the PIER program objectives of improving the environmental costs and risks of California’s electricity.

For more information on the PIER Program, please visit the Commission's Web site at: <http://www.energy.ca.gov/research/index.html> or contact the Commission's Publications Unit at 916-654-5200.

Executive Summary

In 2003, the National Academy of Sciences found that EPA's current methodologies for estimating air emissions from animal feeding operations are inadequate and called for "process-based" modeling instead of an "emission factor" approach. Applied Geosolutions, LLC, University of New Hampshire, University of California at Davis and University of California at Riverside conducted a study for the California Energy Commission (Energy Commission) to design and develop a process-based modeling framework for estimating greenhouse gas emissions from California dairies.

The objectives of this study are fourfold: (1) to perform a series of controlled chamber studies to measure greenhouse gases (GHG) from dairy cows, (2) to develop, test and use a Fourier Transform InfraRed Spectroscopy (FTIR) for measuring nitrous oxide (N₂O) emissions from dairy corrals, (3) to build a process-based biogeochemical modeling tool for estimating GHG emissions from dairies and (4) to apply this tool with spatial data on soils, climate, and dairy locations to demonstrate the use of the tool for regional GHG emission inventories.

There are approximately 2.5 million dairy cows in California. Emission inventories list dairy cows and their manure as the major source of regional air pollutants, but data on their actual emissions remain sparse, particularly for smog-forming volatile organic compounds (VOC) and greenhouse gases (GHG). We report measurements of alcohols, volatile fatty acids (VFAs), and phenols, as well as methane and nitrous oxide emitted from non-lactating (dry) and lactating dairy cows and their manure under controlled conditions. The experiments were conducted in an environmental chamber that simulates commercial concrete-floored freestall cow housing conditions. The fluxes of methanol, ethanol, and methane (CH₄) were measured from cows and/or their fresh manure. The average estimated methanol and ethanol emissions were 0.33 and 0.51 g cow⁻¹ h⁻¹ from dry cows and manure, and 0.7 and 1.27 g cow⁻¹ h⁻¹ from lactating cows and manure, respectively. Both alcohols increased over time coinciding with increasing accumulation of manure on the chamber floor. Volatile fatty acids and phenols were emitted at concentrations close to their detection limit. Average estimated CH₄ emissions were predominately associated with enteric fermentation from cows rather than manure and were 12.35 and 18.23 g cow⁻¹ h⁻¹ for dry and lactating cows, respectively. Lactating cows produced considerably more gaseous VOC and CH₄ emissions than dry cows (P<0.001). While elevated N₂O emissions were measured with

cows in the chamber indicating direct emissions from the cows, the accuracy of the emission measurements is in question due to calibration procedures. In summary, dairy cows and fresh manure have the potential to emit considerable amounts of alcohols and methane.

In a separate study, a total of 96 pregnant, non-lactating Holstein cows were housed in four, totally enclosed cattle pen enclosures (CPEs) and were fed a total mixed ration (TMR) *ad libitum*. Eight cows were housed in each of the four CPEs during each of three, 14 day replications. Cows were randomly sorted into four groups and stratified by weight. Treatments were: (1) control, manure accumulated for 14 days (CON), (2) harrowing (HAR), three times weekly, (3) surface acidifier application (sodium bisulfate, SBS), twice weekly, and (4) scraping (SCR), which was complete manure removal once weekly. Emissions of the smog-forming alcohols ethanol (EtOH) and methanol (MeOH) as well as the greenhouse gases (GHG) carbon dioxide (CO₂), nitrous oxide (N₂O), and methane (CH₄) were measured continuously from the CPEs' air inlets and outlets. Gaseous concentrations were sampled using a photoacoustic gas-analyzer (INNOVA 1412) and emission rates (kg/cow/yr) calculated. Data were analyzed using Proc MIXED procedures in SAS. Overall, alcohol emissions for SBS were lower ($P < 0.05$) compared to all other treatments. The EtOH emission rates for SBS, HAR, SCR, and CON were 3.88, 12.57, 11.81, and 12.41 kg/cow/yr, respectively. MeOH, emission rates for SBS, HAR, SCR, and CON were 1.57, 8.49, 8.05, and 8.67 kg/cow/yr, respectively. SCR compared to SBS, HAR, and CON showed reduced ($P < 0.05$) emission rates for N₂O and CH₄. Emission rates for CH₄ and N₂O were higher in SBS ($P < 0.05$) compared to the other treatments ($P < 0.05$). There were no differences across treatments for CO₂ emissions. This study suggests that surface acidifier (SBS) applied to dairy corrals can reduce alcohol emissions, thus lowering smog pollution. Results suggest that SBS increases greenhouse gases. Scraping and harrowing of corral surface manure show little promise to reduce emissions of both smog forming compounds and greenhouse gases from dairies.

A third measurement study collected ambient concentrations of N₂O at 4 separate elevations, 1,2,5 and 10 meters above a dairy dry lot at California State University Fresno (CSUF). These data were collected using an FTIR system with a 10 meter sampling tower which was also configured to collect corresponding meteorological data. The data were then used to make approximate estimations of N₂O flux using the flux gradient method. Typical values over this study ranged from 10-40 ng/sec m² during ideal meteorological conditions. Ambient N₂O concentrations were observed to be elevated just after a rain event, typically by around 10%.

Ambient N₂O concentrations were observed to be slightly higher above a compost pile relative to the dry lot. A large peak in N₂O concentrations was observed immediately after the compost pile was disturbed. Ideally a longer term continuous monitoring of N₂O in an open path format would be able to better define annual variability, lead to less variable calculations in the emission rates and factors, and provide data more suitable for validating process models. General baseline fluxes of N₂O were observed to range from 25 to 30ng/sec/m². These fluxes are equivalent to an annual emission of 7.9 to 9.57 kg/ha, indicating that dry lots can be a significant source of nitrous oxide emissions.

For this project, the team modified an existing process-based biogeochemical model called Denitrification-Decomposition (DNDC) to simulate crop growth, soil carbon dynamics, and trace gas emissions under various dairy management systems in California. While the DNDC biogeochemical model has been used and tested extensively across a wide range of cropping, climate, and soil conditions, this is the first time it has been used specifically for animal feeding operations. A virtual farm was constructed in Manure-DNDC to generalize or represent a wide range of animal farms in California or other parts of the world. The virtual farm consists of seven components namely housing, outdoor corrals, grazing plot, lagoon, compost, digester and field where the manure is produced, stored, treated or applied, respectively. These components are integrated into a processing entity that tracks the entire the manure life cycle. The Manure-DNDC model runs at daily or hourly time step. Daily fluxes of NH₃, CH₄, N₂O and CO₂ as well nitrate leaching are calculated for each of the seven farm components. The sum of the fluxes from all seven components constitutes the farm emissions.

The framework of Manure-DNDC was accomplished through this effort including field measurements, information/data collection, algorithm development and code integration. The preliminary tests proved the model had a healthy framework to handle the mass balance and biogeochemical dynamics across the entire components of animal farms. However, for a complex, process-based model such as Manure-DNDC, setting up of framework is only the first step of the model development. Calibration and validation with the data observed at each of the farm components are crucial to make the model reliable and applicable. Unfortunately, so far, we have only obtained very limited amount of field data to fulfill the unavoidable stage of the model development. New field data for 2007 and 2008 collected through this project and a companion project will be available 2008 for more model validation.

A suite of spatially explicit geographic information systems (GIS) data for soils, climate, dairy locations, dairy cow populations, and dairy management was developed and assembled to define the biophysical characteristics for driving the Manure-DNDC model. Spatial databases of climate (using CIMIS data), soils (using NRCS soil surveys), dairy location (from Department of Water Resources land use maps) and manure management practices (derived from Air District Dairy permits) were used to create input files for Manure-DNDC. We used 2004 statistics and climate data to estimate CH₄ and N₂O emissions from all dairies in California. Total CH₄ emissions for 2004 were 10.2 Million Metric Tons (MMT) CO₂eq. Total N₂O emissions from cows themselves (enteric), manure management and land application of manure were 0.3 MMT CO₂eq, 2.0 MMT CO₂eq and 12.5 MMT CO₂eq, respectively. Our process-based model estimates of CH₄ emissions are comparable to the 2004 CEC emission inventory estimates of 10.4 MMT CO₂eq. Our model estimate of N₂O from manure management is approximately one third of the CEC 2004 estimate. It is not possible to compare our estimate of N₂O from land application with the CEC 2004 estimate from agricultural soils without disaggregating their estimate to just cropland receiving dairy manure.

In summary, this project achieved its main goals of designing and building a process-based modeling tool for estimating GHG emissions from individual dairies or regions with dairies, developing and testing FTIR approaches for measuring N₂O emissions from components of dairies, collecting new emissions data in controlled chambers to improve our understanding of enteric sources of GHG emissions, and building spatial databases for regional model simulations. This modeling effort is attracting more interest and support from the dairy industry, which has funded a project to extend the model to dairies throughout the country. We expect Manure-DNDC will become a useful tool for livestock industry in the coming years after the thorough calibration and validation activities planned for 2008. Further work is needed to perform more extensive model validation to improve our understanding of the accuracy and uncertainties of model estimates. We recommend the following next steps:

1. Collect additional GHG emission data specifically for model validation. Data should be collected using automated chambers (to capture the episodic nature of N₂O emissions). Chamber data can be used to assess the efficacy of using open path FTIR technology for area emission estimates.
2. Perform additional studies on N₂O emissions directly from dairy cows, including testing various feed regimes impact on emissions.

Introduction

Background and Overview

In 2003, the National Academy of Sciences found that EPA's current methodologies for estimating air emissions are inadequate and called for "process-based" modeling instead of an "emission factor" approach. The measurement and monitoring of dairy-related air emissions and emission reductions is complex because the emission sources are dispersed and largely driven by biological activity with significant variability over time, space, and management practices. Emissions are further affected by local and regional meteorological conditions. This complexity results from the interaction of a suite of biogeochemical processes such as decomposition, nitrification, denitrification, fermentation, and ammonia volatilization. This project will modify an innovative, internationally recognized "process-based" model called the Denitrification-Decomposition (DNDC) model, which already contains these biogeochemical processes, to create a scientifically sound tool for significantly improved estimates of emissions from California dairies.

Need for Process-based Biogeochemical Models

Accurate assessment of air emissions from dairies with emission factors is difficult due to: (1) high variability in the quality and quantity of animal waste, and (2) the numerous factors affecting the biogeochemical transformations of manure during collection, storage and field application. Measurement programs are essential but expensive and thus have not been extensively implemented. Therefore, process-based models that incorporate mass balance constraints are needed to extrapolate air emissions in both space and time (NRC, 2003). EPA has not yet developed such a model, relying instead on a simplified methodology for estimating air emissions from individual dairies, using "model" farms based on typical animal confinement, manure collection, solid separation, manure storage and stabilization, and techniques for land application of manure (EPA 2002).

Although it is well known that constant emission factors are not effective for quantifying GHG, ammonia, and ROG emissions from CAFOs (NRC 2003), managers and regulators generally lack access to tools that are both scientifically sound, capture the biogeochemical processes that

impact emissions, and are relatively easy to use. There are a number of advantages to developing process-based models of element transformations and emissions from the *combined* components (animal feedlot, manure storage and handling, land application of manure) of dairies:

- Dynamic, process-based models, developed from laboratory and field studies, **do not rely on constant emission factors**. They assess the impact on emission factors of varying conditions (e.g., climate, storage facility, soils). These models will continue to improve as more field studies are conducted and published, and they do not obviate the need for a strong measurement program.
- By **enforcing a mass balance** in the model (i.e., conservation of mass), the sum of all emission factors are constrained to be $\leq 100\%$ of inputs. This is both good bookkeeping and essential for evaluating trade-offs in mitigation strategies.
- Full system analysis with dynamic, process-based models can inexpensively and efficiently **evaluate mitigation scenarios** under various conditions, and can help target mitigation toward facility component(s) and/or operation(s) that cause the greatest emissions.
- Simultaneously provide estimates of all emission for **comprehensive assessments** of mitigation efforts. For example, *efforts to reduce methane may result in increased nitrous oxide emissions that could more than offset gains from methane reductions and result in a net increase in total greenhouse gas emissions*. Therefore, **well validated models are critical for comprehensive analyses that capture all emissions to air and water**.

Background on DNDC Model and Capabilities:

During the past decade, multi-agency support from EPA, NASA, and NSF has guided the development, testing, and application of a research biogeochemical model of nitrogen (N) and carbon (C) cycling in soils. The process-oriented computer simulation model, Denitrification-Decomposition (DNDC), was developed based on the biogeochemical concepts for predicting soil biogeochemistry (Li et al. 1992, 1994, 1996; Li 2000). The first component, consisting of the soil climate, crop growth and decomposition sub-models, predicts soil temperature, moisture, pH, redox potential (Eh) and substrate concentration profiles (e.g. ammonium, nitrate, dissolved organic carbon) based on ecological drivers (e.g., climate, soil, vegetation and anthropogenic activity). The second component, consisting of the nitrification, denitrification and fermentation sub-models, predicts nitric oxide (NO), nitrous oxide (N₂O), methane (CH₄) and ammonia (NH₃) fluxes based on the environmental variables in the soil. Classical laws of physics, chemistry and

biology, and empirical equations generated from laboratory observations, were used in the model to parameterize each specific reaction. The entire model forms a bridge between basic ecological drivers including management of agro-ecological systems, and water, carbon, and nitrogen cycles. DNDC utilizes GIS databases with spatially and temporally differentiated information on climate, soil, vegetation and farming practices for local, regional and national scale analyses.

The core of DNDC is a soil biogeochemical model, which can be linked to vegetation models to predict carbon sequestration and nitrogen cycling for different ecosystems. DNDC has been linked to a crop model (Zhang et al. 2002) to simulate soil organic carbon (SOC) dynamics and emissions of dinitrogen (N_2) and several trace gases including N_2O , NO , NH_3 and CH_4 from both upland and wetland agricultural ecosystems. DNDC is a unique process-based biogeochemical model because it (1) simulates both aerobic and anaerobic conditions, (2) tracks redox potential (Eh), (3) can provide a comprehensive simulation of nutrient releases to air and water, including emissions of ammonia, greenhouse gases and nitrate leaching, and (4) contains tools for examining sensitivity and uncertainties in emission estimates. These capabilities are critical for quantifying whole farm emissions from California dairies. This model has been independently tested and validated by many researchers and under a wide range of conditions worldwide and now is utilized for national trace gas inventory studies in the U.S., Canada, the U.K., Germany, Italy, New Zealand, China, Japan, Thailand and the Philippines. The extensive validation and applications worldwide indicate that the fundamental processes embedded in DNDC have provided a sound basis for modeling C and N dynamics across a broad range of climatic zones, soil types and management regimes.

Project Objectives

The project will modify DNDC to create a tool for simulating carbon (C) and Nitrogen (N) biogeochemical cycling in a dairy operation, tracking the manure life cycle (production, storage/processing, field application) and determining the fate of manure C and N (volatilized, incorporated into soils or vegetation, lost via leaching) for California dairies. This task will extend DNDC's applications by integrating the fundamental biogeochemical processes with animal housing and manure management practices. The new model elements will include: (1) integration of detailed biogeochemical processes under animal housing and manure storage conditions; (2) characterization of environmental factors under housing or storage conditions; and

(3) characterization of quantity and quality of animal waste at each dairy. The new version of DNDC will include features to analyze the fate of manure through the incorporation of dairy specific management conditions and local climatological and soil conditions. An example of the model framework for ammonia is provided in the Appendix. The resulting tool will be used to provide improved estimates of releases of C and N to air (e.g. CH₄, NO, N₂O, NH₃, VOC, etc) and water (nitrate leaching from field application phase).

The objectives of this Work Authorization are as follows:

- Develop the GIS Databases and tools that can be used to collect input data necessary for estimating GHG emissions from dairies operations in California.
- Enhance the DNDC model creating a new tool (Manure-DNDC) for simulating carbon and nitrogen biochemical cycling in dairy operations, tracking the manure life cycle (volatilized, incorporated into soils or vegetation, lost via leaching) for California dairies.
- Complement existing measurement programs to include N₂O measurements (develop leveraged project at California State University at Fresno).
- Use laboratory data to be collected by UC Davis to generate improved understanding of air emissions from dairy cows and drylot conditions.
- Develop an FTIR system at UC Riverside for measuring N₂O emissions from drylot conditions.
- Use laboratory and field data to calibrate the Manure-DNDC model.

To meet the project objectives a set of tasks were selected to:

- incrementally create a suite of individual tools for improved emission estimates for each major phase (e.g. housing, manure storage/treatment and land applications phases) of manure management in California dairies,
- validate process model utilizing extensive field data being collected under other externally funded projects,
- provide full accounting to be consistent with current IPCC and EPA approaches for estimating both direct and indirect emissions,
- be applicable at scales ranging from individual dairies to county and state level emission inventories, and
- provide tools that can be readily and easily be used to improve state wide emissions estimates and evaluate mitigation projects.

Report Organization

Final report presents major components of the research project as separate chapters in the report. Each chapter will include a short description of the objectives, approach and outcomes. All tables and figures are provided at the end of each component section. Conclusions and recommendations from each of the components are presented in each section and then summarized in the final project conclusions/recommendation section.

Component 1: Air Emission Chamber Studies

Several sets of chamber studies were conducted at University of California, Davis research facilities. Here we report in detail on three studies that were supported primarily by this contract. We also present a brief overview of two studies that were funded with other funding that leveraged off this contract.

Study 1: Alcohol, Volatile Fatty Acid, Phenol, and methane Emissions from Dairy Cows and Fresh Manure

Abstract

There are approximately 2.5 million dairy cows in California. Emission inventories list dairy cows and their manure as the major source of regional air pollutants, but data on their actual emissions remain sparse, particularly for smog-forming volatile organic compounds (VOC) and greenhouse gases (GHG). We report measurements of alcohols, volatile fatty acids (VFAs), and phenols, as well as methane emitted from non-lactating (dry) and lactating dairy cows and their manure under controlled conditions. The experiment was conducted in an environmental chamber that simulates commercial concrete-floored freestall cow housing conditions. The fluxes of methanol, ethanol, and methane (CH₄) were measured from cows and/or their fresh manure. The average estimated methanol and ethanol emissions were 0.33 and 0.51 g cow⁻¹ h⁻¹ from dry cows and manure, and 0.7 and 1.27 g cow⁻¹ h⁻¹ from lactating cows and manure, respectively. Both alcohols increased over time coinciding with increasing accumulation of manure on the chamber floor. Volatile fatty acids and phenols were emitted at concentrations close to their detection limit. Average estimated CH₄ emissions were predominately associated with enteric fermentation

from cows rather than manure and were 12.35 and 18.23 g cow⁻¹ h⁻¹ for dry and lactating cows, respectively. Lactating cows produced considerably more gaseous VOC and GHG emissions than dry cows (P<0.001). In summary, dairy cows and fresh manure have the potential to emit considerable amounts of alcohols and methane and research is needed to determine effective mitigation.

Introduction - Background and overview

California is the leading dairy state in the United States producing 21% of the nation's milk supply. The highest concentration of dairies is in the San Joaquin Valley (SJV) in Central California (Agricultural Statistics Board, 2005), a region with the worst air quality in the nation that is in extreme non attainment of state and federal ozone standards. Smog-forming volatile organic compound (VOC) and greenhouse gas (GHG) emissions from dairies are believed to contribute to the impairment of health and well-being of humans and animals, and to affect the regional and global environment (IPCC, 2001; California Air Resources Board, CARB, 2005).

Ozone is formed through the interaction of VOCs and oxides of nitrogen (NO_x) in the presence of sunlight. There is limited data on emission rates of VOCs emitted from dairy cows and manure. Rabaud et al. (2003) identified 35 different VOCs from a small dairy farm in California with alcohols as a main compound group. Filipy et al. (2006) also identified and quantified VOCs from a lactating cow open stall on a commercial dairy in Washington. They determined an emission rate of ethanol and dimethyl sulfide of 3693.6±1846.8 mg cow⁻¹h⁻¹ and 49.68±37.08 mg cow⁻¹h⁻¹, respectively, using an atmospheric tracer method. Miller and Varel (2001) measured VFA and alcohol concentrations in both fresh and aged cattle slurries under laboratory conditions. A high concentration of ethanol (25- 40 mM) was found in both slurries. Aged cattle manure produced twice the concentration of VFA compared to fresh manure during anaerobic incubation. Martensson et al. (1999) monitored VFAs in dairy barns and detected acetic, butyric, lactic, and formic acids in the air. Sonesson et al. (2001) identified 70 different VOCs on eight dairy farms in Sweden. They found *p*-cresol, 2-butanone ethyl acetate, α-pinene and Δ³-carene at levels well below the occupational exposure level (ACGIH, 1999). With respect to ozone-forming VOCs, no comprehensive research that characterizes emissions from dairy cows and their fresh manure has been conducted .

The Intergovernmental Panel on Climate Change (IPCC; 2001) reported that since 1750, the atmospheric concentration of the greenhouse gases carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) has increased by 31%, 150%, and 16%, respectively. The Intergovernmental

Panel on Climate Change (IPCC; 2001) estimated that agriculture contributes 21-25% of global CO₂ emissions, 55-60% of global CH₄ emissions, and 65-80% of global N₂O emissions, respectively. Processes and sources generating GHG include burning of fossil fuels, deforestation, rice paddies, biomass burning, enteric fermentation of ruminants, fermentation of animal manure, and application of nitrogenous fertilizers. Dairy cows and their manure are considered to be important contributors to CH₄ and to a lesser extent N₂O emissions (IPCC, 2001; Jarvis and Pain, 1994; Phetteplace et al., 2001). Considering that the 100-year global warming potential (GWP) of CH₄ and N₂O is 20 and 300 times higher than CO₂, respectively (IPCC, 2001; Kuczynski et al., 2005), the effect of cows and their manure on the global GHG emissions becomes even more important. Both CH₄ and N₂O can be produced from both enteric fermentation in the cow and decomposition of manure (Kaspar and Tiedje 1981; Jungbluth et al., 2001). Previous studies predicted CH₄ emissions from dairy cows based on the physiology and feed energy consumption of the animal (Crutzen et al., 1986; Holter and Young, 1992; IPCC, 2001). Methane emission factors of 5.79 g LU⁻¹ h⁻¹ (LU, livestock unit = 500 kg live weight animal) for dry cows and 11.17 g LU⁻¹ h⁻¹ for lactating cows were obtained (Holter and Young, 1992). Direct measurement of CH₄ emissions from cows and dairy facilities were also conducted in previous studies but not under controlled conditions (Jungbluth et al., 2001; Kinsman et al., 1995; Kirchgessener et al., 1991; Sneath et al. 1997). Many factors such as feed intake, animal size, growth rate, milk production and particularly energy consumption can affect CH₄ emissions from dairy cows (Jungbluth et al., 2001). Compared to studies of CH₄ emissions, there is a scarcity of literature on N₂O emissions from dairy cows (Jungbluth et al., 2001). Generally, ruminant animals are considered as a small source of N₂O emissions (IPCC, 2001). The direct measurements of N₂O emissions from dairy facilities had yielded emission factors in the range of 0.01-0.08 g LU⁻¹ h⁻¹ (Amon et al., 2001; Jungbluth et al., 2001; Sneath et al., 1997). However, no studies have quantified N₂O emissions from cow enteric fermentation.

Objective

The objective of the present study was to quantify VOC and GHG emissions from dry (not lactating) and lactating cows (enteric fermentation) and fresh manure under environmental chamber conditions.

Project approach

Environmental Chambers

Experiments were conducted inside of an environmentally controlled chamber (4.4m×2.8m×10.5m) at the Department of Animal Science, University of California, Davis. The chamber (142 m³ volume) has a continuous ventilation rate of 2,219 m³/h (at 20°C and 1 atm), resulting in a chamber residence time of approximately 6 min and equivalent to 15.8 air exchanges per h. A balometer® (TSI Inc, Shoreview, MN) was used to check the ventilation rate before and after the experiment. The chamber temperature was maintained at 20°C and controlled via air conditioning. The relative humidity of air in the chamber was 56 ± 11 %. Typical dairy freestall housing conditions for three cows were simulated by assembling three steel freestall stanchions at the West end of the chamber where animals could rest. Head gates were installed at the East end of the chamber where cows accessed feed *ad libitum*. Animals had *ad libitum* access to water by a water trough. Ambient temperature and relative humidity were measured in 10 min intervals using two HOBO sensors (Onset Computer, Bourne, MA) located inside the chamber. Cow excreta (urine and feces slurry mix) accumulated on the concrete floor until the chamber was cleaned. The environmental chamber facility is certified by the Association for Assessment and Accreditation of Laboratory Animal Care International (AAALACI), and the Institutional Animal Care and Use Committee (IACUC) approved the project to certify the health and welfare of the animals.

Animals

The present work describes emission rates on a ‘per cow’ basis. The average body weights of dry and lactating cows were 770 and 656 kg, respectively and the feed intake (on a dry matter basis) was 17.7 and 19.1 kg per day, respectively. The average milk yield was 31 kg cow⁻¹ day⁻¹. A total of nine dry (pregnant but not lactating) and nine mid-lactating Holstein dairy cows from the UC Davis dairy herd were used for the experiments in groups of three cows. Cows were fed a total mixed ration (TMR; Table 1) diet *ad libitum*, formulated to meet the 2001 National Research Council (NRC) requirements for either dry or lactating cows. Both diets were analyzed for crude protein (CP) (AOAC, 1997a), total digestible nutrients (TDN) (AOAC, 1997b), acid detergent fiber (ADF) (AOAC, 1997b), neutral detergent fiber (NDF) (Van Soest et al., 1991), and minerals (Ca, P, Mg, K; Sah and Miller, 1992). The chemical composition is listed in table 1.

Gas Sampling and Analysis

The environmental chamber has one incoming and one outgoing air duct. Analytical instruments located in the attic space above the chamber pulled air through Teflon tubing (12.7 mm ID, 0.25 m long) from each air duct immediately above the ceiling. Background samples of the 'empty chamber' were collected during the first day of each (two days) experimental period to assess the VOC and GHG concentrations in the incoming and outgoing air. After two h of empty chamber measurement, three cows were placed inside the chamber. The first two h after cows entered the chamber were used to measure air emissions in the 'cows only' phase (enteric fermentation; no manure). In the following 'cows and manure' phase, the animals were kept inside the chamber for additional 22 h and manure accumulated over time. The lactating cows were milked with a mobile milking unit before placement in the chamber and a second time inside the chamber at 19:00. After 24 h, cows were taken out of the chamber, but the accumulated animal manure was left undisturbed on the chamber floor for second day measurements (24 h; 'manure only' phase).

Ethanol, methanol, N₂O, and CH₄ from dairy cows and their excreta were continuously measured using an INNOVA model 1412 Field Gas Monitor (INNOVA AirTech Instrument, Ballerup, Denmark). This gas analyzer can selectively measure up to 5 component gases and water vapor simultaneously through the use of optical filters. The detection limits of the INNOVA 1412 are 0.08 µg L⁻¹ for methanol, 0.10 µg L⁻¹ for ethanol, 0.21 µg L⁻¹ for CH₄, and 0.04 µg L⁻¹ for N₂O. The INNOVA is approved as a reference method for alcohol measurements by the California Air Resource Board (CARB, MSO 2000-08) as well as by the Environmental Protection Agency (EPA) for the measurement of ethanol and chlorinated VOC (EPA-VS-SCM-28). In the present study, the INNOVA analyzer was calibrated monthly by the instrument manufacturer. The sampling interval for inlet and outlet air was 20 min. To avoid the responding error, only data logged between minute 5 and 17 of each sampling interval was used for later analysis. Data corresponding to the short interval of time when the chamber door was opened to allow entry and exit of cows (at 7:00 on the first day and 9:00 on the second day, respectively), were omitted for calculation of emission fluxes.

Emissions of both VFAs and phenolic compounds were measured using a modified sorbent tube EPA TO-17 method (Woolfenden and McCleney, 1997). Measured VFAs were acetic, propionic, isobutyric, butyric, isovaleric, valeric, and hexanoic. Phenols and cresol compounds were phenol, 2-methylphenol, 2-ethylphenol, 3-methylphenol, 4-methylphenol, indole, and 3-methylindole. Four sorbent tube gas samplers (GS 301, Gerstel, Muehlheim, Germany) were connected to both the inlet and outlet air ducts from the air handling system for the environmental chamber, respectively, using both quick-connect fittings and flexible Teflon tubing. Samples

were collected in duplicate on glass sorbent tubes (178×6 mm diameter) containing a multi-bed sorbent packing of Carboxen 1000 and Carboxen 1000 X (from Supelco, Bellefonte, PA) (1:2 ratio v/v) at flow rate of 100 mL min^{-1} for a total volume of 12 L. Samples were taken at 0, 6, 12, 18, and 24 h after cows entered the chamber for dry cows, and at 0, 3, 6, 9, and 24 h for lactating cows. More samples for 'manure only' phases were taken at 0, 6, 12, 18 and 24 h after cows left the chamber. During the lactating cow experiments, sorbent tube sampling was not conducted during night time. All samples were refrigerated and analyzed within 14 days of the time they were sampled in the field.

Sorbent tubes were analyzed by thermal desorption-gas chromatography-mass spectrometry (TDS-GC-MS). The TDS was a Gerstel TDSA (Gerstel, Muehlheim, Germany) interfaced to a 6890 GC (Agilent Technologies, Wilmington, DE) and 5973N Inert mass selective detector (Agilent Technologies, Wilmington, DE). Thermal desorption parameters were as follows: splitless mode; initial temperature, 60°C ; final temperature, 300°C ; initial time 0.5 min; final hold time 3 min; ramp, $60^\circ\text{C min}^{-1}$; with a transfer line temperature of 320°C . The 6890 GC was equipped with programmed temperature vaporizer (PTV) inlet (CIS 4, Gerstel, Muehlheim, Germany) and a $30\text{m} \times 0.25\text{mm} \times 0.25\ \mu\text{m}$ FFAP (free fatty acid phase) column (J&W Scientific, Inc., Wilmington, DE). The PTV inlet used the following parameters: solvent vent mode; initial temperature, -30°C , final temperature, 320°C , initial time, 0.2 min, final time, 3 min; ramp, $12^\circ\text{C sec}^{-1}$, vent flow 20 mL min^{-1} , and purge split flow 20 mL min^{-1} . This method is essentially a 20:1 split injection from TDS to analytical column. Helium was used as the carrier gas in constant flow mode at 1.4 mL min^{-1} . The GC oven temperature program was: 1) initial temp, 80°C hold 0.05 min; 2) ramp 10°C to 220°C ; and 3) ramp 50°C to 240°C and hold 5 min. The MS transfer line and source temperatures were maintained at 240 and 150°C , respectively. The mass spectrometer was operated under Single Ion Monitoring mode using the following monitoring ions: 1) VFA compounds monitored 43, 57, 60, 73, 74, and 87, 94, 101 m/z from 3-14.1 min, and 2) phenolic compounds monitored 39, 66, 77, 94, 107, 108, and 122 m/z.

A stock standard solution for VFAs including acetic, propionic, isobutyric, butyric, 2-methylpropanoic, isovaleric, valeric, and hexanoic acids was prepared in HPLC grade water (Burdican and Jackson, Mustegon, MI). A reference standard stock solution for seven aromatic compounds, including phenol, 2-methylphenol, 2-ethylphenol, 3-methylphenol, 4-methylphenol, indole, and 3-methylindole was prepared in methanol (Capillary GC Grade, Sigma Aldrich, St. Louis, MO). All chemicals were 99% pure or higher (GC grade) and provided by Aldrich (Sigma-Aldrich, St. Louis, MO).

Calibration curves were generated using external standards loaded onto sorbent tubes using the ATIS™ system (Supelco, Inc. Bellefonte, PA). The ATIS™ system was maintained at 110°C and purged with nitrogen at 100 mL min⁻¹ for a minimum total volume loading of 250 mL for each sorbent tube. The Limit of Quantification (LOQ) for the VFAs ranged from 0.8 to 3.8 µg m⁻³ air for acetic acid and 2-methylpropanoic acid, respectively. The LOQ for phenolic compounds ranged from 0.38 ng (2-methylphenol) to 5.43 ng (4-methylphenol) which corresponded to 0.02 (2-methylphenol) to 2.7 µg m⁻³ air for 2-methylphenol and 4-methylphenol, respectively.

The emission flux rate was calculated using the equation:

$$E = \frac{\sum_n Q \times (C_{out} - C_{in})}{n \times N} \quad (1)$$

where:

E = Gas emission rate from the chamber, mg cow⁻¹ h⁻¹,

C_{out} = Mass concentration in the outlet air, mg m⁻³,

C_{in} = Mass concentration in the inlet air, mg m⁻³,

Q = Ventilation rate at 20°C and 1 atm, m³ h⁻¹,

n = Total effective measurement numbers,

N = Cow numbers.

Validation Experiment

Validation experiments were conducted to evaluate the performance of the environmental chamber and gas monitoring system. Pure CH₄ (Airgas Inc., Radnor, PA) was continuously and evenly distributed into the chamber through Teflon tubes at a flow rate of 1.3 L min⁻¹. Pure methanol (99.9%, Fisher Scientific Inc, Fair Lawn, NJ) and ethanol (99.5+%, Sigma-Aldrich Inc., St. Louis, MD) filled into glass plates were placed on a microbalance (Mettler-Toledo, Columbus, OH) that was situated on a table (40 cm height) in the chamber center. The amount of alcohol evaporated was continuously measured using a microbalance and the data were visually recorded with a PC-based web camera. The gas concentrations at the chamber inlet and outlet were continuously monitored using the INNOVA field gas analyzer that was used during the actual animal studies. Air ventilation rate was measured prior to and after the validation experiment. Background concentrations in the chamber were also measured for 24 hours prior to and after the validation experiment.

Mass balance calculation was conducted to evaluate the total recovery efficiency of the system. The recovery efficiency (RE) was calculated using the equation

$$RE = \frac{E'}{M_c} \times 100\%$$

E' = Gas emission rate from the chamber during certain period, mg,

M_c = Total gas mass input into the chamber during same period, mg.

Statistical Analysis

The Proc Mixed procedure (SAS Inst. Inc, Cary, NC) was used for statistical analysis. The model comparing air emissions from dry and lactating cows included animal type (dry vs. lactating cows), time, and an animal type \times time interaction with the groups (hosting different animals for each group) as the random factor. The model investigating the effects of animal and manure on air emissions included animal type (dry vs. lactating cows), phases (three periods of “animal only”, “animal and manure”, and “manure only”), and animal type by phase interaction. Groups were treated as a random factor. Time was a continuous variable; all others were categorical variables. For all measures, the predicted difference test in Proc Mixed procedure in SAS was used to separate means when the overall F-value was significant ($P < 0.05$).

Project outcomes

The validation results indicated that the environmental chamber is well suited to accurately measure GHG and VOC emissions from animals and waste. The mass balance calculation showed approximately 90% of the total CH_4 input, 90% of the total methanol input, and 98% of the total ethanol input into the chamber were recovered at the outlet. The background concentrations of CH_4 , N_2O , methanol and ethanol prior to and after the validation experiment were approximately 1.40, 0.67, 0.08, and 0.13 $\mu\text{g L}^{-1}$, respectively

Both methanol and ethanol were emitted at average fluxes ranged from 0.25 to 0.70 $\text{g cow}^{-1} \text{h}^{-1}$ during all periods in which fresh manure was present in the chamber (Fig. 1, 2). Enteric fermentation contributed to alcohol emissions but fresh slurry appeared to be the main emission source. Upon entry of cows into the chamber, methanol and ethanol fluxes increased moderately (possibly enteric fermentation contribution). Major alcohol increases occurred over time coinciding with increasing accumulation of fresh manure (Fig. 1, 2). In the ‘manure only’ phase without cows present, both alcohols remained at high albeit decreasing levels for several h confirming manure was indeed the main alcohol source. The decrease over time within the ‘manure only’ phase might be related to a decrease in fermentable sugars and cellulose in the feces and a decrease in microbial activity (Williams, 1983), as well as the decrease of moisture on the manure surface that affects the mass transfer of alcohols from manure to air. The estimated average emission rates of

methanol were 0.33 and 0.70 g cow⁻¹ h⁻¹ from dry and lactating cows, respectively, as well as their fresh manure (Table 2). The dry and lactating cows' manure emitted 0.27 and 0.53 g cow⁻¹ h⁻¹ methanol, respectively, during the second experimental day ('manure only' phase after cows were removed from the chamber). The estimated average emission rates of ethanol were 0.51 and 1.27 g cow⁻¹ h⁻¹ from dry and lactating cows as well as their fresh manure, respectively. The 'manure only' phase resulting from dry and lactating cows' emitted on average 0.33 and 0.70 g cow⁻¹ h⁻¹ ethanol, respectively. Lactating cows and their fresh manure produced considerably more methanol and ethanol than dry cows and their fresh manure (P<0.001) most likely because of the larger amount of fermentable substrate in their feed (Table 1) (Wilkerson et al., 1995).

Filipy et al. (2006) predicted ethanol emission rates from fresh and aged dairy manure based on data by Miller and Varel (2001), who predicted ethanol emission factor was 0.63 and 4.41 g cow⁻¹ h⁻¹ for fresh and aged beef cattle manure, respectively. Furthermore, Filipy et al. (2006) measured ethanol emissions under lactating cow freestall conditions on a commercial dairy. Their measured emission rate of ethanol was 3.69 ±1.85 g cow⁻¹ h⁻¹ using an atmospheric tracer method and analysis on a GC/MS. The measured ethanol values in the present study were 0.51 for dry cows and 1.27 g cow⁻¹ h⁻¹ for lactating cows, which is close to the fresh manure values calculated by Filipy et al. (2006). It is important to mention that most modern dairies in the SJV use water to flush manure into a liquid storage pond (a.k.a. 'lagoon') three times per day. Since the present study left the manure accumulating on the concrete floor (w/o flushing), we conducted a mitigation pilot study in which manure was flushed out of the chamber at 11:00, 15:00, and 19:00 leading to ten fold reduction of both ethanol and methanol emissions (data not shown). Since alcohols are very water soluble, a manure flush system might be effective in keeping these compounds in the liquid phase thus preventing volatilization to the atmosphere.

Both VFAs and phenols were apparently emitted from cows and fresh manure (Fig. 3, 4). However, both VFA and phenol concentrations were measured close to the lower detection limit of the assay and instrumentation. The only VFA consistently above its LOQ was acetic acid (Fig. 3). On an emission mass basis, acetic acid contributed from 32 to 100% of total VFA emissions. The higher level of acetic acid emission compared to other VFAs is consistent with what has been reported for both dairy farms and cattle feedlots (Martensson et al, 1999; McGinn et al., 2003; Moller et al., 2004, Spinhirne et al., 2004). Martensson et al. (1999) monitored VFAs in dairy barns and determined that acetic acid concentrations in air ranged from 31 to 78 µg m⁻³, while butyric acid concentration ranged from 4 to 11 µg m⁻³. If data from the present study were scaled to reflect a similar population size (ignoring factors like diet, ventilation, etc.) as the study by Martensson et al. (1999) the acetic acid concentration would range from 36 to 247 µg m⁻³ and the butyric acid concentrations from 0 to 64 µg m⁻³. Butyric acid was typically above the method LOQ during at least one sampling event per replicate (Fig. 3). High variability across the three cow groups and concentrations near the lower detection limit of the assay make further interpretation of trends difficult.

On an emission mass basis in the present experiment, 3/4-methylphenol was the most significant phenolic compound amounting to 50% of these compound group emissions (Fig. 4). All phenolic

compounds were typically above method LOQ for outlet air samples, whereas inlet air samples were typically below method LOQ. Besides 3/4-methylphenol, the most significant phenolic compounds were phenol, 2-methylphenol and 2-ethylphenol. Sonesson et al. (2001) reported detection of phenol (3-50 $\mu\text{g m}^{-3}$), 4-methylphenol (0.6-100 $\mu\text{g m}^{-3}$), and 4-ethylphenol (0.4- 10 $\mu\text{g m}^{-3}$) on eight dairy farms in northern Sweden (farm size ranged from 10 to 82 milking cows). If data from the present study were scaled to reflect the Sonesson et al. (2001) dairy population size (again, ignoring potential different conditions between studies like diet, etc.) our phenol concentration would have ranged from 9.6 to 50.7 $\mu\text{g m}^{-3}$ and our 4-methylphenol concentrations would have ranged from 21.9 to 200 $\mu\text{g m}^{-3}$. In summary, studies by Martensson et al. (1999) and Sonesson et al. (2001), agree with the present findings that emissions of VFAs and phenol compounds from dairy cows and fresh manure are generally low and in our case close to the method LOQ.

Upon entry of both dry and lactating cows into the chamber, CH_4 fluxes immediately increased indicating that enteric fermentation is the main process responsible for production of this gas ('empty chamber' vs. 'cows only' phases; $P < 0.01$) (Fig. 5). After removal of cows from chambers ('manure only' phase), CH_4 flux went back to background levels ('empty chamber'; Table 2), indicating that fresh manure did not produce noticeable CH_4 fluxes ('empty chamber' vs. 'manure only'; $P > 0.05$). The emissions of CH_4 from dairy cows also showed a clear diurnal pattern; maintaining higher rates during the day than at night. Decreasing emission rate were found from 20:00 (when the light was turned off) to 8:00 the next day. Kinsman et al. (1995) reported a similar pattern, with fluxes increasing at 7:00 and decreasing at 21:00. Differences in CH_4 emissions between dry and lactating cows were anticipated and observed (Fig. 5, Table 2). Lactating cows produced approximately 1.3 times more CH_4 than non-lactating dry cows per animal ($P < 0.01$). This difference can be largely explained by the larger amount of readily fermentable substrate (i.e. corn) in the lactating vs. dry cows' diet, necessary to meet the nutritional requirements for cows at this stage of milk production (Table 1) (Wilkerson et al., 1995). In the present study, the estimated emission rate of CH_4 averaged 12.35 $\text{g cow}^{-1} \text{h}^{-1}$ from dry cows and manure, and 18.23 $\text{g cow}^{-1} \text{h}^{-1}$ from lactating cows and manure, respectively. The average weights of dry and lactating cows were 770 and 656 kg, respectively. Therefore, per 500 kg livestock unit, the lactating cow produced approximately 1.7 times more CH_4 than dry cows, which is close to the ratio reported by Holter and Young (1992). The CH_4 fluxes observed in the present study for lactating cows were greater than the 13.03 $\text{g cow}^{-1} \text{h}^{-1}$ determined for adult Holstein and Jersey cows (EPA, 1998;) that is being used by some air regulatory agencies. Since fresh manure did not produce noticeable CH_4 fluxes and under commercial conditions is usually flushed out of the animal housing area on average three times per day, the CH_4 emissions from animal housing components of a dairy can be estimated largely on animal emissions. Several recent reports showed 17.47 $\text{g cow}^{-1} \text{h}^{-1}$ of CH_4 flux from lactating cows' facilities (Kinsman et al., 1995; Sneath et al. 1997), which is in a good agreement with findings obtained in the present study.

Kaspar and Tiedje (1981) reported that a small quantity of N_2O can be emitted by the cow most likely produced during nitrate reduction reactions occurring in the gut. The present study found elevated N_2O

emissions (vs. the background) when the cows stayed in the chamber. However, the N₂O emissions could not be accurately quantified due to an error during calibration procedures. Although N₂O emissions from cow enteric fermentation appear to be minor, additional research is needed due to its considerable heat forcing potential.

Conclusions

Dairy farms may produce high fluxes of alcohol (>0.25 g cow⁻¹ h⁻¹) including methanol and ethanol, and CH₄ (>12 g cow⁻¹ h⁻¹) from animals and their fresh manure. Both ethanol and methanol were emitted at average flux rates ranged from 0.25 to 0.70 g cow⁻¹ h⁻¹ from cows' fresh manure. However, flushing of animal housing has a high potential to reduce alcohol emissions due to their high water solubility.

Enteric fermentation was the main process responsible for production of CH₄, while fresh manure did not produce noticeable fluxes. Lactating cows and their manure produced more CH₄, methanol and ethanol than dry cows and manure most likely due to the larger amount of fermentable substrate in both feed and feces. Compared with alcohol and methane emissions, the emissions of VFAs and phenol compounds from dairy cows and their manure were very low, and close to the lower detection limit of the assay and instrumentation. Variation in VFA and phenol concentrations across the three cow groups, as well as low concentrations near the lower detection limit of the assay make further interpretation of trends difficult. Current emission inventories in the San Joaquin Valley in California underestimate alcohol emissions and may overestimate VFA emissions from dairy cow housing considerably. Future research needs to address the mitigation of VOC emissions that occur during fermentation of feedstuff and fresh manure as well as CH₄ from cow digestive processes.

Figures for Component 1, Study 1

Fig. 1. Methanol emission rates from three groups of dry and lactating cows (n=3), respectively. SEM = pooled standard error.

Fig. 2. Ethanol emission rates from three groups of dry and lactating cows (n=3), respectively. SEM = pooled standard error.

Fig. 3. Acetic, propionic, butyric, and valeric acid emission rates from three groups of dry and lactating cows (n=3), respectively. SEM = pooled standard error.

Fig. 4. 2-methylphenol, phenol, 2-ethylphenol, 3/4 methylphenol emission rates from three groups of dry and lactating cows (n=3), respectively. SEM = pooled standard error.

Fig. 5. Methane emission rates from three groups of dry and lactating cows (n=3), respectively. SEM = pooled standard error.

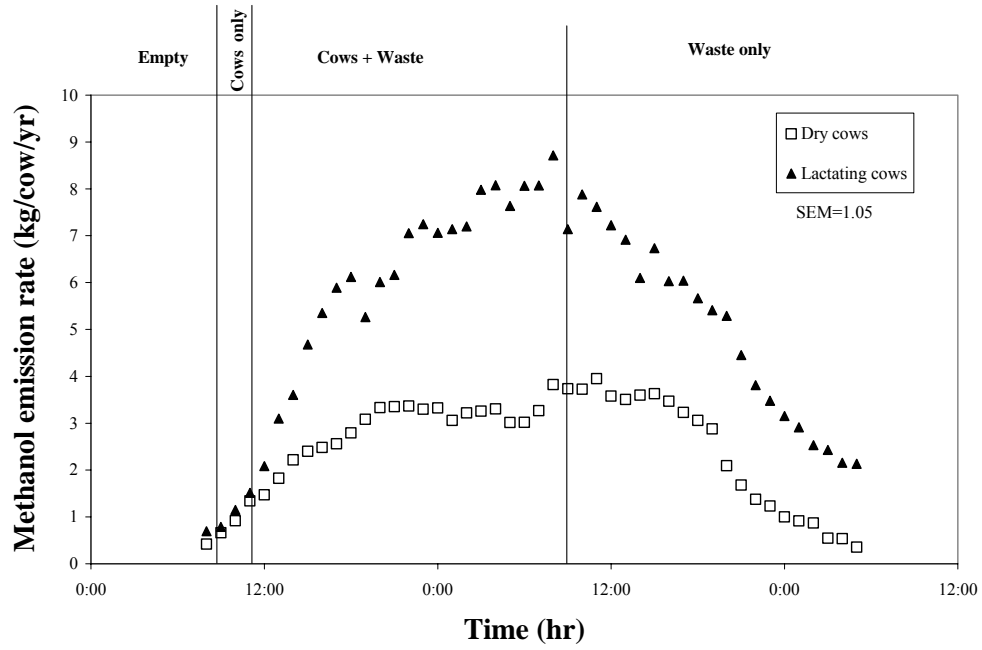


Fig. 1

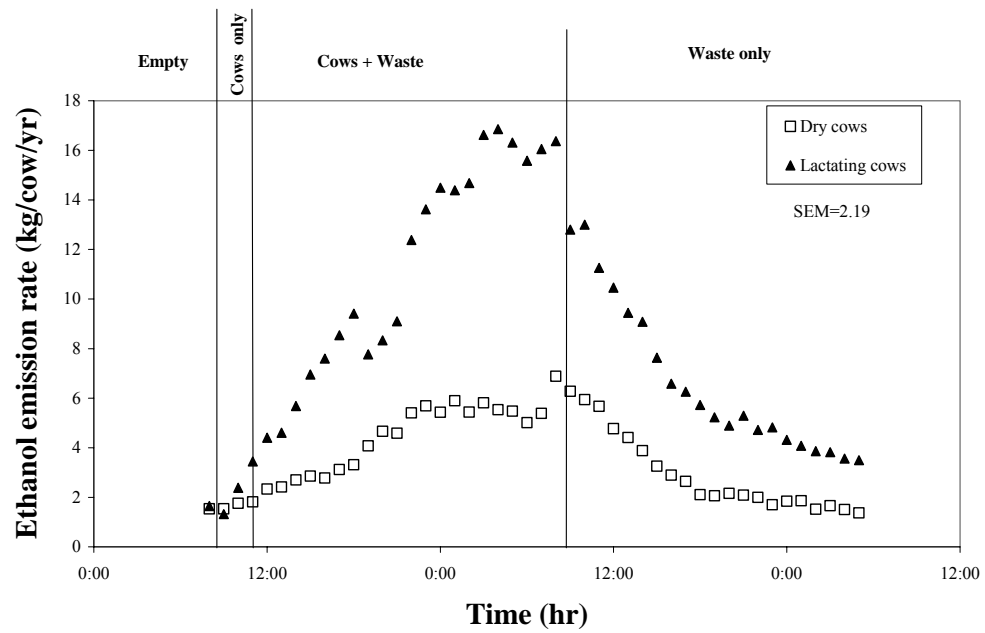


Fig. 2

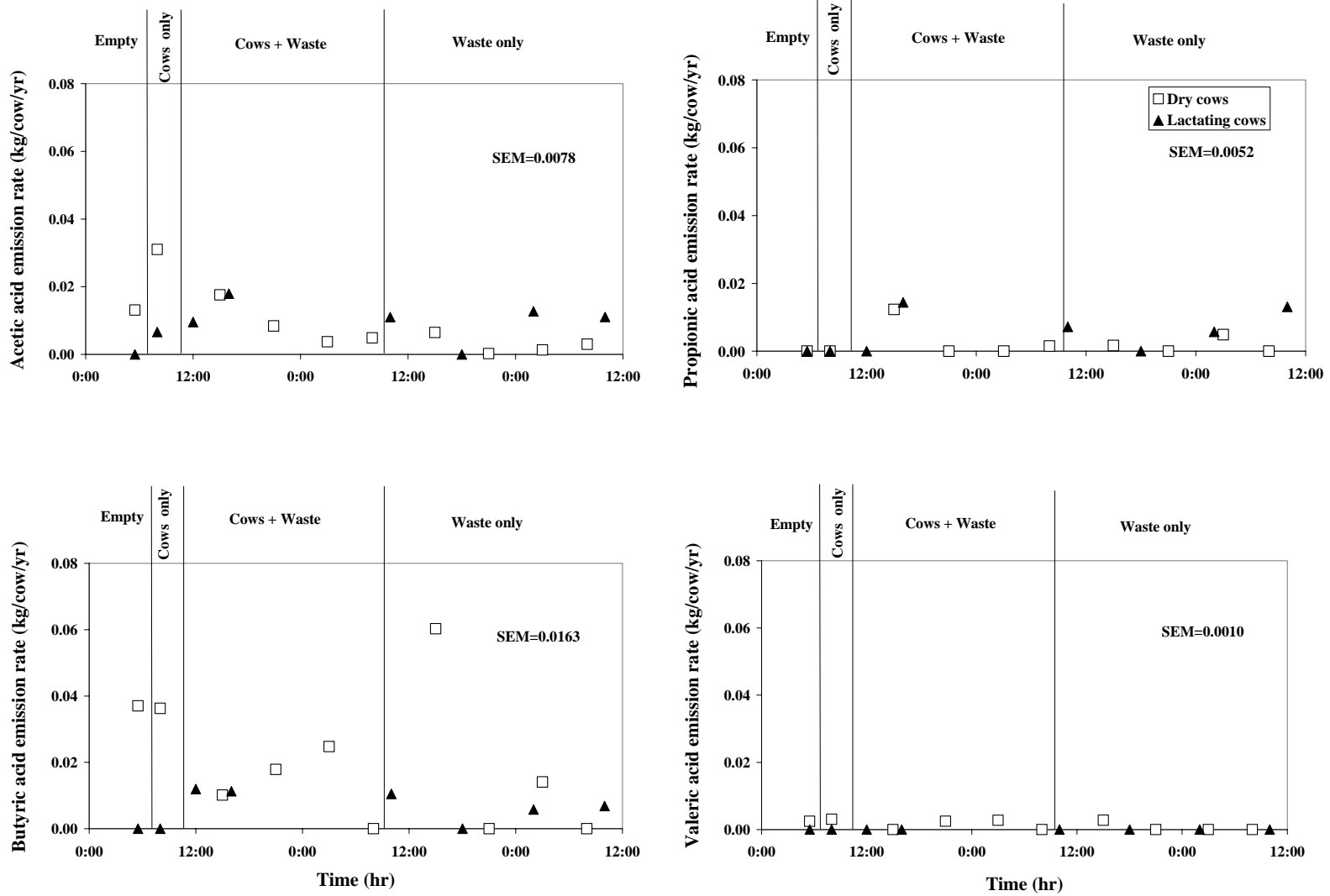


Fig. 3

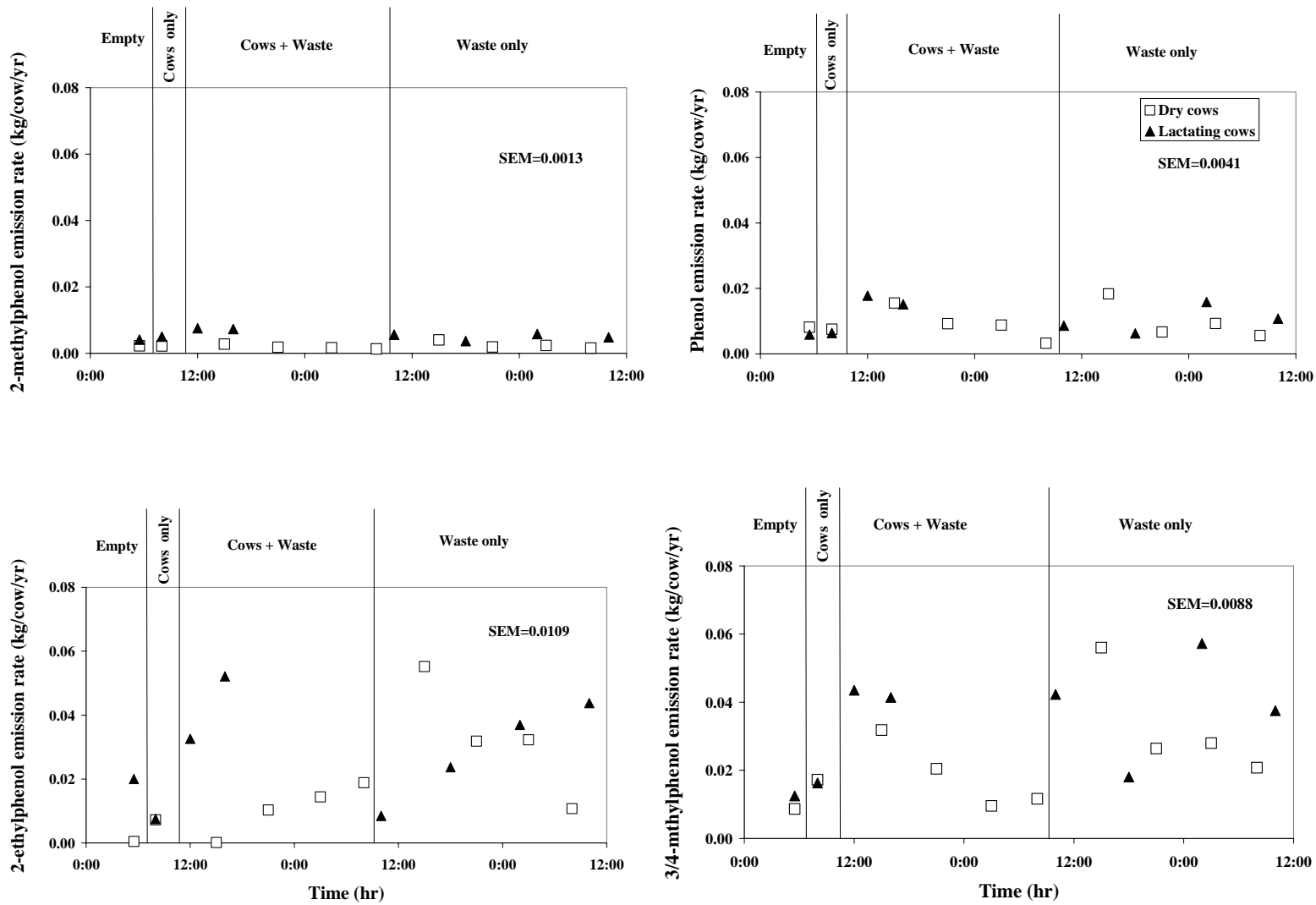


Fig. 4

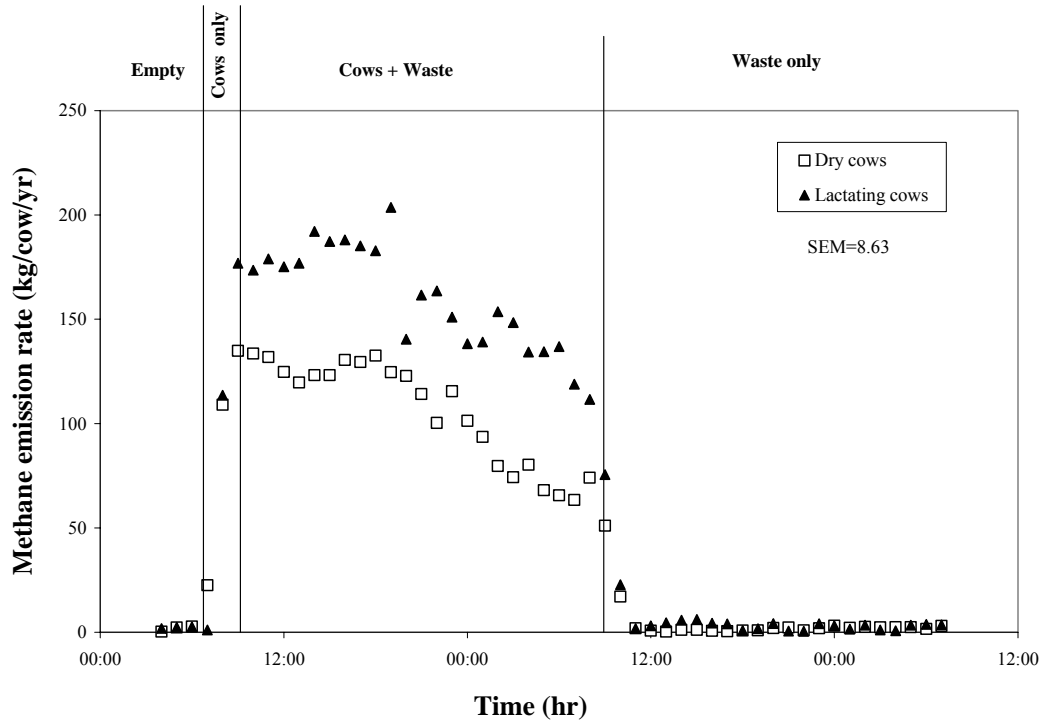


Fig. 5

Tables for Component 1, Study 1

Table 1. Diet ingredients used for dry and lactating cows.

	Dietary composition	
	Dry cow	Lactating cow
Grain	0	34.8
Alfalfa	31.0	39.2
Oat Hay	61.0	0
Whole Cottonseed Meal	0	11.3
Almond Hulls	0	8.1
Soybean Meal	0	4.0
Milk Mineral	0	1.6
Energy Mix	0	0.6
Salt	0	0.3
Dry Cow Pellet	8.0	0

Table 2. Average methane, methanol, and ethanol emission rates from dairy cows and their fresh waste.

	Dry Cows	Lactating Cows
Average methane emission rate (kg cow ⁻¹ yr ⁻¹)		
Empty chamber	1.8 ± 1.0 ^a	2.3 ± 1.0
Cows & Waste (24 hr)	108.2 ± 14.1	159.7 ± 15.9
Day time (10:00 am to 8:00 pm)	126.9 ± 4.9	180.4 ± 12.5
Night time (10:00 pm to 8:00 am)	83.3 ± 12.1	139.1 ± 10.1
Waste only	2.4 ± 0.8	3.0 ± 1.0
Average methanol emission rate (kg cow ⁻¹ yr ⁻¹)		
Empty chamber	0.30 ± 0.16	0.72 ± 0.21
Cows & Waste	2.89 ± 1.83	6.14 ± 0.99
Waste only	2.33 ± 0.66	4.60 ± 1.03
Average ethanol emission rate (kg cow ⁻¹ yr ⁻¹)		
Empty chamber	1.53 ± 0.28	1.31 ± 0.50
Cows & Waste	4.47 ± 0.74	11.13 ± 2.25
Waste only	2.93 ± 0.79	6.13 ± 1.40

^a Standard error; (n = 3)

Study 2: Effects of Dairy Corral Management on Air Emissions

Abstract

A total of 96 pregnant, non-lactating Holstein cows were housed in four, totally enclosed cattle pen enclosures (CPEs) and were fed a total mixed ration (TMR) *ad libitum*. Eight cows were housed in each of the four CPEs during each of three, 14 day replications. Cows were randomly sorted into four groups and stratified by weight. Treatments were: (1) control, manure accumulated for 14 days (CON), (2) harrowing (HAR), three times weekly, (3) surface acidifier application (sodium bisulfate, SBS), twice weekly, and (4) scraping (SCR), which was complete manure removal once weekly. Emissions of the smog-forming alcohols ethanol (EtOH) and methanol (MeOH) as well as the greenhouse gases (GHG) carbon dioxide (CO₂), nitrous oxide (N₂O), and methane (CH₄) were measured continuously from the CPEs' air inlets and outlets. Gaseous concentrations were sampled using a photoacoustic gas-analyzer (INNOVA 1412) and emission rates (kg/cow/yr) calculated. Data were analyzed using Proc MIXED procedures in SAS. Overall, alcohol emissions for SBS were lower ($P < 0.05$) compared to all other treatments. The EtOH emission rates for SBS, HAR, SCR, and CON were 3.88, 12.57, 11.81, and 12.41 kg/cow/yr, respectively. MeOH, emission rates for SBS, HAR, SCR, and CON were 1.57, 8.49, 8.05, and 8.67 kg/cow/yr, respectively. SCR compared to SBS, HAR, and CON showed reduced ($P < 0.05$) emission rates for N₂O and CH₄. Emission rates for CH₄ and N₂O were higher in SBS ($P < 0.05$) compared to the other treatments ($P < 0.05$). There were no differences across treatments for CO₂ emissions. This study suggests that surface acidifier (SBS) applied to dairy corrals can reduce alcohol emissions, thus lowering smog pollution. Results suggest that SBS increases greenhouse gases. Scraping and harrowing of corral surface manure show little promise to reduce emissions of both smog forming compounds and greenhouse gases from dairies.

Introduction - Background and overview

Twenty-one percent of the nation's milk supply comes from California, making it the leading dairy state in the United States (California Agricultural Resource Directory, 2005). There is concern that the large number of dairy cows (approximately 1.8 million) impacts environmental quality. The San Joaquin Valley of California is the leading dairy region of the United States but also known as the worst non-attainment area for smog. Cows, feed, and waste are sources of volatile organic compounds (VOCs), which are major contributors to tropospheric ozone (smog), and also greenhouse gases, which increase global warming.

The formation of ground level ozone is caused by the gas-phase interaction of emitted VOCs and oxides of nitrogen (NO_x) in the presence of sunlight. The current regulatory VOC emission factor for dairy cows is 8.75 kg/head/year, which suggests that San Joaquin Valley (SJV) dairies emit VOCs at higher rates than vehicles, and thus contribute significantly to the region's extreme ozone non-attainment status (SJVAPCD, 2005). Studies conducted in the Mitloehner lab at UC Davis (Shaw *et al.*, 2007) have shown that fresh waste in animal housing areas and fermented feed are the main VOC sources from dairies, with the main VOC group being alcohols (ethanol and methanol). Effective best management practices are needed to reduce emissions from fresh waste under dairy cow housing conditions (Dragosits *et al.*, 2002).

In addition to VOCs, greenhouse gases (GHGs) are also regulated by California law. Greenhouse gases are gaseous components of the atmosphere that contribute to global warming by absorbing radiated energy from the earth (originating from the sun). Greenhouse gases include nitrous oxide (N₂O), methane (CH₄), and carbon dioxide (CO₂). Sources of greenhouse gases from dairies include cows (enteric fermentation occurring in the rumen), manure in animal housing and outdoor storage, treatment of manure and slurry (e.g., composting and anaerobic treatment), land application, and chemical fertilizers (Monteny *et al.*, 2001).

On most California dairies, waste management techniques differ between the concrete floored freestall barns where lactating cows are housed and the dirt floored corrals where dry cows and heifers are typically housed. Manure that collects in freestall barns is flushed or scraped several times daily, and the resulting waste stream is stored in large manure ponds (lagoons). Manure from open dirt corrals is typically scraped to storage piles several times a year. Alcohols are highly water soluble, therefore flushing and lagoon storage keeps these pollutants in the liquid phase. However, water is not applied to the waste in the dirt corrals and this leads to alcohol emissions from the fresh solid waste into the atmosphere. Complete and frequent removal of waste in drylot corrals, using techniques such as scraping, may be an effective mitigation strategy for reducing GHGs in the immediate area (Monteny *et al.*, 2001, Weiske *et al.*, 2006). However, GHG emissions may increase in the manure storage areas (Weiske *et al.*, 2006).

Both methanol (MeOH) and ethanol (EtOH) are produced during anaerobic fermentation in the cow's rumen by microbes like *Streptococcus bovis* and *Ruminococcus albus*. These microbes survive for several hours after excretion in waste. Although most CH₄ and CO₂ are released from the animals, some of these gaseous emissions, as well as emissions of N₂O, also result from microbial processes in the excreta or after manure is land applied (Clemens and Ahlgrim, 2001). Therefore, it is important to also consider the management of waste when determining appropriate mitigation strategies for greenhouse gases from dairies. The growth of microbes in fresh waste may be impaired by environmental factors such as pH, temperature, and oxygenation of the waste. Therefore, it is important to address at least one of the main factors (e.g., pH) to effectively disrupt the microbial and enzymatic activity in order to reduce the

gaseous emissions released into the atmosphere (Jongebreur and Monteny, 2001). Adding oxygen to the slurry to prevent the anaerobic activity responsible for much of the gaseous emissions can be achieved by frequently raking (aka harrowing) the waste with a chain harrow. Since growth and activity of rumen bacteria are inhibited at low pH (Stewart, 1977, Russell and Dombrowski, 1980, Thurston *et al.*, 1993), application of acidifying agents may also reduce the gaseous emissions from fresh waste.

When considering an acid to use for pH reduction in dairy slurry, it is important to consider the compatibility of the acid with the presence of animals. Sodium bisulfate (SBS, Jones Hamilton, OH) is a dry, granular acid salt that has been used for many years as a pH reducer in a variety of agricultural, industrial, and food applications. The anti-bacterial properties of SBS have been exploited in its application as a sanitizer (EPA Reg #1913-24-AA). Sodium bisulfate has been used for bacterial reduction in poultry, dairy, and equine waste and bedding due to its pH reducing and antimicrobial properties, and has been found to significantly decrease ammonia emissions in these facilities (Sweeney *et al.*, 1996, Ullman *et al.*, 2004). Research is needed to determine the effects of SBS on VOC and GHG emissions from dairies.

The hypothesis for the present study is that gaseous emissions resulting from microbial processes in dairy waste can be mitigated by using corral waste management techniques that are believed to disrupt growth and activity of anaerobic microbes.

Objective

The objective of this study was to evaluate the effects of drylot corral waste management on emissions of smog-forming volatile organic compounds and greenhouse gases.

Project Approach

General

A total of 96 pregnant, non-lactating Holstein cows were used to evaluate different waste management techniques in drylot corrals at the Environmental Quality Research Facility located at the University of California, Davis. Experiments were conducted during the periods of August 21 through September 25, 2006, and from April 13 through April 27, 2007. Animals were housed and treated in accordance with the Guide for the Care and Use of Agricultural Animals in Agriculture Research and Teaching (FASS, 1999), and the approved Animal Care and Use protocol for the University of California, Davis.

The cows were housed in the Cattle Pen Enclosure (CPE) facility, which consists of four, completely covered, dirt-floored corral pens (18.5 x 10 m each) that allow for simultaneous air emission testing of four mitigation treatments. Enclosures were oriented west (W) (front) to east (E) (back). A 10 m

feed bunk, situated on a 3 m wide cement feed apron, was situated along the W side of each corral. The remainder of the corral was dirt floored with a 3% slope. In each corral, 14 locking head gates were situated along the feed bunk. A water trough with a float-activated water supply, providing the cows with *ad libitum* access to water, was located along the E side of the corral.

Each corral pen was enclosed with a CPE, a dome-like, 22 x 11 m structure (Figure 6). The construction was steel framed, consisting of welded truss arches with parallel 0.06 m diameter steel tubes spaced 0.3 m apart and strengthened by continuous 0.025 m diameter structural webbing that reached a height of 5.79 m at the top of the arch (36' Legend Series Cover-all Building, Saskatoon, Saskatchewan, Canada). The steel construction was covered with a white Dura Weave cover, consisting of 100% Marquesa Lana with a double stacked weave (Intertape Polymer Group, Montreal, Quebec, Canada). The CPE was equipped with a roll-up door located on the E side, enabling cattle and equipment to be moved in and out of the facility. A feed flap, located on the W side of each CPE alongside the feed bunk, could be opened and closed as needed, and provides an efficient means of feed delivery into the bunks within each CPE.

Each CPE has a cooling pad on the E side to allow for air inflow and two fans in front of ventilation openings on the W side allowing for air outflow from the CPE. A panel, used to control cooling pad operation and fan speed, is located on the E side of each CPE. Two optical sensors (Monarch Instruments, Amherst, NH) are mounted on the two fans to provide constant monitoring of the fan's rotation rate per minute (RPM). The mA usage of each fan as well as the static pressure were recorded with data loggers (Onset Computer Corporation, Bourne, MA) at 10 minute intervals to allow for calculation of air flow. The 4.88 x 1.22 m cooling pad located on the E side of the CPE allows for ambient air inflow and also provides evaporative cooling as water runs down the pad using a pump (Beckett Corporation, Model W3500, Irving, TX).

Negative pressure is generated that is created by the fans blowing air out of the CPE. Due to the negative pressure mechanical ventilation (wind tunnel system) in each CPE, there is constant directional airflow from E to W within the CPE.

Experimental Treatments

The study consisted of three replications of fourteen days each. The Holstein cows were randomly sorted into 4 groups of 8 animals each on day 1 of each period. Sorting occurred after the cows were weighed and the groups stratified by weight to ensure that the four randomized groups would be uniform in total weight. The four treatment groups were: 1) a control (CON); manure accumulation for 14 d without disturbance, 2) harrowing (HAR), which was raking three times weekly, 3) application of sodium bisulfate acidifier (SBS) on slurry, twice weekly, and 4) frequent corral scraping (SCR), once weekly. The four CPEs were randomly assigned a treatment, and this assignment was consistent throughout each replication of the study.

The CON did not experience any waste management technique intended to mitigate emissions. After the cows entered the CPE on day 1 of each experimental period, the waste was neither removed nor manipulated in any way for the entire 14 days. In addition, the cows assigned to CON remained in the enclosure for the entire period, with the infrequent exception of health checks and treatments of individual animals, usually lasting no longer than an hour.

On days 3, 5, 8, 10, and 12 of each experimental period, the corral surface of the CPE that was assigned to HAR was raked with a 4 x 4 chain harrow (Gearmore Inc., Model H4x4, Chino, CA). The cows were removed from the CPE and moved into an adjacent, open corral area while this treatment was implemented. The chain harrow was pulled on the back of a Honda all-terrain vehicle (ATV). This treatment took an average of 20 min. Upon completion of the harrowing treatment, the cows were moved back into the CPE.

On days 2, 4, 8, and 10 of each experimental period, SBS was applied to the ground surface of assigned CPE. The SBS acidifier was applied using a fertilizer spreader (Scotts®, AccuGreen 1000 Drop Spreader, Marysville, OH) at a rate of 0.37 kg/ m². SBS was spread evenly across the corral floor, on both the cement and dirt areas of the CPE. The animals were not moved out of the CPE during the time of application.

On days 5 and 12 of each 14 d period, the cows in SCR were moved from their CPE into an adjacent, uncovered dry lot corral for approximately one hour. During this time, the floor of the CPE was scraped, using a front loader (Bobcat, West Fargo, ND), and the manure was completely removed. The waste was moved away from the CPE and dumped into waste storage piles in a remote area to prevent possible contamination of inlet air. Once all manure was removed from the ground surface in the corral, the cows were moved back into the CPE.

Animal Performance

Feeding and Body Weight Gain

In each period, the cows were weighed initially upon arrival to the facility (day 1) and again on the day of departure (day 14). Body weight (BW) was determined and average daily gain (ADG) calculated.

All animals were fed an identical total mixed ration (TMR) (Table 3) *ad libitum* once daily in the morning. The feed fed into each of the four CPE troughs was weighed at each feeding using the scale connected to the feed wagon (Kirby, Merced, CA). Feed amount was continuously adjusted to allow for approximately 10% refusals. Feed refusals were collected daily and weighed prior to feeding.

Grab samples were taken from the refusals in each of the CPEs and from the feed wagon once weekly for dry matter analysis. The refusal samples were taken from five different areas within the trough

and a composite sample generated. The samples were weighed and placed into an oven (Precision Scientific Co., Chicago, IL) at 107.2°C for 12 hrs. The five samples were weighed again, dry matter (DM) percentages of feed and refusals determined, and dry matter intake (DMI) of animals in each CPE calculated.

Animal Health

Animal health was monitored by a veterinarian (SLB). Cows were observed upon arrival to the facility and throughout the duration of the trial. Individual animals that displayed any signs of poor health were examined more closely in a portable chute (Comfort Hoof Care, Model H*Series, Baraboo, WI), which was transported to the research facility as needed, and proper medical treatments were administered.

Environmental and Emissions Measurements

Climatic Measures

Climatic measurements of ambient temperature (°C) and relative humidity (%) were measured continuously within each CPE. These climatic measurements were recorded using data loggers (HOBO Pro Data Logger Series, Onset Computer Corporation, Bourne, MA) that were placed above the feed flap inside each CPE. These temperature and relative humidity measurements were recorded at 10 min intervals. Climatic measurements were also taken from outside the CPEs using an automated weather system (Novalynx, Model 110-WS-16, Auburn, CA) at 15 min intervals. Measurements from the weather system included temperature, relative humidity, and black globe temperature (BGT).

Surface Measurements

Measurements of soil pH and temperature were taken in all four CPEs once weekly. Additional pH and temperature measurements were conducted in the SBS treatment group 48 hours post treatment. Measurements were taken in ten different locations throughout the CPE using a portable pH meter (Fisher Scientific, Accumet AP84, Pittsburgh, PA) and a laser radiation thermometer gun (Raytek, Raynger ST, Santa Cruz, CA). The ten measurement locations were spread evenly throughout each CPE, in a grid fashion (Figure 7), and were representative of the entire enclosure.

Air Emission Measurements

The alcohols ethanol (EtOH) and methanol (MeOH), and the greenhouse gases nitrous oxide (N₂O), methane (CH₄), and carbon dioxide (CO₂) were continuously measured using an INNOVA model 1412 Photoacoustic Field Gas-Monitor (INNOVA, AirTech Instruments, Ballerup, Denmark). This gas analyzer can selectively measure up to five component gases and water vapor simultaneously through the use of optical filters. The equipment was located in a centralized air conditioned cabinet outside of the

second CPE. A total of 48.8 m of Teflon tubing (with 12.7 mm ID) was used to connect the equipment to all four enclosures. To minimize tubing length as a confounding factor, tubes in each enclosure were of identical length. Samples were sequentially taken at an inlet location and from the outlet locations in each of the four CPEs for twenty minutes at a time.

Gaseous concentrations and air flow were measured continuously and emission rates were calculated.

Emission rates (kg/cow/year) were calculated using the following equation:

$$\text{MIX} * \text{FL} * 60 * 1000 / 22.4 * \text{MW} / 1000000 * 24 * 365 / \text{cow\#} / 1000$$

where MIX is the net concentration in ppm

FL is the ventilation flow rate (m³/min)

60 is the conversion from min to hr

1000 is the conversion factor from m³ to L

22.4 is the volume of one molar ideal gas at standard temperature (L/mole)

MW is molecular weight (g/mole)

1000000 is ppm

24*365 is the conversion from hours to year

cow# is the number of cows in each CPE (8)

and 1000 is the conversion from grams to kilograms.

Statistical Analysis

The statistical analysis of the MeOH, EtOH, N₂O, CH₄, and CO₂ emissions was completed using Proc Mixed procedures in SAS. Observations were repeated over time. The model included replication, treatment, day, and treatment*day interactions as fixed effects. The PDIF option was added to an LSMEANS statement to test all possible pairwise comparisons between the four study treatments and was adjusted with Bonferroni and Tukey tests. Proc Mixed procedures in SAS were also used to statistically analyze the above gaseous emissions at day 0, prior to animals entering the CPEs, to insure that the enclosures did not differ prior to implementation of treatments. Animal performance measures (BW, ADG, and DMI) were analyzed using Proc GLM procedures in SAS. All data was analyzed at a significance level of P < 0.05.

Project Outcomes

Animal Performance

Feeding and Body Weight Gain

The mean initial BW of cows prior to entering the CPEs was 732.17 kg (ranging from 722.44 kg to 736.99 kg in the four treatment groups). The body weight did not differ across treatments (Table 4). On average, the cows gained 1.60 kg/head/day. Average daily gain ranged from 1.41 kg/head/day to 1.72 kg/head/day across the four treatment groups. Average DMI was 14.97 kg/head/day (ranging from 14.80 kg/head/day to 15.11 kg/head/day in the four treatment groups). Animal performance (ADG and DMI) were similar across the four treatments, but differed across the three replications (Table 4).

Animal Health

Two cows were observed limping during initial weighing in the chute prior to study treatments. Upon examination in a hydraulic hoof trimming chute (Comfort Hoof Care, Model H*Series, Baraboo, WI) they were observed to have toe ulcers (one from the first and one from the second replication) and were treated by opening and removing all damaged and necrotic tissue, bandaging, and placing orthopedic blocks on the opposite, sound claws. During the second replication, a cow in CON was found to have a white line abscess on the medial claw of the left rear hoof. This condition was treated by removing the undermined horn in the heel, opening the abscess, and placing a block on the lateral claw. A cow in SCR was found to have symmetrical swelling around the coronary band during the second study replication. No wounds were found, but swelling was more pronounced on the lateral side and there was evidence of trauma. The cow was treated with a non-steroidal anti-inflammatory drug (Banamine, Schering-Plough Animal Health, Kenilworth, NJ) and was given a parenteral antibiotic (Naxcel, Pfizer Animal Health, New York, NY) for three days. She recovered uneventfully.

One CON cow during day 12 of the first replicate aborted a 7-month old fetus. The fetus was taken to the California Animal Health and Food Safety Laboratory for diagnostic workup, which was inconclusive. The cow had a retained placenta and was lethargic and febrile. She was treated symptomatically with a non-steroidal anti-inflammatory drug (Banamine, Schering-Plough Animal Health, Kenilworth, NJ) and parenteral antibiotic (Polyflex®, Fort Dodge Animal Health, Fort Dodge, IA). She recovered and remained in the study. In the third replicate, a cow assigned to CON slipped on the concrete prior to being weighed on day 1. She was injured and was found to be non-ambulatory the following day. She was transported to the Veterinary Medical Teaching Hospital (VMTH), where she was treated by floating in a warm water bath (Aquacow rise system, St. Johnsbury, VT) several times and treated with fluids. She did not recover and was replaced in the study with another cow.

None of the health problems discussed above were thought to be a result of the study treatments.

Environmental and Emissions Measurements

Climatic Measures

Average outdoor ambient temperature ranged between 14°C - 23°C (Table 5) over the three periods. Average temperatures in the four CPEs during the experimental period were slightly lower than the outdoor temperatures, and ranged from 14°C - 20°C. Average outdoor ambient relative humidity ranged from 40% - 60% across the three experimental periods. Average relative humidity within the CPE was always higher than the outdoor relative humidity conditions, and ranged from 79% - 87%.

Temperature and relative humidity within each of the four CPEs were similar and followed the same trends. Dramatic deviations (e.g., increase in temperature in a CPE) were only experienced temporarily and can be explained by factors that were immediately remedied, such as a broken pump in one of the enclosures.

Surface Measurements

Average soil temperature measured once weekly (with each replication consisting of two weeks) was 19.58°C (ranging from 19.34°C – 19.76°C in the four CPEs). Average soil temperature was similar across the four treatments; however, there were differences within the CPE floor locations ($P = 0.02$) and over time ($P < 0.0001$). Average soil pH, measured prior to first SBS application each week, differed across treatments ($P < 0.0001$). The average pH values ranged from 8.16 – 8.98 in the four CPEs, and the soil of the CPE assigned to SBS had a lower pH than the other three treatment groups. Average pH in CON, HAR, and SCR were similar across treatments.

Soil measurements taken immediately prior to weekly SBS application compared with measurements made two days post application showed differences in temperature and pH ($P < 0.0001$). Average temperatures were 19.58°C prior to SBS application and 17.53°C two days post treatment. Soil average temperatures in the SBS treated CPE varied over time ($P < 0.0001$). Average soil pH values were reduced by application of SBS acidifier, from a pre-treatment value of 8.16 to 4.53 two days post-treatment.

Air Emissions

Air emissions of MeOH, EtOH, N₂O, CH₄, and CO₂ did not differ across CPEs on day 0, prior to cows entering the enclosures and to the initiation of study treatments. Figures 8 to 12 show that day 0 gaseous emission factors were low and similar across treatments. Emissions increased drastically at day 1 when cows entered the CPEs and waste accumulation began. Gaseous emissions differed across replications (Table 6).

Volatile Organic Compounds

Emissions of VOCs differed across treatments ($P < 0.0001$) and over time ($P < 0.05$) (Table 6). Average MeOH emission rates for SBS, HAR, SCR, and CON were respectively 1.57, 8.49, 8.05 and 8.67 kg/cow/year. The SBS group had considerably less MeOH emissions than HAR, SCR, and CON (Figure 8), with no differences across the latter three groups. Average EtOH emission rates for SBS, HAR, SCR, and CON were 3.88, 12.57, 11.81, and 12.41 kg/cow/year, respectively. Emissions of EtOH were three to four times lower in the SBS treatment group compared to the other three treatment groups (Figure 8). Emission rates of EtOH across CON, HAR, and SCR treatment groups did not differ. Figures 8 and 9 show that even as early as day 1, EtOH and MeOH emissions are lowered by surface application of SBS.

Greenhouse Gases

The emission rates for the greenhouse gases N_2O and CH_4 differed across treatments ($P < 0.05$), but CO_2 emission rates were similar across treatments (Table 9). All measured GHG emissions differed over time ($P < 0.05$).

Average N_2O emission rates for SBS, HAR, SCR, and CON were 2.99, 1.65, 1.59, and 2.20 kg/cow/year, respectively. The N_2O emissions were higher in SBS vs. the other treatments, and both HAR and SCR showed lower emissions than SBS and CON (Figure 10). Average CH_4 emission rates for SBS, HAR, SCR, and CON were 137, 117, 107, and 122 kg/cow/year, respectively. The SBS treatment group had the highest CH_4 emission rates (Figure 11), CON and HAR were similar, and SCR had the lowest emissions.

Average CO_2 emission rates for SBS, HAR, SCR, and CON were 5929, 6249, 5659, and 6539 kg/cow/year, respectively. CO_2 had a significant Day*Treatment interaction ($P = 0.0066$). Therefore, differences in CO_2 emissions between treatments are time dependant. Over time, all treatments differed in CO_2 emission rates. Lowest to highest emissions were in the SCR, SBS, HAR, and CON treatment groups (Figure 12).

Project Discussions

In the present study, application of SBS to the ground surface manure was effective in reducing emissions of the smog forming alcohols, ethanol and methanol. Previous studies have shown that acidic conditions inhibit the growth and activity of rumen microbes, such as *Ruminococcus albus* (Stewart, 1977, Russell and Dombrowski, 1980, Thurston *et al.*, 1993). Because microorganisms from the digestive system of ruminants are able to survive in waste after excretion and are responsible for the incomplete anaerobic fermentation of manure that lead to VOC emissions (Miner, 1997, Wang *et al.*, 2004, Casey *et*

al., 2006), the results from the present study point to the conclusion that alcohol forming microbes from the rumen are inhibited in the waste if subjected to acidic environments. Based on the findings that application of SBS lowered the soil pH by almost half and that alcohol emissions were reduced, it is speculated that acidification of waste creates an atmosphere that is not conducive to the microbial fermentation of the sugars that lead to alcohol emissions.

Application of SBS acidifier increased N₂O and CH₄ emissions in the present study. Nitrous oxide emissions are primarily produced as a gaseous intermediate in the microbial process of denitrification. Denitrification is the stepwise anaerobic microbial reduction of nitrate (NO₃⁻) to nitrogen gas (N₂) (Mosier *et al.*, 1998a, Wrage *et al.*, 2001). Several intermediates, including N₂O, are produced and could be emitted into the atmosphere (Wrage *et al.*, 2001). Several studies have found that the proportion of N₂O produced during denitrification increases at low pH (Nägele and Conrad, 1990, Daum and Schenk, 1998, Stevens and Laughlin, 1998). Therefore, it is not unexpected that the highest N₂O emissions occurred in the more acidic conditions of the SBS treatment group. Higher N₂O emissions are produced under acidic conditions because N₂O reductase, the enzyme that catalyzes the reaction that converts N₂O to N₂, is inhibited in low pH conditions (Knowles, 1982, Granli and Bøckman, 1994, Thomsen *et al.*, 1994). The mechanisms resulting in the high emissions of CH₄ in the SBS treatment group are currently unknown and are not explained by the literature.

In the present study harrowing decreased emissions of N₂O, but did not affect the other measured gases. The process of harrowing aerates the soil and manure pack (Steinmann, 2002). Therefore, the microbes in the harrowed manure were introduced to oxygen. The measured gaseous emissions result from processes from anaerobic bacteria. The results from the present study indicate that oxygen permeation of the manure due to harrowing is insufficient to inhibit methanogenic bacteria and the microbes responsible for alcohol emissions. However, the results suggest that the anaerobic process responsible for N₂O emissions on dairies, denitrification, is hindered by the harrowing waste management technique. Research on the effect of harrowing on gaseous emissions is limited; however, a previous study by Steinmann (2002) showed that mineral nitrogen content was higher in harrowed soil when compared to a control. Therefore, harrowing may promote conditions that keep nitrogen in the soil rather than emitted into the atmosphere.

Completely removing waste from the corral areas by scraping once weekly reduced N₂O and CH₄ emissions. Previous research by Osada *et al.* (1998) found that frequent removal of slurry from pig houses led to 10% reductions in N₂O and CH₄ emissions. Alcohols were not decreased due to scraping. Shaw *et al.* (2007) found that methanol emissions were high in fresh waste. Therefore, the alcohols may have already entered the air prior to the time of waste removal and harrowing.

Emissions of CO₂ did not differ across treatments. This outcome agrees with other work showing that the main source of the CO₂ from dairy cows is from enteric fermentation (Amon *et al.*, 2001, Jungbluth *et al.*, 2001). The experimental treatments implemented in the present study were waste

management techniques and therefore were not expected to effect gaseous emissions emitted directly from cows in the processes of respiration and enteric fermentation.

Project Conclusions

The surface acidifier SBS reduces the ozone forming alcohols, ethanol and methanol, from dairies. This may help reduce smog production in areas such as San Joaquin Valley of California that have many dairies and also do not meet federal regulations for ozone. The San Joaquin Valley Air Pollution Control district has recently adopted Rule 4570, which requires large confined animal facilities to select and implement methods of mitigating VOC emissions from their facilities. The results of the present study suggest that application of an acidifier, such as SBS, may be a very effective technique that dairies can use to reduce emissions of alcohols from waste, which have been shown in previous studies (Miller and Varel, 2001, Filipy *et al.*, 2006, Shaw *et al.*, 2007) to be the most important VOC type from dairies.

While SBS may be an effective mitigation technique in reducing VOCs, it may increase greenhouse gases. In the present study, emission rates of the greenhouse gases N₂O and CH₄ were higher in the SBS treatment group.

Results from the present study suggest that scraping and harrowing are not effective mitigation techniques for the most relevant gaseous emissions. Scraping, the most common waste management technique used in dairy drylot corrals, was shown to effectively reduce greenhouse gas emissions, but not VOC emissions. Further research is needed to show the overall effects of scraping on emissions of greenhouse gases. Manure is scraped into storage piles, and it is likely that emissions of greenhouse gases increase in the location of the manure storage piles while simultaneously being reduced in the corral areas.

In the present study, SBS application was the waste management technique that had the largest impact on gaseous emissions. Using SBS may help dairies meet air quality requirements for ozone. However, further research is required to determine effective dosages of SBS. In the present study, SBS was applied uniformly across the entire corral floor and at a rate that would be cost-prohibitive on commercial dairies. It is possible that applying SBS topically on areas of highest manure concentration (i.e. near feed and water troughs) may achieve the same outcome while using less of the acidifier, which would also make this waste management approach more cost effective.

SBS acidifier application drastically decreased VOC emissions, but also seemed to increase greenhouse gas emissions. Therefore, the decision to use this waste management technique would depend upon the objectives of the dairy as well as environmental concerns in the area at the time of application.

Tables Component 1, Study 2

Table 3. Feed Ingredients in the Diet

Item	% in diet ^a
<i>Feed Components</i>	
Oat Hay	42.80
Cracked Corn	22.13
Alfalfa Hay	17.31
Almond Hulls	13.43
UC Davis Dry Cow Pellet ^b	4.33
<i>Chemical Components</i>	
Dry Matter	93.1
Protein	10.75
Ash	6.39
C	45.4
N	1.77
Ca	0.54
Mg	0.24

^a Reported on an a dry matter basis.

^b UC Davis Dry Cow Pellet contained (%DM): 20.0 Crude Protein, 3.5 Crude Fat, 3.0 Crude Fiber, 2.8-3.3 Calcium, 1.0 Phosphorous, 0.8 Sodium, and 3.2 – 3.8 ppm Selenium.

Table 4. Least squares means, standard errors, and p-values for body weight at day 0, average daily gain, and dry matter intake ^a.

Item	Treatment				SEM	P-values	
	SBS	HAR	SCR	CON		Trt	Rep
BW at day 0, kg	733.21	736.05	736.99	722.44	8.19	0.91	0.004
ADG, kg/hd-d	1.62	1.72	1.41	1.64	0.33	0.74	<.0001
DMI, kg/hd-d	15.09	14.80	15.11	14.87	0.27	0.90	<.0001

^a Every treatment was replicated three times and had eight non-lactating cows per replicate group.

SBS = Sodium bisulfate acidifier application treatment (two times / week)

HAR = Frequent harrowing treatment (three times / week)

SCR = Frequent scraping treatment (one time / week)

CON = Control

Table 5. Air temperature and relative humidity during the three experimental periods.

Climatic Parameter	Period 1	Period 2	Period 3
	8/21/06 – 9/4/06	9/11/06 – 9/25/06	4/13/07 – 4/27/07
Air temperature ^a, °C			
Ambient	22.59 ± 7.8	21.77 ± 6.6	14.53 ± 5.7
Cattle Pen Enclosure ^b	19.76 ± 6.0	18.04 ± 5.3	14.36 ± 5.8
Relative Humidity ^c, %			
Ambient	52.73 ± 23.0	39.89 ± 19.4	60.31 ± 23.0
Cattle Pen Enclosure ^b	87.01 ± 19.6	82.88 ± 17.6	79.28 ± 25.4

^a Average daily temperature ± standard deviation

^b Average of measurements from all Cattle Pen Enclosures

^c Average daily relative humidity

Table 6. Least squares means, standard errors, and p-values of methanol, ethanol, nitrous oxide, methane, and carbon dioxide (in kg/cow/year)^a

Item	Treatments					P-values			
	SBS	HAR	SCR	CON	SEM	Trt	Rep	Day	Day*Trt
MeOH	1.57	8.49	8.05	8.67	0.32	<.0001	<.0001	.0003	0.57
EtOH	3.88	12.57	11.81	12.41	0.40	<.0001	<.0001	<.0001	0.60
N ₂ O	2.99	1.65	1.59	2.20	0.07	<.0001	<.0001	0.003	0.030
CH ₄	137	117	107	122	1.39	0.020	0.004	<.0001	0.14
CO ₂	5929	6249	5659	6539	61.9	0.42	<.0001	<.0001	0.004

^a Every treatment was replicated three times and had eight non-lactating cows per replicate group.
 SBS = Sodium bisulfate acidifier application treatment (two times / week)
 HAR = Frequent harrowing treatment (three times / week)
 SCR = Frequent scraping treatment (one time / week)
 CON = Control

Figures for Component 1, Study 2



Figure 6. UC Davis Cattle Pen Enclosure (CPE) Research Facility, E Side

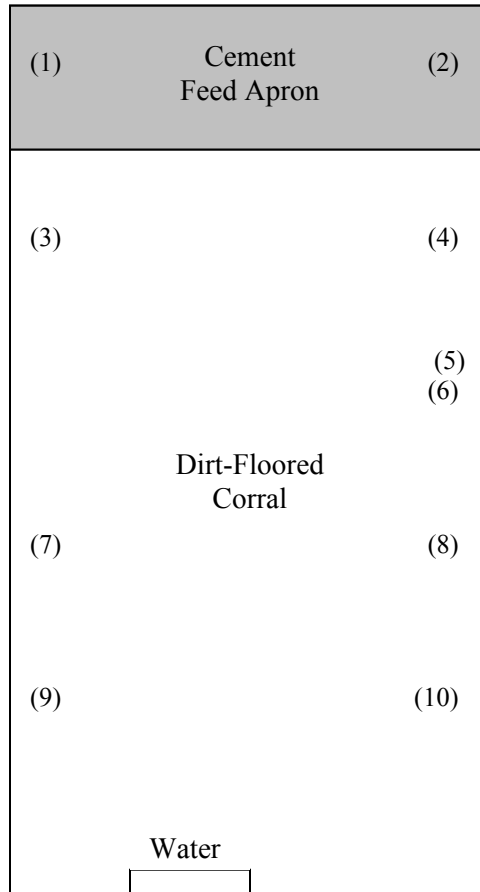


Figure 7. Corral layout and sample location map for soil pH and temperature measures. The top of the corral, adjacent to the feed apron, faces west, and the back of the corral faces east. Numbers represent sampling locations.

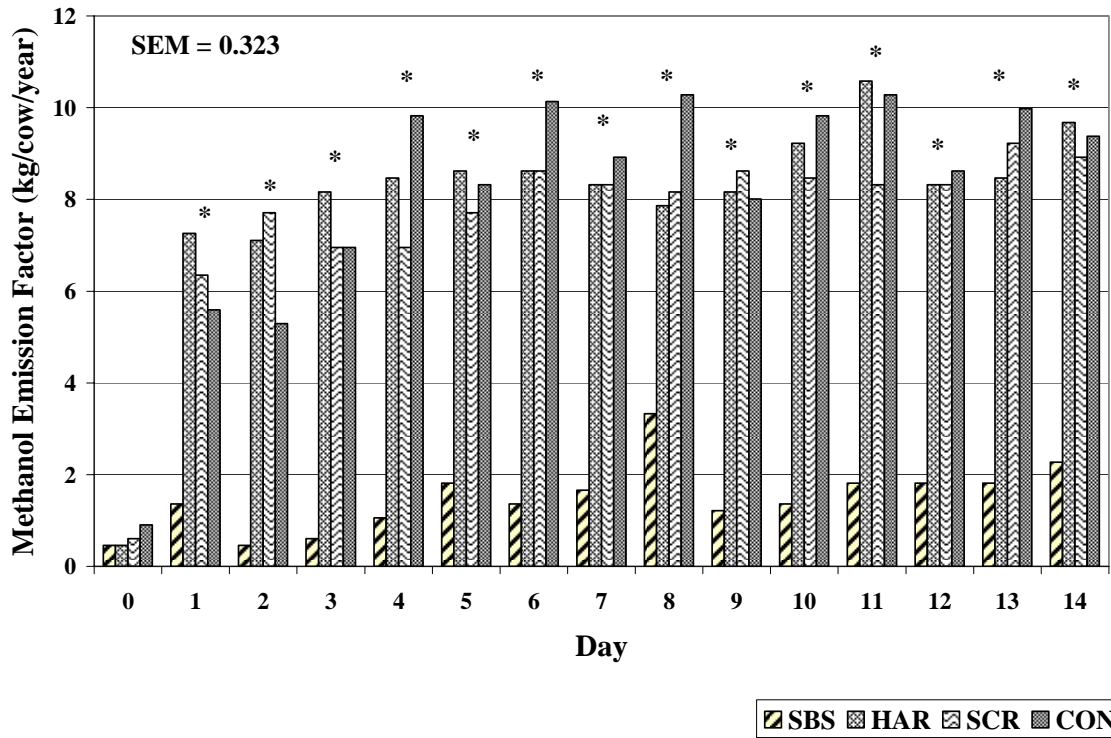


Figure 8. Methanol emission factor (kg/cow/year) over time from cows housed in CPEs. Treatments are sodium bisulfate application twice weekly (SBS), harrowing three times weekly (HAR), scraping once weekly (SCR), and control (CON). Asterisks indicate differences across treatments.

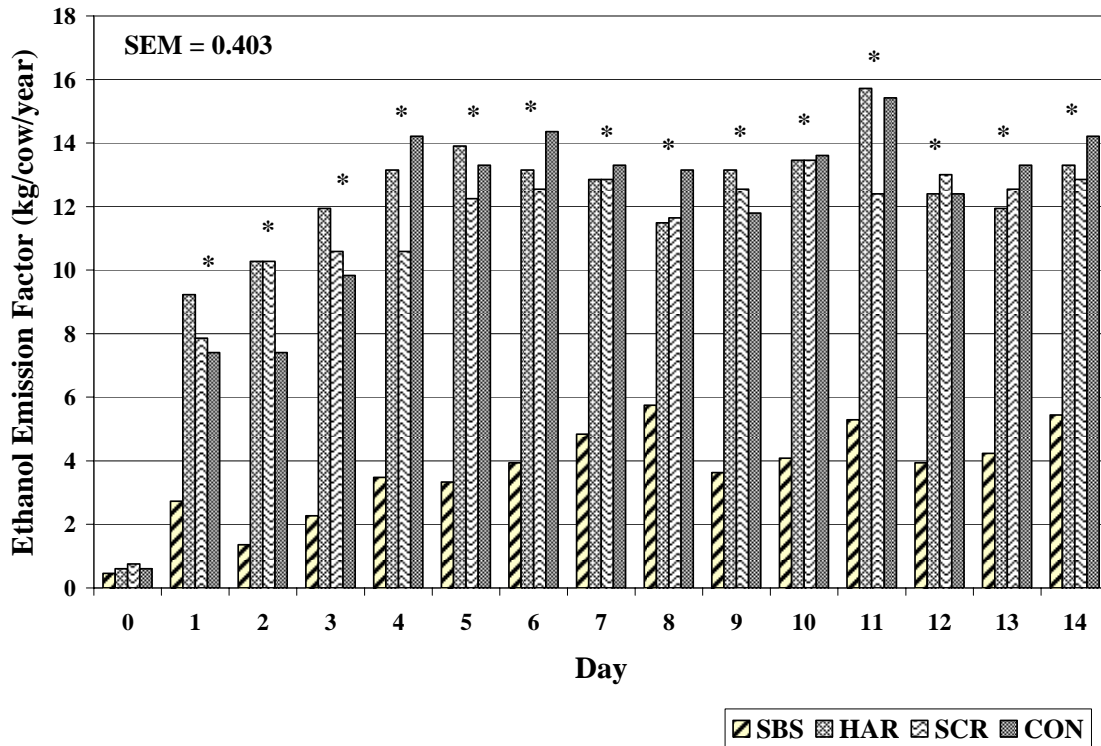


Figure 9. Ethanol emission factor (kg/cow/year) over time from cows housed in CPEs. Treatments are sodium bisulfate application twice weekly (SBS), harrowing three times weekly (HAR), scraping once weekly (SCR), and control (CON). Asterisks indicate differences across treatments.

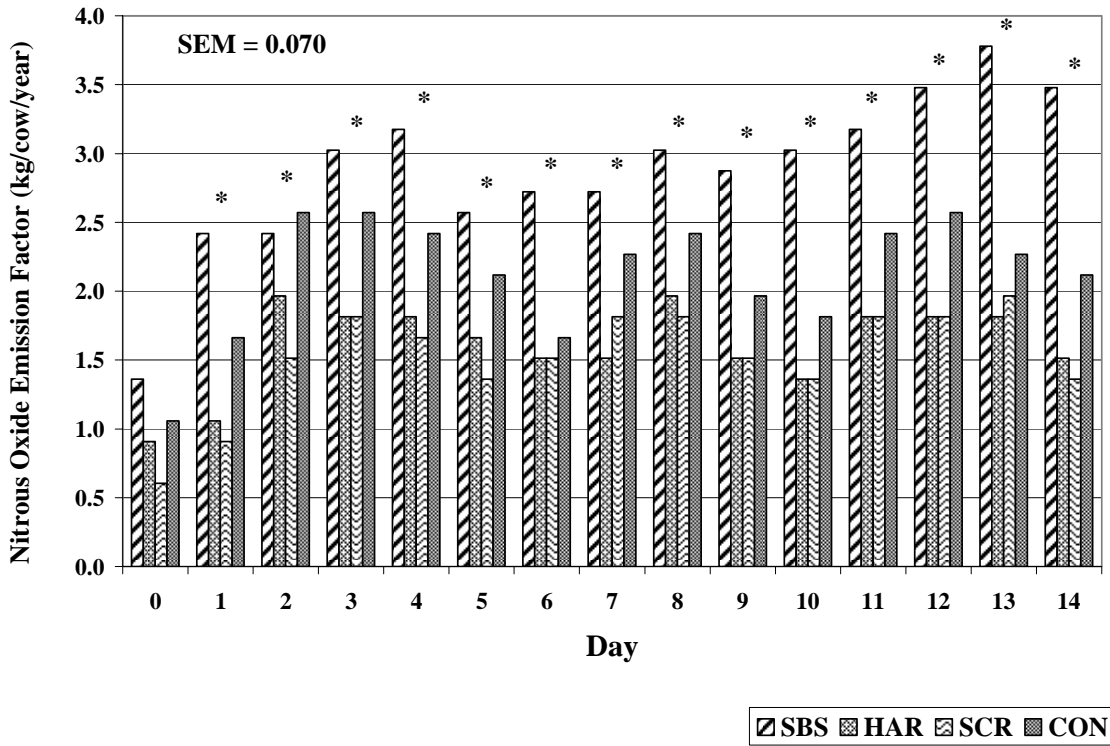


Figure 10. Nitrous oxide emission factor (kg/cow/year) over time from cows housed in CPEs. Treatments are sodium bisulfate application twice weekly (SBS), harrowing three times weekly (HAR), scraping once weekly (SCR), and control (CON). Asterisks indicate differences across treatments.

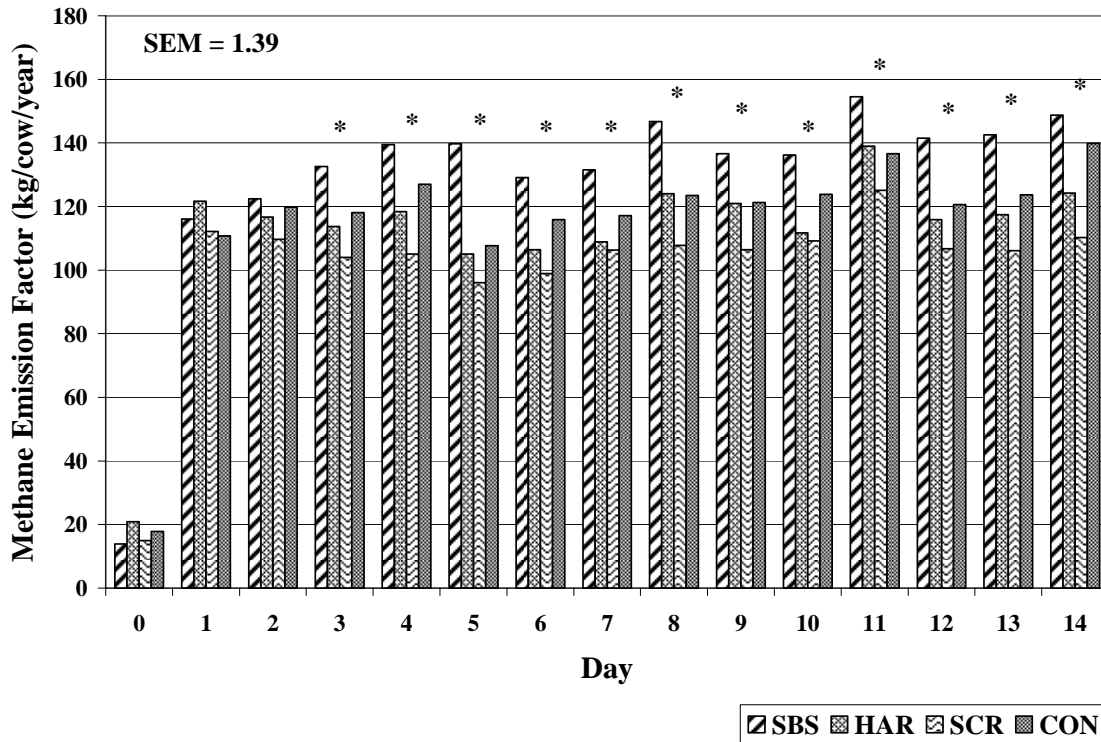


Figure 11. Methane emission factor (kg/cow/year) over time from cows housed in CPEs. Treatments are sodium bisulfate application twice weekly (SBS), harrowing three times weekly (HAR), scraping once weekly (SCR), and control (CON). Asterisks indicate differences across treatments.

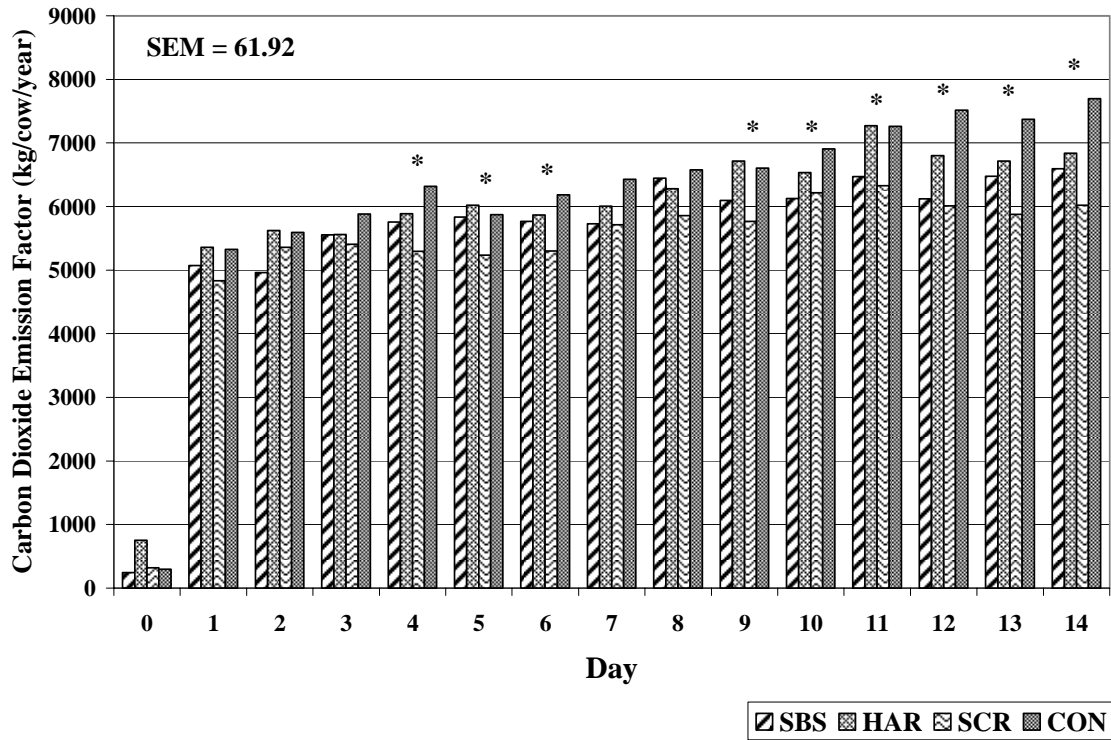


Figure 12. Carbon dioxide emission factor (kg/cow/year) over time from cows housed in CPEs. Treatments are sodium bisulfate application twice weekly (SBS), harrowing three times weekly (HAR), scraping once weekly (SCR), and control (CON). Asterisks indicate differences across treatments.

The following contains brief description of three additional studies that were performed to provide additional information for model development and testing.

Study 3: Effects of A Simulated Rain Event on GHG and VOC in Drylot Corrals.

Abstract

The objective of this study was to assess the effects of a simulated rain event on GHG emissions from drylot corrals that underwent different management treatments.

A total of 96 pregnant, non-lactating Holstein cows were housed in four, totally enclosed cattle pen enclosures (CPEs) and were fed a total mixed ration (TMR) *ad libitum*. Eight cows were housed in each of the four CPEs during each of three, 14 day replications. After the 14 days, cows were removed from the CPE.

Cows were randomly sorted into four groups and stratified by weight. Treatments were: (1) control, manure accumulated for 14 days (CON), (2) harrowing (HAR), three times weekly, (3) surface acidifier application (sodium bisulfate, SBS), twice weekly, and (4) scraping (SCR), which was complete manure removal once weekly. One half quarter inch of water was evenly applied to the corral surface of the HAR treatment at the end of 14 day periods to simulate a rain event.

Emissions of the smog-forming alcohols ethanol (EtOH) and methanol (MeOH) as well as the greenhouse gases (GHG) carbon dioxide (CO₂), nitrous oxide (N₂O), and methane (CH₄) were measured continuously from the CPEs' air inlets and outlets. Gaseous concentrations were sampled using a photoacoustic gas-analyzer (INNOVA 1412) and emission rates (kg/cow/yr) calculated. Data were analyzed using Proc MIXED procedures in SAS.

Overall, the application of water to the surface of the harrowing treatment (HAR) after 14 days of manure accumulation did not lead to an increase or decrease of GHG or VOC emissions (see figures 13 – 17).

Emissions from dry cows and waste

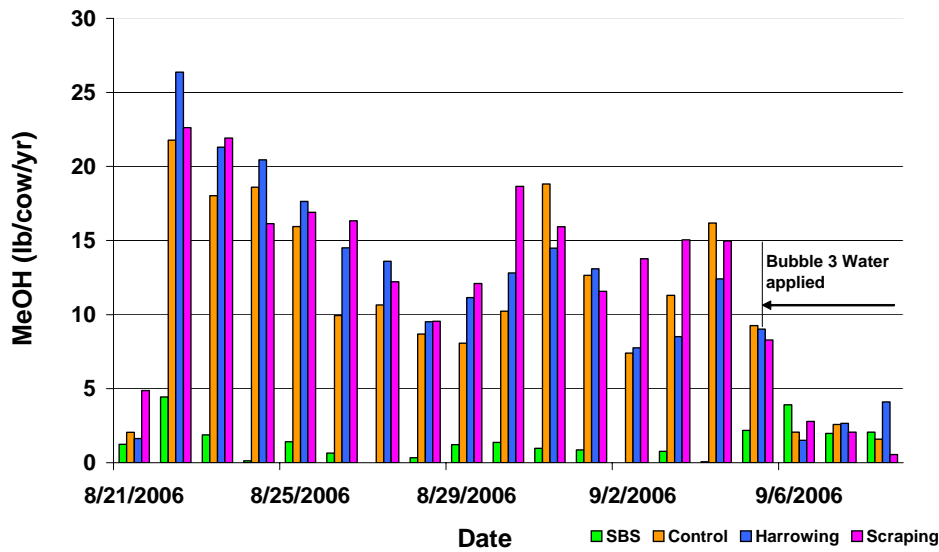


Figure 13. Methanol (MeOH) emission factor (lb/cow/year) over time from cows housed in CPEs. Treatments are sodium bisulfate, twice weekly (SBS), harrowing three times/ wk (HAR), scraping once/wk (SCR), and control (CON).

Emissions from dry cows and waste

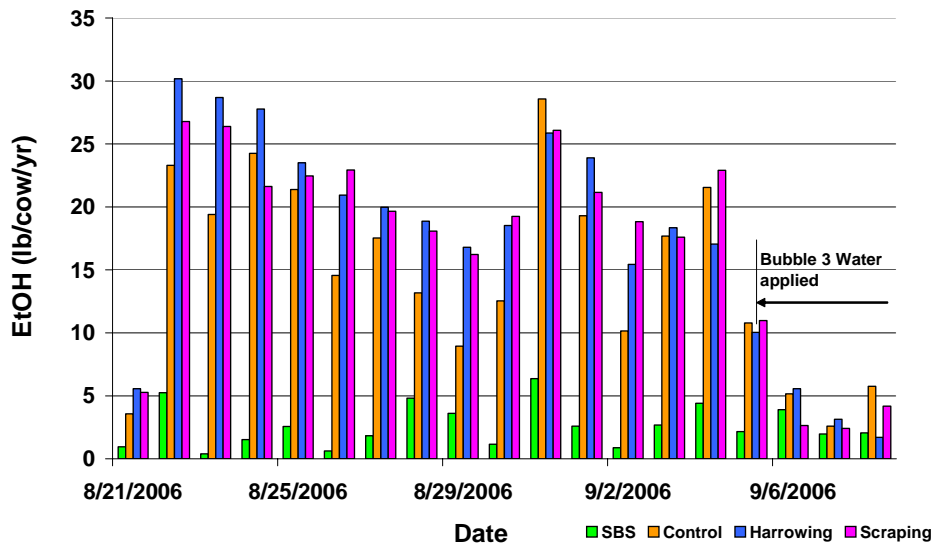


Figure 14. Ethanol (EtOH) emission factor (lb/cow/year). Treatments are sodium bisulfate, twice weekly (SBS), harrowing three times/ wk (HAR), scraping once/wk (SCR), and control (CON).

Emissions from dry cows and waste

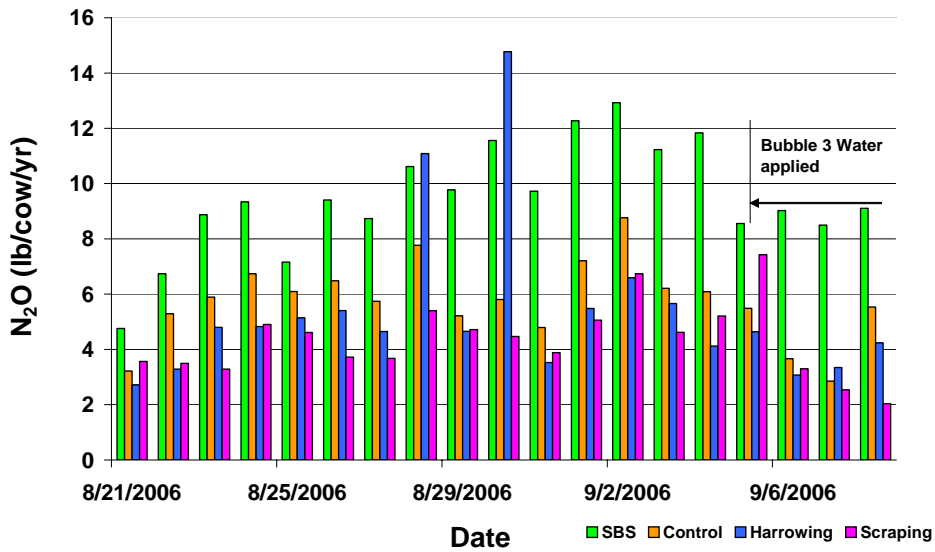


Figure 15. Nitrous oxide (N₂O) emission factor (lb/cow/year) over time from cows housed in CPEs.

Emissions from dry cows and waste

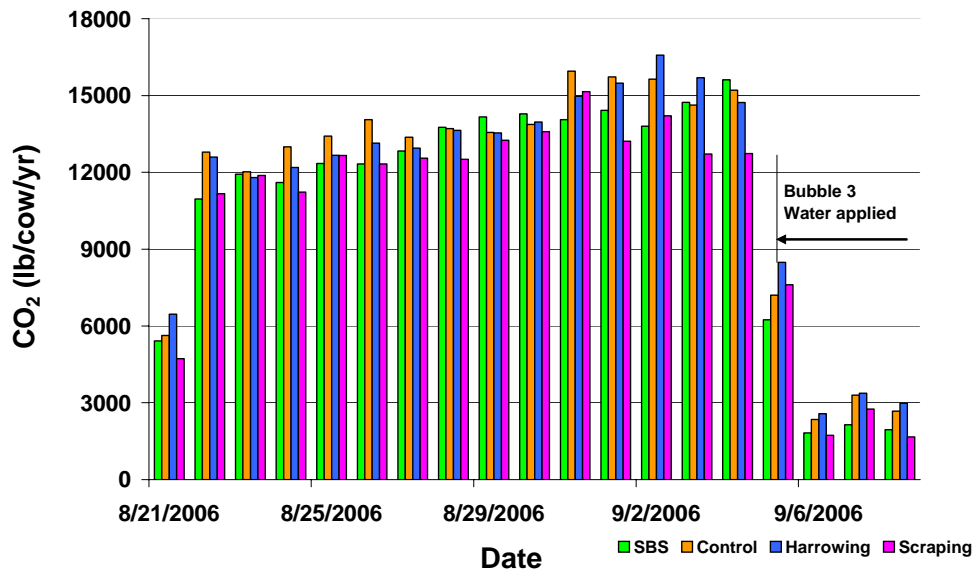


Figure 16. Carbon dioxide (CO₂) emission factor (lb/cow/year) over time from cows housed in CPEs.

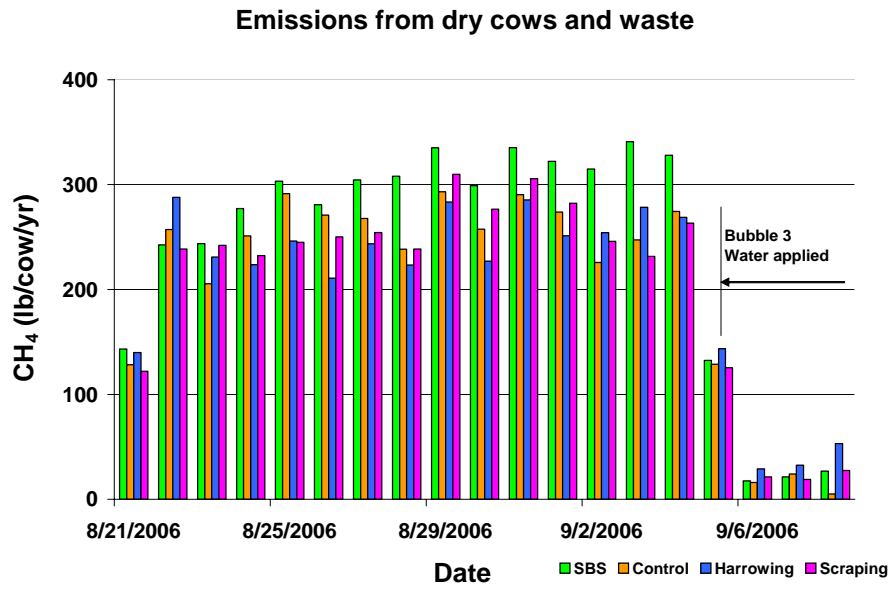


Figure 17. Methane (CH₄) emission factor (lb/cow/year) over time from cows housed in CPEs.

Study 4: Effects of Waste Management Techniques to Reduce Dairy Emissions from Freestall Housing

Abstract

The objective of this study was to reduce smog forming - and green house gas emissions (GHG) from lactating Holstein cows using industry typical freestall waste management. The San Joaquin Valley (SJV) in Central California is the largest milk producing region in the United States. The valley suffers from substantial smog forming gases (aka Volatile Organic Compounds, VOC), and GHG emissions. Typical dairy freestall waste management in the SJV includes flushing and scraping. In the present study, four treatments were compared in groups of three cows/group. A total of nine lactating Holstein cows were randomly assigned into three groups and each group underwent all treatments using a CRD. The four treatments were 1) no waste removal (CON), 2) flushing three times daily (FL3), 3) flushing six times daily (FL6), and 4) scraping three times daily (SC3). Cows were fed a TMR *ad libitum* and housed in freestalls that were located inside an environmental chamber. VOC and GHG emission concentrations were measured using a photoacoustic gas analyzer (INNOVA 1412). Emission rates were calculated in kg/cow/year and analyzed using PROC MIXED in SAS. All emission compounds showed differences across treatments. As a general trend, CON showed highest emissions ($P < 0.05$), followed by SC3, FL3, and FL6. Flush vs dry waste removal techniques (flushing vs scraping) is approximately twice as effective ($P < 0.05$) in reducing VOC emissions under freestall conditions. More frequent flushing of dairy waste (FL6 vs FL3) leads to further reduction of VOC emissions. GHG emissions were similar across treatments. The results of this study indicate that waste removal techniques used on modern dairies can decrease dairy air emissions. Consequently, VOC and GHG that promote smog and climate change can be reduced effectively through management of cow housing.

Study 5: Effects of Dietary Rumensin on Greenhouse Gas and Volatile Organic Compound Emissions from Lactating Dairy Cows

Abstract

The present study investigated the effects of a feed additive and rumen microbial modifier, Rumensin, on selected variables in lactating dairy cows. Rumensin fed cows (RUM) were compared to untreated control cows (CON) with respect to the effects of the feed additive on greenhouse gas (GHG) and volatile organic compound (VOC) emissions along with animal performance (dry matter intake, DMI), milk production, milk components, plasma urea nitrogen (PUN), milk urea nitrogen (MUN), and the microbial population structure of fresh waste. Measurements of GHG and VOC were collected at days 14 and 60 in an environmental chamber simulating commercial dairy freestall housing conditions. Milk production and DMI measurements were collected twice daily over the 60 day experimental period and milk components, PUN, and MUN, were measured on days 14 and 60. The microbial population structure of 6 RUM and 6 CON cow fecal contents were examined on three different occasions.

Rumensin did neither affect emissions of the GHGs methane (CH₄), nitrous oxide (N₂O), and carbon dioxide (CO₂), nor the smog forming VOCs methanol (MeOH), and ethanol (EtOH). Over a 24-hour period, emissions of CH₄, N₂O, and CO₂ emissions decreased, while MeOH and EtOH emissions increased as waste accumulated on the chamber floor in both RUM and CON animals. Animal performance did not differ in RUM versus CON cows. Microbial population structure was similar between treatments.

In summary, the microbial rumen modifier Rumensin fed at 600 mg head⁻¹ day⁻¹ with an alfalfa hay-based total mixed ration did neither effectively reduce GHG and VOC emissions, nor impact animal performance or the microbial population structure of animal fecal contents.

Component 2: FTIR Measurements of N₂O Emissions from Dairy Drylots

Objectives

The objective of this component of project is to design, develop and use an FTIR instrument for collection ambient measurements of N₂O and other pertinent gases, as NH₃, CO, CO₂, CH₄ and NMHC to aid in this process, to estimate fluxes from dairy drylots. To accomplish the flux estimation we will collect concentration data for these gases at 4 elevations, 1, 2, 5 and 10 meters and use a simple gradient model to give first order flux values. The long-term goal (beyond the scope of this project) is to establish realistic flux and emission values which require the use of open-path FTIR measurements. The data presented are the extractive measurements taken at two sites, specifically, one over a dry lot and one over a compost pile. The dry lot measurements consisted of almost continuous sampling for two months. These data provide a strong statistical database that could be examined in the future for model validation. Specifically the long time sampling was performed to examine temporal fluctuations of emissions with the goal of understanding the impact of rain events on N₂O emission from a dry lot. The compost pile measurements were collected to investigate differences in baseline emissions from compost piles and dry lots.

Spectroscopy

Spectroscopy can be defined as the investigation of the interaction that occurs between a defined source of electromagnetic radiation with a target sample. The way the emissive properties of the radiative source, usually some sort of light source, are perturbed depends upon the sample investigated. For example, molecules of gas can absorb electromagnetic radiation leading to molecular vibrations or rotations, with the frequencies that are absorbed by quantum theory being unique to each different type of molecule in the target sample. Therefore each molecule has its own characteristic absorption pattern over the electromagnetic spectrum.

Spectroscopic methods basically evaluate the concentration of the molecule investigated through Beer-Lambert's Law, which states that the fraction of light intensity transmitted through a gas is given by:

$$I/I_o = \exp(-\sigma(\psi)NL) \quad (1)$$

Where I and I_o are the transmitted and incident powers respectively, L is the absorption path length (cms), and N would then be the concentration of the absorbing molecules in number of molecules per

cubic centimeter. In this example $\sigma(\psi)$ is the wavenumber dependent absorption cross section in square centimeters per molecule.

FTIR (Fourier Transform InfraRed Spectroscopy) Description

Fourier transform infrared spectroscopy began to come into its own in the early 1950s when experimental groups first built and tested high-resolution spectrometers. Today, commercial Fourier transform spectrometers are widely available. Aided by fast computers, which perform Fourier transforms quickly, FTIR spectrometers are used to make spectroscopic measurements in many diverse disciplines. This has led to FTIR technology being used in the development of many commercial instruments by companies such as IMACC, Nicolet, Midac, Bruker, Bomem, Unisearch Associates and ABB to name a few. Most of the commercial instruments employed in this type of infrared spectroscopy use an interferometer originally designed by Michelson to measure the speed of light as shown in Figure 18.

The interferometer works by taking the entire incident beam of radiation from the source and dividing it into two paths with a beam splitter. The beam splitter is usually some non-absorbing film whose transmittance and reflectance are both approximately 50%. The beam splitter must also permit the transmission of the wavelengths (nominally 2-10 microns) employed for this type of spectroscopic measurement. Usually they are made of germanium. Therefore the source radiation incident on the beamsplitter is divided into two parts. One of the paths goes to a fixed mirror while the other path goes to a moving (translating) mirror. When the position of the translating mirror is continuously varied along an axis collinear to the source, an interference pattern $I(x)$ is generated as the two phase shifted beams interfere with each other. By smoothly translating one mirror, the optical path difference (OPD) is $x=2L$ (where x is twice the distance L traveled by the translating mirror). This optical path difference (also called retardation,) between the beams traveling to the fixed and the moving mirrors will be the same for all wavelengths of light. This leads to two boundary conditions. First, when the two beams have traveled the same distance, they will be in phase and thus when they recombine at the beam splitter, will interfere constructively. Second, when the movable mirror is at a distance twice that of the fixed mirror, the two beams will be out of phase with each other and interfere destructively. By moving the translating mirror at a constant velocity, the signal at the detector will vary sinusoidally. The time varying component is the only component that is important in spectroscopic measurements and is called the interferogram. The actual signal measured at the detector will depend on the beamsplitter, detector response at different wavelengths and the emission light source.

The specific intensity $I_k(x)$ can be derived for the source energy at a single wave number k by

$$I_k(x) = J(k) \langle T(k) \rangle \frac{1}{2} [1 + \cos(kx)] \quad (2)$$

where $J(k)$ is the incident intensity and $\langle T(k) \rangle$ is the averaged beam splitter transmission function. Since $\cos(kx)$ is an even function, the interferogram will be symmetrical about the white light fringe. Since the resolution of a Fourier transform spectrometer increases with increasing optical path difference, the maximum spectral resolution is achieved by using the entire available translation distance to measure only one side of the interferogram. Figure 19 provides a typical interferogram.

However, in order to maximize the signal-to-noise ratio (by avoiding the slight overhead incurred in switching the direction of stage motion), both sides of the interferogram can be measured, yielding a so-called "two-sided" interferogram. Two-sided interferograms contain two measurements of each interferogram point per scan, but can only achieve half the optical path difference (and therefore half the spectral resolution) of one-sided scans. Because one-sided interferograms transform to real spectra, no explicit information on the interferogram phase is available, although phase problems do show up as anomalous spectral baselines.

Two-sided interferograms transform to complex spectra (they have two pieces of information per frequency), allowing phase errors to be directly measured as a function of frequency. Two-sided scans are therefore extremely useful for examining alignment of the optics and other potential instrumental problems. As already mentioned, a perfectly aligned instrument with no phase errors will produce completely symmetric interferograms whose transform will have zero imaginary part over all frequencies in the passband. The total intensity measured for a given OPD x from radiation at all wave numbers is found by integrating which is equivalent to applying the inverse Fourier cosine transform F_c^{-1}

$$\begin{aligned} I(x) &\equiv \int_0^\infty I_k(x) dk = \frac{1}{2} \int_0^\infty [1 + \cos(kx)] \langle T(k) \rangle J(k) dk \\ &= \frac{1}{2} \int_0^\infty \langle T(k) \rangle J(k) dk + \frac{1}{2} \int_0^\infty \cos(kx) \langle T(k) \rangle J(k) dk \\ &= \frac{1}{2} I(0) + \frac{1}{2} \int_0^\infty \cos(kx) \langle T(k) \rangle J(k) dk \end{aligned}$$

$$= \frac{1}{2}I(0) + \frac{1}{2}\mathcal{F}_c^{-1}[\langle T(k) \rangle J(k)]. \quad (3)$$

The FT-IR spectrometer generates the infrared spectrum of a given sample by calculating the ratio of the signal obtained by scanning air (empty beam) to the signal obtained by scanning the sample gas.

This process is schematically illustrated in figures 20-21, for the FTIR analysis of styrene, (taken from the Columbia University web site (www.columbia.edu/ccnmtl/draft/dbeeb/chem-udl/spectrometer.html)).

First an interferogram of the source (background) is scanned (figure 20 left), and then transformed into a single beam spectrum (figure 20 right) and stored in computer memory. The sample, (in this case containing styrene), is then sampled by many possible ways, either extractively to a sample cell, in-situ or open-air and the interferogram of the sample gas is scanned (figure 21 left), and then transformed into a single beam spectrum (figure 4 right) and stored in computer memory.

The ratio between the two single-beam spectra, in computer memory, is calculated and the "double beam" presentation with a flattened baseline is produced. The features present in the background spectrum correspond to the emission profile of the source, the optical efficiency, or detectivity of the detector, the absorption of atmospheric water, and gaseous CO₂. The ratio process compensates for these effects and they don't appear in the spectrum of the sample as shown in figure 22.

By comparing the resulting IR spectrum of styrene to stored calibration spectra of styrene the concentration of styrene in this sample can be ascertained. It is important to note that calibration spectra are temperature and pressure dependent and accurate IR measurements require stored calibration spectra at the temperature and pressure of the sample gas.

CE-CERT/UCR FTIR

Figure 23 is a picture showing the CE-CERT/UCR FTIR purchased from IMACC in April 2001. This FTIR has been used primarily for the measurement of on road exhaust gases in determining emissions from ULEV (ultra low emitting vehicles) and is now available for this project.

We have also subcontracted IMACC to provide us with an additional FTIR system to conduct open path FTIR measurements in as follow-on to this project. The specifications for the CE-CERT/UCR FTIR are found on table 7.

The CE-CERT FTIR can display data or spectra during real time acquisition or after the fact. The FTIR is configured to open and automatically run a specified script when it is started. The monitor allows for custom windows to be created so that we can graphically display spectra or interferograms, as well as plotted data and tabular lists of diagnostics or gas concentrations. The layout for the monitor is also saved so multiple display layouts can be set up and simply opened to configure the screen for a particular application.

A typical FTIR display is shown in Figure 24. Here the top most window has buttons for loading, starting, and stopping the script. The next window has two panes. The one on the left displays gas concentration data along with the analysis (2 σ) errors.

The window on the right has selected diagnostic parameters displayed. In this case these are the current system status, the percent complete for the current averaging interval, the number of scans complete, the number of “batches” or averaging intervals of data produced, the number of good scans in the last averaging interval, the number of bad scans in this interval (if any), the averaged pressure and temperature for the last completed measurement interval, and the peak interferograms voltages.

The lower window was set up as a tab window with two tabs. One tab brings up plots of the gas concentrations and the tab selected here shows spectra.

In this case the single beam and absorbance spectra are displayed. In all windows, a right mouse click brings up configuration menus that allow the user to select the type of plot/tabulation displayed and the parameters or data to be shown. Once the monitor is set up as desired and linked to a script, all that is required to start data acquisition, processing, and display is to start the monitor.

FTIR Suitability for N_2O Measurements

IR spectra for N_2O was generated using certified calibration gas of 25 ppmV (which is approximately 75 times that found in ambient air) and measured in an 8-meter White cell that was heated at 20 C with pressure controlled at 740 torr.

The IR spectra for N₂O can be found on figure 25 and shows that there are two distinctly identifying regions for N₂O. The first occurs around the 2150-2250 cm⁻¹ region, with peak N₂O absorbance occurring at approximately 2240 cm⁻¹. This region has been used as the defined characteristic absorption region for past FTIR N₂O measurements. The second occurs around the 1250-1300 cm⁻¹, with peak N₂O absorbance occurring at approximately 1290 cm⁻¹. Detection limits were determined by using the generated calibration spectra at 25 ppmV and measuring the response of the FTIR to zero gas for the stronger responding 2150-2250 cm⁻¹ region. The minimum detection limit (MDL) at two times the standard deviation (2σ) of zero air response with five-second averaging was found to be 0.021 ppmV or 21 ppbV. Since background levels are approximately 315 ppbV, the FTIR with the 8-meter White Cell has a MDL that is 16 times more sensitive than background levels and is therefore highly suitable for these measurements.

Since the MDL is approximately 21 ppbV at five second integration, we expect that with thirty second integration, which we used, we will have sufficient resolution to detect changes of better than 10 ppbV from background as the technique has better sensitivity with longer intergration times.

Experimental Preparation and Method Development

FTIR Preparation

An IMACC FTIR was readied for use in ambient measurements of N₂O. The FTIR is based on a Nicolet intereferometer, the unit has been encased in a Nema 4 enclosure and structurally designed for field use by the manufacturer IMACC. The FTIR was removed from its previous sampling system. A sampling pump, sampling lines, and purge lines were installed. The FTIR was moved and set up in the Atmospheric Processes Laboratory. Operating parameters for the IMACC FTIR appropriate for identification of N₂O in non-dried ambient samples were chosen and set up. The parameters for the interferometer and gas cell are listed in tables 8 and 9.

A quantification method file and standard spectra files appropriate for identification and quantification of N₂O in ambient samples were configured in the methods system. The species selected are listed in Table 10 as are the standards of the stored spectrum in the method. For example the stored spectrum for CO was done with a calibration gas of 10.5 ppmV at 25 C at a path of 8.3 meters (our test cells pathlength). These stored spectra, at known pressures, temperatures and concentrations, are used to determine the

concentrations of the measured spectra when a classical least square fit is applied to the measured spectra with the stored calibration spectra. The wavelengths of analysis for the species measured are listed below in Table 11, these represent the frequencies of interest for the entire method, which incorporates the 7 subject species. Table 12 lists the subject species and whether the other gases measured and included in the method development are an interferent to the subject species.

Spectra of dry zero nitrogen were collected for use as background spectra. Spectra of nitrogen, ambient air, and an N₂O gas standard (100 ppmV N₂O, balance N₂) were collected in order to evaluate noise levels and response to N₂O.

Figure 26 shows the single beam power spectrum for zero nitrogen. The small power absorption that occurs near 2350 cm⁻¹ is due to residual CO₂ in the sample path. The numerous lines centered around 1500 cm⁻¹ are due to residual water in the sample path. This single beam spectrum is used as a background spectrum. The transmittance spectrum for a sample is calculated by dividing the single beam spectrum of a sample by the single beam spectrum of the background.

Figure 27 shows a transmittance spectrum for ambient air. In regions of the spectrum where the sample absorbs little power, the transmittance is near 100%. In regions near 2350 cm⁻¹ and 1500 cm⁻¹ nearly all of the power is absorbed by CO₂ gas and H₂O gas respectively, and the transmittance is nearly zero.

Absorbance is calculated as the negative logarithm of transmittance

$$\text{abs} = -\log(I_{\text{sample}}/I_{\text{background}}) \quad (4)$$

where I_{sample} and $I_{\text{background}}$ are the single beam spectra of the sample and background respectively. Figure 28 shows the absorbance spectrum of the ambient sample.

Figure 29 shows the absorbance spectrum of 100 ppmV N₂O in nitrogen, using our cylinder calibrated gas standard. When this method is applied to laboratory indoor ambient air, the method reports concentrations ranging from 0.250 to 0.320 ppm, with uncertainty on the order of +/- 0.030 ppmV.

Sampling System Preparation

The sampling configuration was designed and has been constructed to have 7 inputs and 1 outlet. Figure 13 shows the sampling layout for the instrument configuration. All valves are Teflon with 3/8 inch orifices. The inlets are for the following:

- 1) 1-meter elevation on tower
- 2) 2-meter elevation on tower
- 3) 5-meter elevation on tower
- 4) 10-meter elevation on tower
- 5) Trailer Interior
- 6) Spare
- 7) spare

The single outlet is to the FTIR.

We set longer integration times at each elevation, basically three minutes, so that we can give a complete measurement cycle once every 15 minutes which includes cell purge times. The longer integration times will improve the sensitivity for the N₂O measurement.

Also that all lines from the FTIR sampling system to the individual measuring points were made to be the same length and same volume to reduce anomalies or artifacts from sampling. Also note that the sampling system has been made automatic with computer control. The valve system was programmed using a Campbell data logger, which recorded the sequence of sampling and set each sampling interval at each height for a period of three minutes. This allowed time to completely purge the sampling cell of the previous sample. This system was designed and operated to collect the following:

- H₂O Concentration
- CO₂ Concentration
- CO Concentration
- N₂O Concentration
- CH₄ Concentration
- NH₃ Concentration
- Hydrocarbon Concentration

Field Measurements and Results

Sampling Site

The FTIR was set up on the campus dairy at California State University Fresno (CSUF) at the south end of the dairy dry lot. The dairy is located north and west of the intersection of E Barstow Ave and North Chestnut Ave in Fresno. Figure 31 is an aerial image of the dairy, and the red block is the general location of the sampling site. The actual sample collection point is north of the red block visible in the figure, and is located about two meters south of the fence bordering the southernmost lot. The sampling points were on a ten-meter tower to collect gas samples and meteorological data from various elevations. CSUF provided the site, a trailer, and the tower.

CE-CERT collected gas samples at heights of one, two, five, and ten meters. CSUF collected wind speed and wind direction at heights of one, two, and ten meters, and collected temperature and relative humidity at a height of two meters. The support trailer was located as far south of the tower as possible to minimize its effect on northerly winds. Distance from the trailer to the tower was a few meters. Figures 32-35 illustrate the equipment setup and general characteristics of the dairy.

Sample Transport and Sequencing

Inside the trailer, CE-CERT set up a Fourier Transform Infra-Red (FTIR) Spectrometer to measure N₂O. The FTIR sampled through a bank of five valves that switched sequentially through a sequence of five sample valves. Each of the four sample lines leading to the collection points on the tower were the same length: 100 feet. The fifth line was very short and sampled from inside the trailer. This fifth sample line is available for testing bag samples or cal gases without disrupting normal sampling. The lines to the elevated sampling points on the tower were sampled in this order: 1 m, 2 m, 5 m, 10 m, indoor. The sample flow switched from one elevation to the next every three minutes. A complete sampling cycle took 15 minutes. Sample flow rate was nominally 7 liter per minute (lpm), so that transit time through the 100 foot sample line was about 9 seconds. The air sampling information is summarized in Table 13.

Field Setup of FTIR

The FTIR was set up to measure sub-ppm levels of nitrous oxide (N₂O) with a resolution of roughly 10 ppb.. Details of the FTIR operating parameters are shown in table 14.

These parameters also allow measurement of CH₄, NH₃, CO, and CO₂ at the same time. The calibration method used to quantify the spectra is based on spectral measurements made at temperatures and pressures slightly different than the temperature and pressure used to collect samples in this study.

Factors to correct for temperature and pressure were developed with the assistance of the instrument manufacturer and incorporated in the final data set.

The FTIR measures light absorption in a continuously flowing gas cell having a path length of 8.28 meters and a cell volume of 2.0 liters. Twenty spectral scans are collected and averaged for each sample, which leads to a sample collection time of slightly less than 30 seconds.

The valve system collects at each sample height for 3 minutes, therefore six samples will be measured by FTIR at each height. The first point and the sixth point at each height are discarded because the sample switching period and the FTIR sampling periods are not exactly synchronized, and therefore the first or sixth points can include a sample line transition. Points two and three are discarded to allow sample transit time and cell flushing time. Points four and five are retained as samples.

Figure 36 shows the inside of the CSUF trailer where the FTIR was installed. Note that the computer controlled sampling system was located in the trailer as well.

Sampling Schedule

The trailer, tower, meteorological sensors, and FTIR were set up on October 19, 2007. Trial sample runs of various durations were made beginning at that time. On October 20, the system was set up to run essentially continuously 24 hours per day until December 12th, a period of nearly two months. As can be expected a large database was achieved. CE-CERT provided oversight through October 26. During this time sampling was periodically interrupted to verify sample flow switching and to download data. Since October 26, the FTIR has been kept operating by CSUF staff. The FTIR requires filling with liquid nitrogen twice each day, and CSUF staff were trained in the procedures for that task. CE-CERT visited the site approximately weekly to verify operation and to download data.

A second location was chosen for February 8 and 9 to look at compost emissions.

Results

Preliminary results are shown on Figures 37-39. Figure 37 shows an example of CO₂ data and sample line marker. The blue points are CO₂, the pink points are valve position marker. The points were collected every 30 seconds, the valves switched every three minutes. Valve 0 controls the sample line inside the trailer. This valve has a more restrictive orifice than the other valves, which causes the pressure

in the sample cell to be much lower than when sampling the tower lines. The reduced cell pressure during valve 0 sampling means that the mass of CO₂ in the cell for a given ppm is lower than the mass of CO₂ for the same ppm in the cell at normal pressure. Thus, the FTIR signal is lower.

This is useful to keep for the entire data set as we could flag when the data was measured in the trailer and time synchronize the valve switching measurements with the FTIR as the FTIR was not exactly 30 seconds but was approximately 29.7 seconds. This alleviated any mix up in combining the data sets.

Because the data have not yet been corrected for pressure and temperature, the reduced signal is apparent in the figure. The yellow points in the figure are the fifth data point collected during each three minute sample collection period.

The figure demonstrates the correct alignment of FTIR sample selection with valve position.

Figure 38 shows the same type of plot except for N₂O. The N₂O shows the same reduction in signal as the CO₂ for the same reason during valve 0. Both figures show very little variation in CO₂ or N₂O concentration among the other sampling heights. Figure 39 show the N₂O data over the next couple of hours. The N₂O sampled at one meter and two meters is measurably higher than the N₂O measured at five meters and ten meters.

In particular examine the sample periods beginning at 18:45, 19:30, and 19:45. This is representative of a gradient from an area source, although we are only measuring over a small area, with an open path FTIR we would be able to make measurements over the whole area source monitored.

Dry Lot Measured Results

Since the data was taken continuously for such a long period of time (almost two months) to combine the data set into a way that could be analyzed, a program was written using LabView to extract the data for each of the species, with respect to the height sampled. The data analysis software was written to extract the data per elevation at the 4th point at each elevation as described earlier. The amount of data and the synch deviation from the FTIR to the valve control system required that the Labview program be written to extract the pertinent data point at each level and then search for the next synch point Figure 40 shows the method to assign each data point specific for each elevation. The data set was then assembled with corresponding meteorological data.

The project requirement was to estimate N₂O flux using the gradient flux method, suitable periods over the data set were chosen to do this. Improvements to the N₂O flux measurements can be made by using an open path FTIR measurement over the area source. This open path work was not funded but may be consideration for future funding, as UCR will be capable of doing open path measurements by summer 2008.

Appendix A contains plots of all the field data taken during the 2007 field measurement program. The data are presented in eight 7-day periods. These 7-day time periods are provided in Table 15. For each series, ten data plots are presented (content of the 10 plot series is listed in Table 16).

Therefore there are 80 plots in Appendix A. This data set is extremely large and would require detailed analysis far beyond the scope of this project to try to estimate fluxes for all the individual species and for all the times measured. Hence, here we report N₂O flux measurements, representative periods of the data set, the concentrations of the other species only are presented here for completeness. These representative periods were selected using a program that matched the criteria of consistent wind speed and direction, clear discreet gradient to the surface as would be expected from a ground source.

Figure 41 depicts a typical representative spatial N₂O distribution. Note that N₂O levels near the surface are in the 365 to 385 ppbV range and that levels at 10 meters are around 340 ppbV, this is fairly consistent with most of the data set when winds were relatively constant in direction. Typically the levels of N₂O measured were above nominal ambient measurements of 315 to 320 ppbV from the dry lot, showing a gradient to the 10 meter level. Detection limits were calculated in the lab to around 10 ppbV with the methodology developed for this project and the sampling time used. Note error levels were also usually in the plus or minus 10 ppbV range at two times the standard deviation of the signal noise over the sampling interval.

The long term testing was to meet the requirement of trying to measure the dry lot concentrations of N₂O after a rain event. Such an event happened on December 7th. During the evening prior to the data reported here (Figure 42) 0.2 inches of rain precipitated. Note that N₂O levels near the surface are in the 360 to 460 ppbV range and that levels at 10 meters are around 350-380 ppbV, this is fairly consistent with most of the data set when winds were relatively constant in direction during a rain event. These levels are somewhat elevated when compared to normal dry lot conditions, by an average of 40-80 ppbV near the surface and 20 ppbV at 10 meters. However there were very few rain events during the period of sampling, so we are unable to assess if the observed changes in N₂O concentration are consistent with changes in soil moisture or if the observed increases was due to other factors.

Typical wind conditions were used to try and evaluate the N₂O flux via the flux gradient method. Refer to Figures 43 and 44 which show the spatial distribution of N₂O during a period of ideal wind direction and relatively low wind speeds which facilitate an estimate of the flux.

Concentrations ranged from a high of 400 ppbV at the lower levels to a low of 365 at the highest elevation. This strong gradient observed under ideal conditions was used to estimate the flux of N₂O via the gradient method for this period of sampling. For this 30 minute period N₂O flux was calculated from a high of 37 ng/sec m² to a low of 13 ng/sec m² (equivalent to an annual emission of 4.1 to 11.7 kg N₂O /ha). Typical values over this study averaged around 25-30 ng/sec m² (annual rates of 7.5 to 9.5 kg N₂O /ha) during similar conditions.

Measurement Height During a Period with Nominal Wind Conditions (November 7th, 2007)

Compost Pile Results

Figures 45 and 46, show the setup of the sampling/meteorological tower over the compost site. Note that the winds were very weak and predominantly from the southwest blowing over the compost site. Note also that the equipment trailer is to the left (east) of the tower. Significantly, the compost pile was disturbed around 8:45 am, on the 9th of February. Figure 46 shows that the compost piles had been pushed into larger piles by a backhoe.

Average concentrations measured over the compost pile were slightly higher than average concentrations measured over the feed lot, but what was really significant was that concentrations of N₂O and CH₄ went significantly higher once the compost pile was disturbed. The observed average N₂O concentrations were almost 5 times higher on average to those when the compost pile was left undisturbed. Figure 47 shows the data from just prior to the disturbance of the compost pile till just after. Further study into this and to the extent that compost piles are disturbed may lead to higher than expected N₂O emissions from such practices. Also during this period there was a significant increase in CH₄ around 30% from disturbing the compost pile.

Conclusions

An FTIR method was developed to measure concurrently N₂O, CO₂, CO, N₂O, CH₄, NH₃, Hydrocarbon Concentrations. The data were used to make approximate estimations of N₂O flux using the flux gradient method. Typical values over this study averaged around 25-30 ng/sec m² during ideal meteorological conditions. This emission rate is equivalent to an annual emission of 7.9 to 9.5 kg N₂O/ha. Ambient N₂O concentrations were observed to be elevated just after a rain event, typically by around 10%. Ambient N₂O concentrations were observed to be slightly higher above a compost pile than the dry lot. Concentration increased dramatically after the compost pile was disturbed.

Ideally a longer term continuous monitoring of N₂O in an open path format would be able to better define annual variability, lead to less variable calculations in the emission rates and factors, and would improve the utility of the data for validating process models.

Simply extractive sampling, as was done in this project can only yield initial considerations of the N₂O flux but more measurements considering the size of the source, and variability over the area source would lead to better understanding of the spatial and temporal variability of N₂O emission from dry lots.

We would like to thank Dr. Charles Krauter of CSUF for the use of his meteorological tower, site selection and his staff for keeping the IR detector filled with LN₂ during the study. We would also like to thank John Bergmans of Bergmans Mechatronics for software development to match the FTIR data with the time sequenced channel data.

Figures Project Component 2

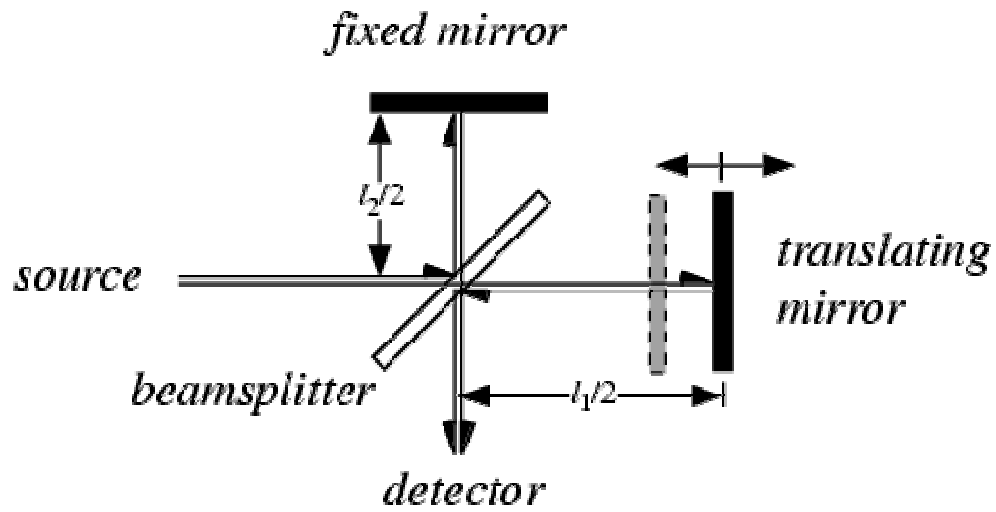


Figure 18: Typical Michelson Interferometer.

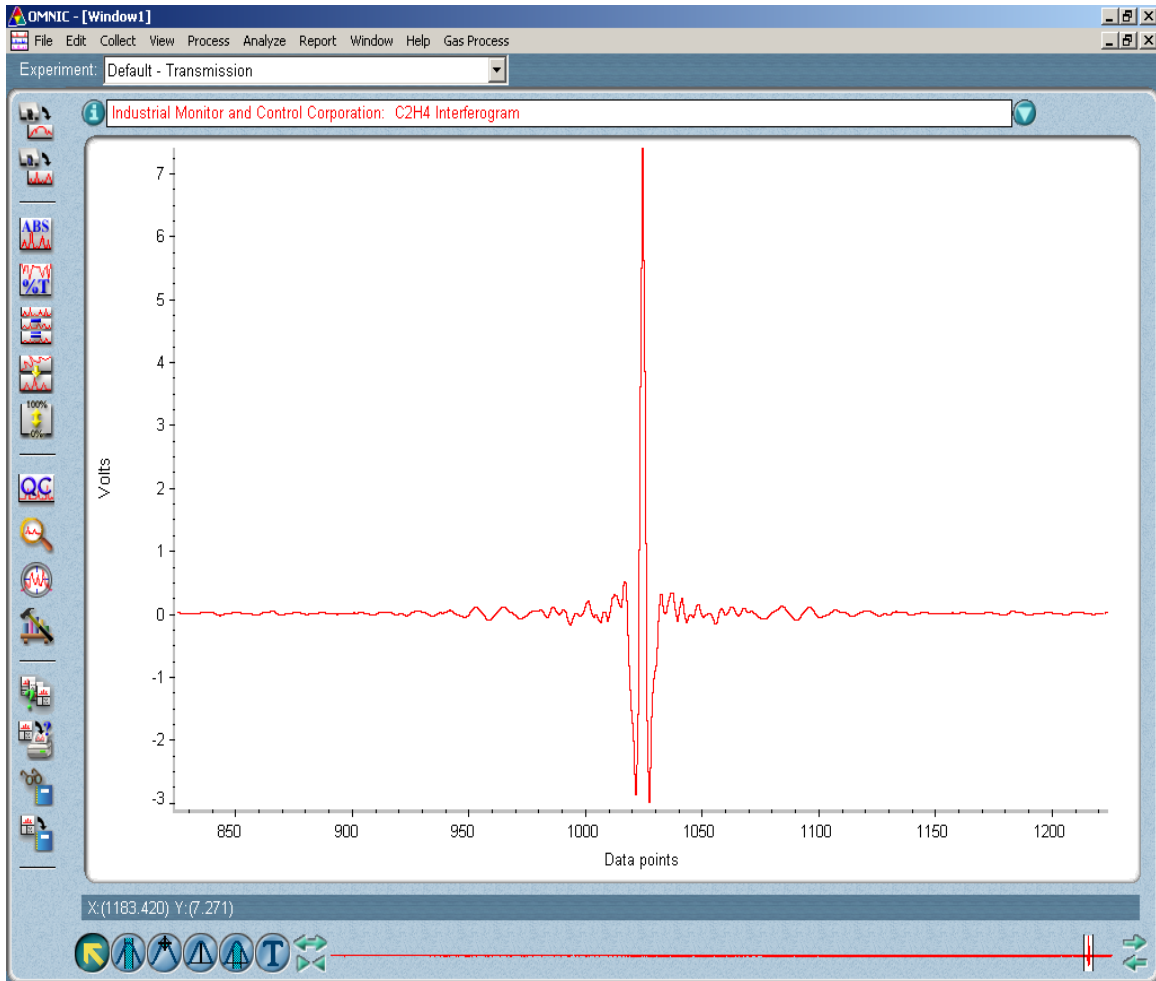


Figure 19: Typical Interferogram, In This Example Ambient Air Containing High Level of C₂H₄

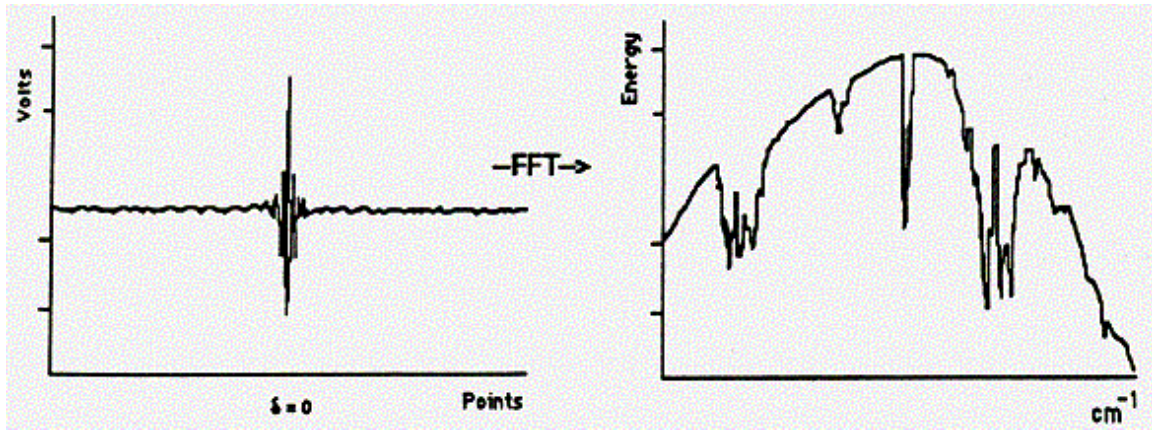


Figure 20: Interferogram Of The Source Background (Left), And Resulting Transformed Single Beam Spectrum (Right)

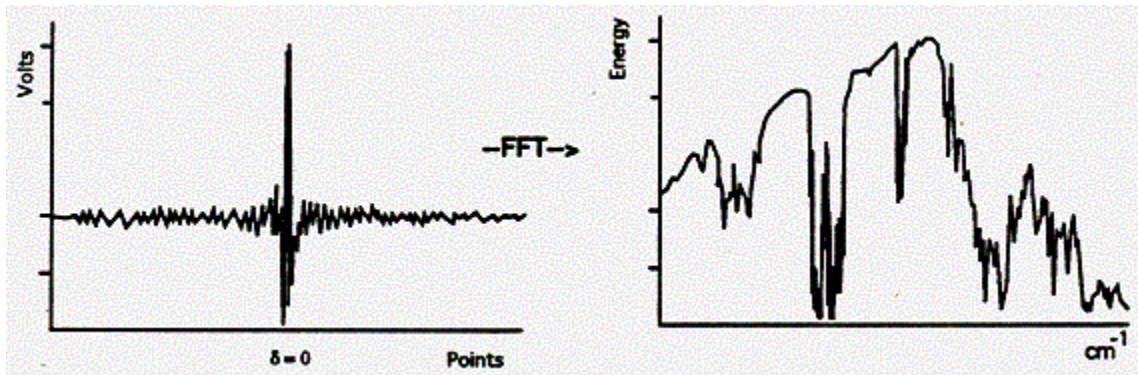


Figure 21: Interferogram Of The Gas Sample Containing Styrene (Left), And Resulting Transformed Single Beam Spectrum (Right)

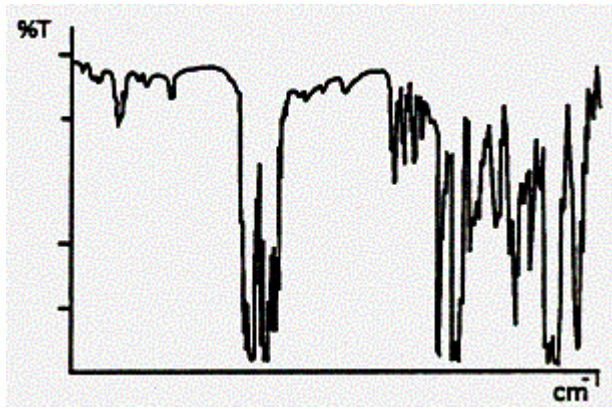


Figure 22: Resulting IR Spectrum of Styrene



Figure 23: The CE-CERT/UCR FTIR (left) purchased from IMACC and the 8.3 meter cell (right)

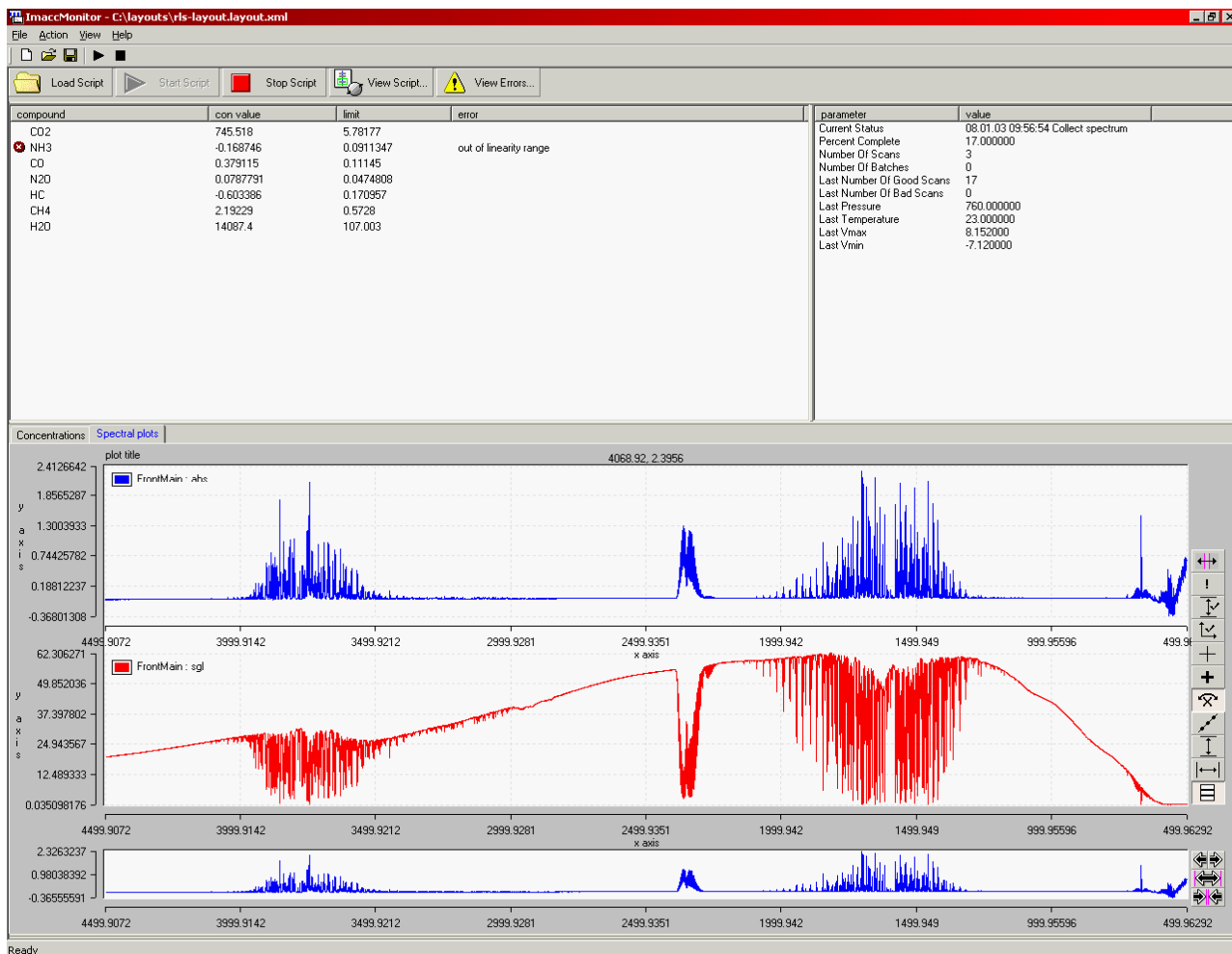


Figure 24: A typical FTIR display from the UCR/CE-CERT FTIR

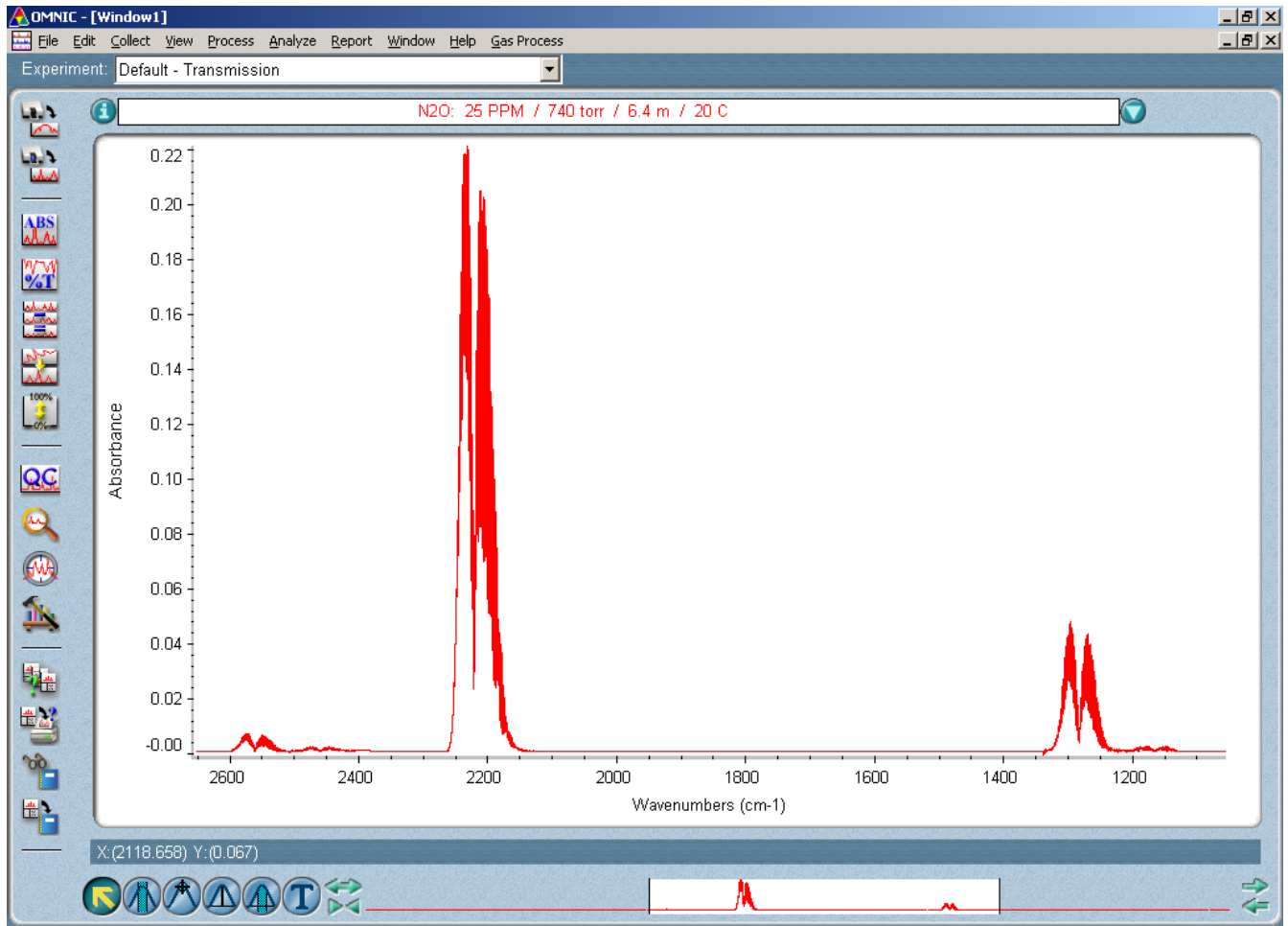


Figure 25: Plot of N₂O Spectra using 25 ppmV certified calibration gas into a 8.3-meter White Cell that was controlled at 10 C and 740 torr.

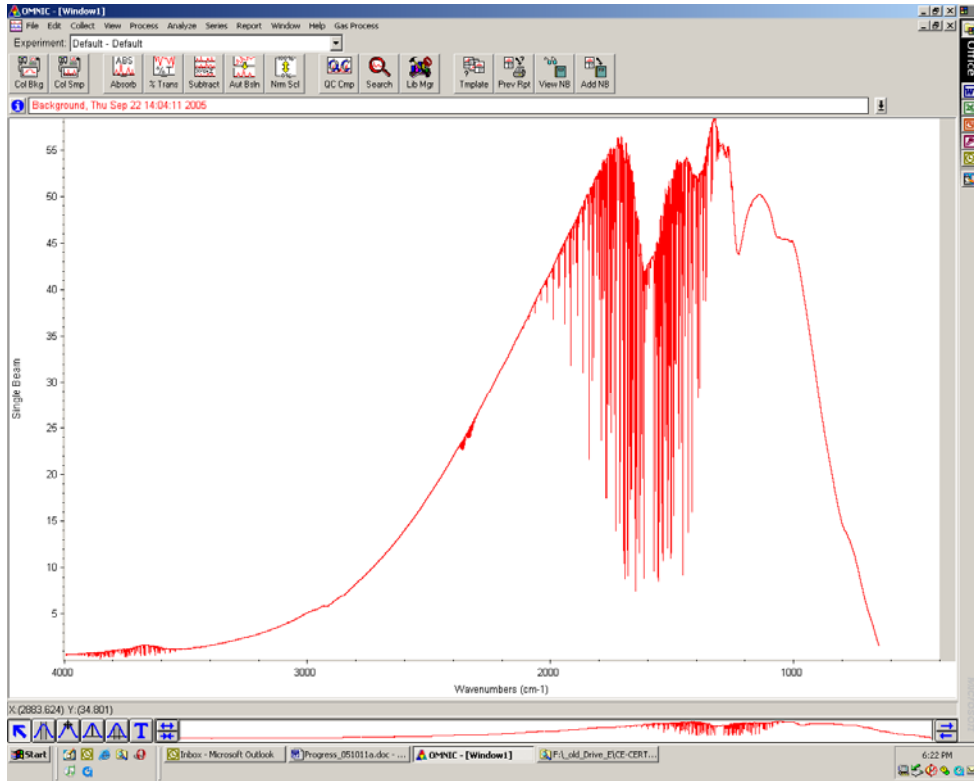


Figure 26: Single Beam Spectrum of Nitrogen

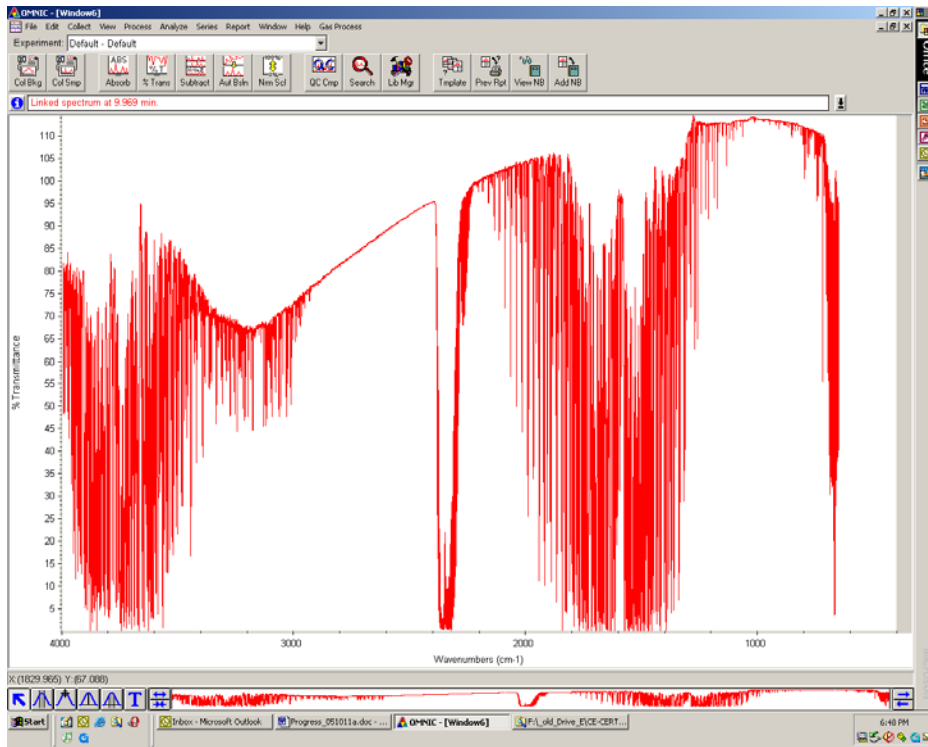


Figure 27: Transmittance Spectrum of Ambient Air

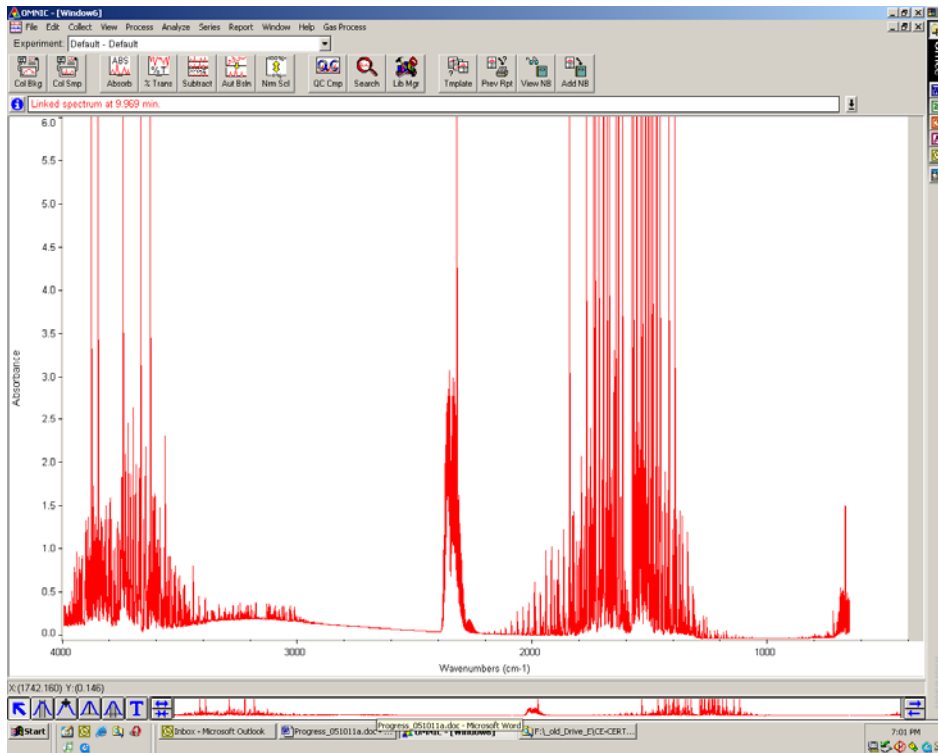


Figure 28: Absorbance Spectrum of Ambient Air

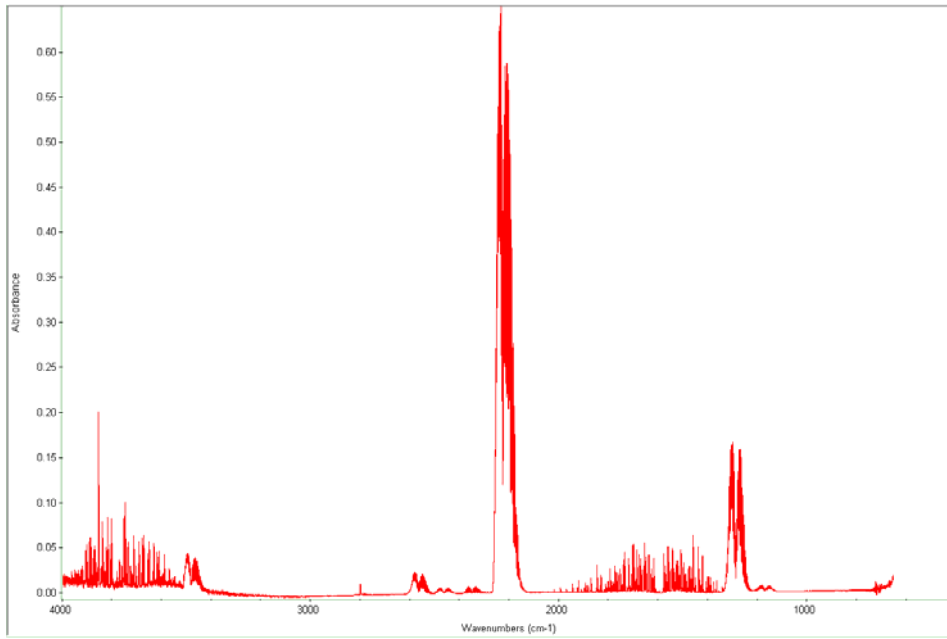


Figure 29: Absorbance Spectrum of Nitrous Oxide (100 ppm) in Nitrogen

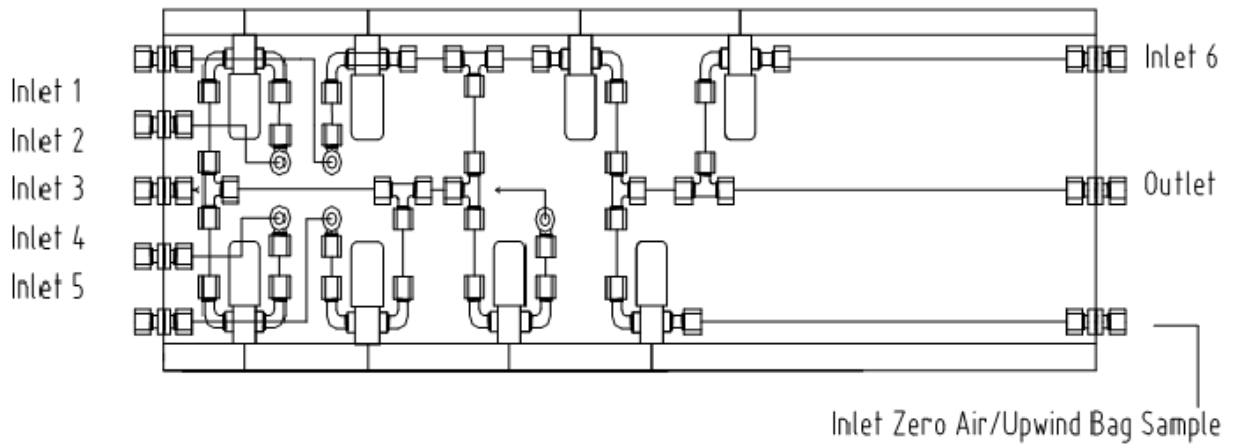


Figure 30: Physical layout of the Constructed Sampling System for the N₂O



Figure 31: Aerial view of dairy and sampling site location

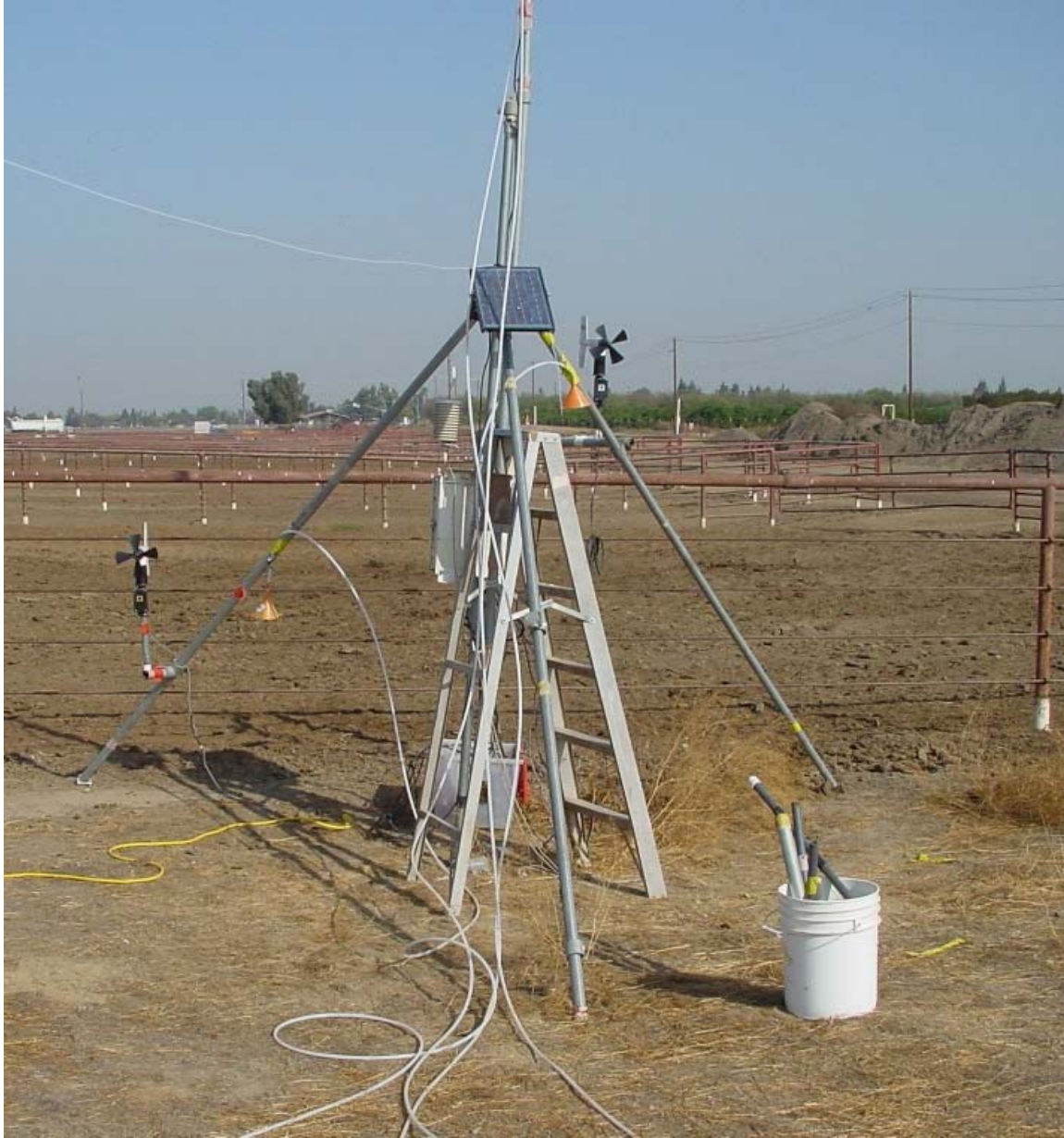


Figure 32: **Sample collection tower.** It shows wind sensors at one and two meters, the temperature/RH sensor at two meters, and gas sampling points at one and two meters. The figure also shows the proximity to the dry lot.



Figure 33: View of site, photo taken from the southeast. It shows the relationship of the tower to the trailer, and the five meter gas sampling point can also be seen.



Figure 34: Dry lot surface (and nearby cows) indicating the proximity of cows to the sampling points from time to time.



View from tower to North



View from tower to East



View from tower to South



View from tower to West

Figure 35: Views from tower to points of compass, looking due north, east, south, and west.



Figure 36: IMACC FTIR Instrument in Instrumentation Trailer (left) with UCR Built Sampling System (right)

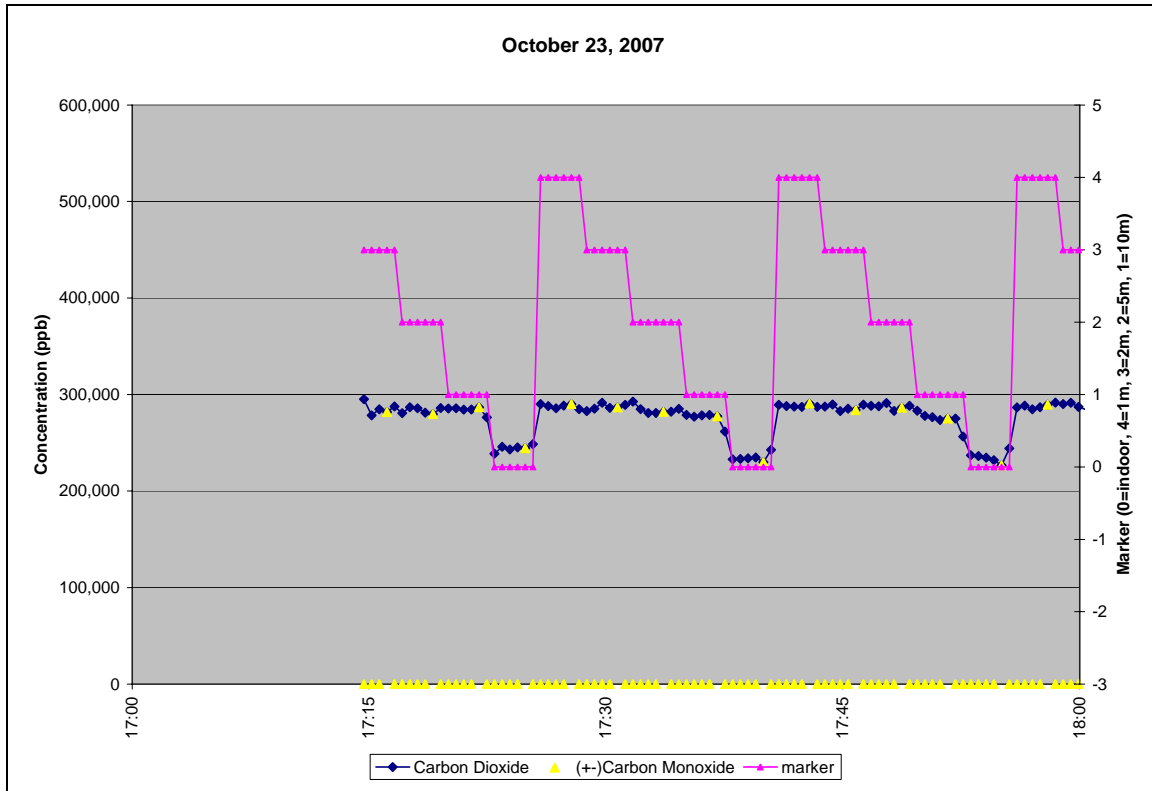


Figure 37: Example of sequential CO2 data and valve marker

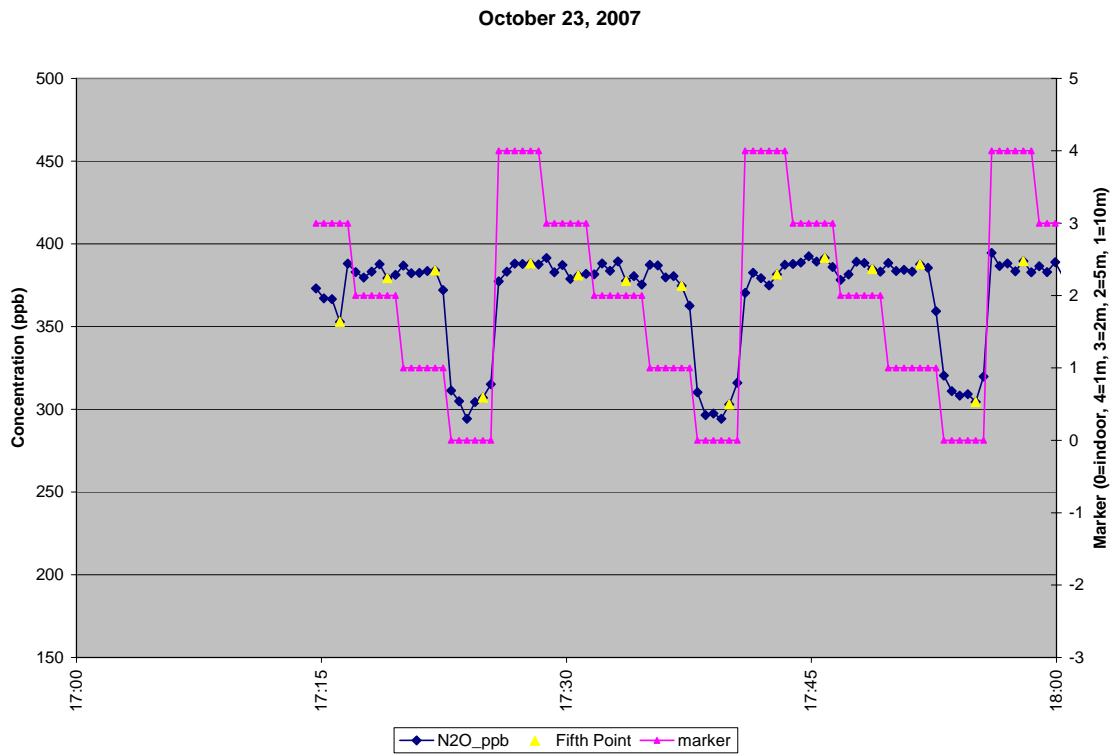


Figure 38: Example of sequential N₂O data and valve marker

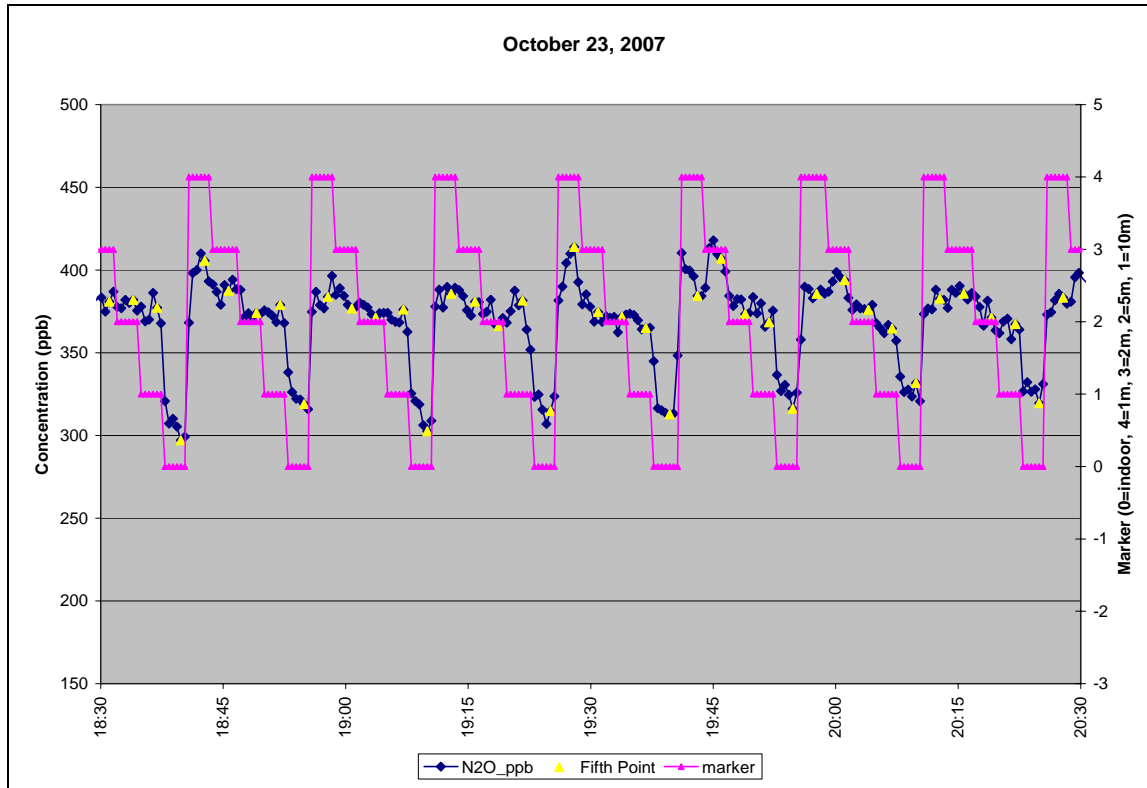


Figure 39: Example N₂O data showing variation with sample height

N₂O Spatial Distribution Assignment Method (Data from 11/6/07)

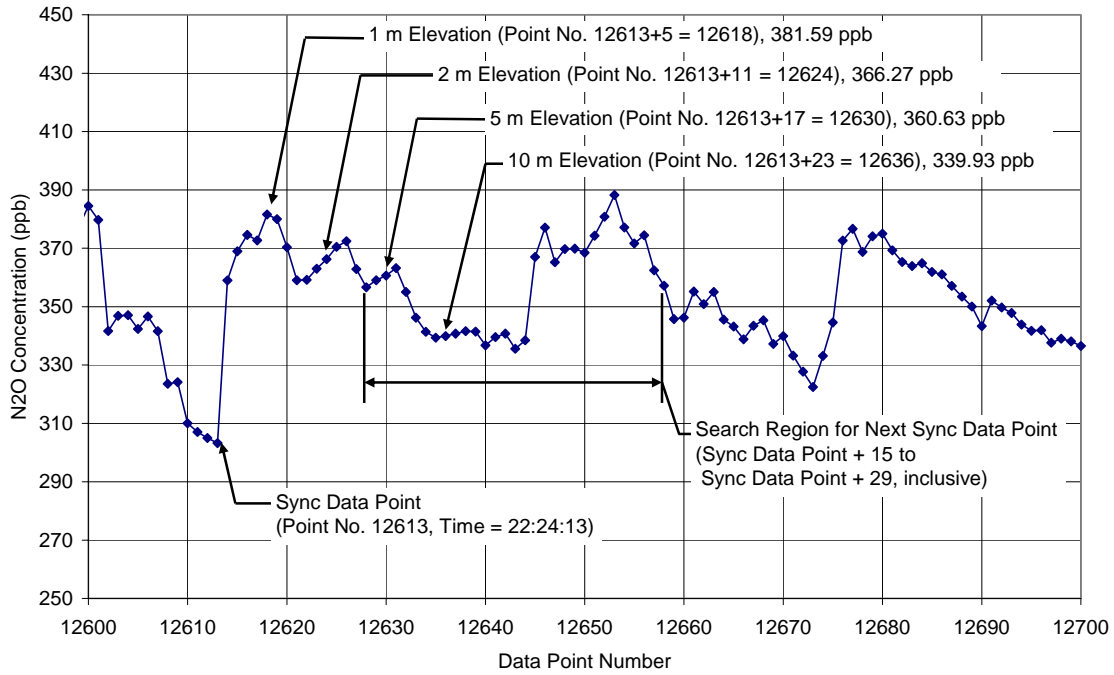


Figure 40: Illustration of Method to Assign N₂O Measurements to Each Measurement Location

Representative Spatial N₂O Distributions

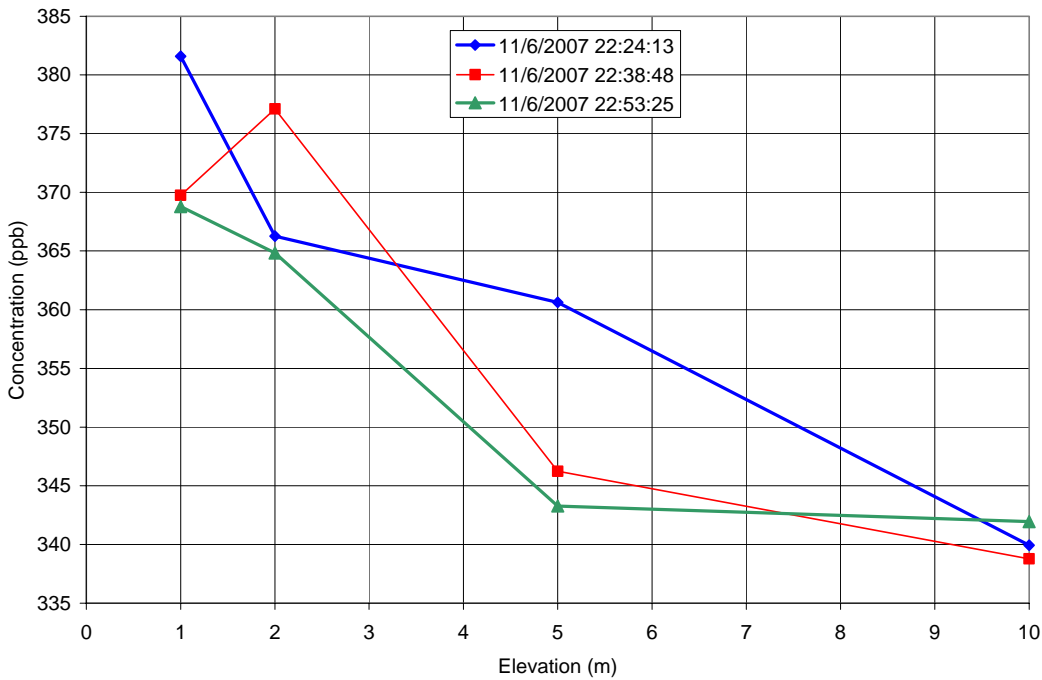


Figure 41: Representative Spatial N₂O Distributions to Each Measurement Height

Spatial N₂O Distribution Following Precipitation

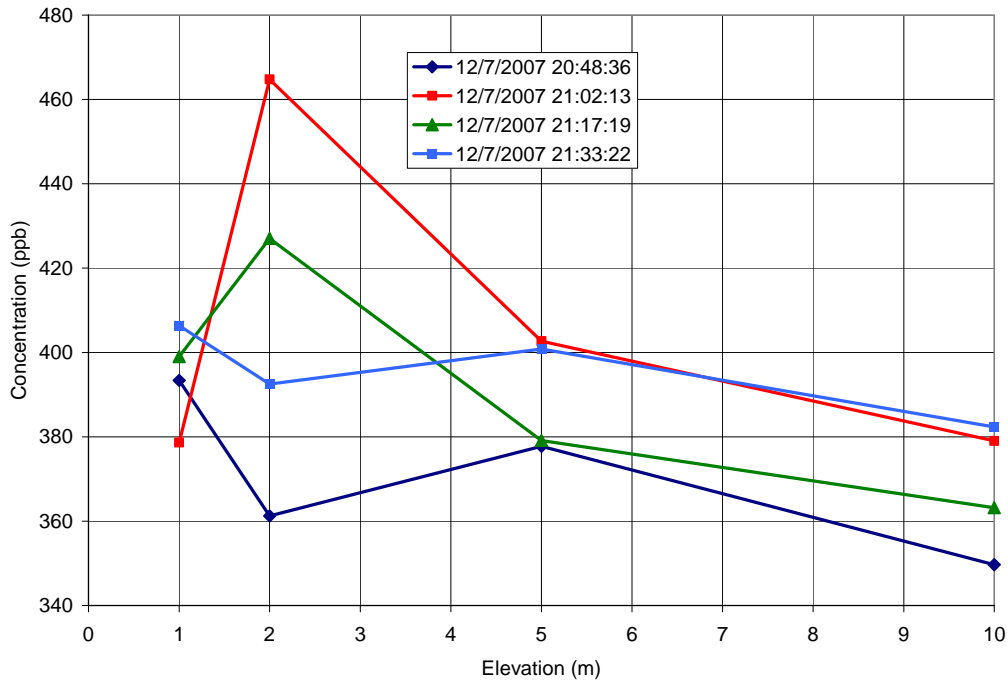


Figure 42: Representative Spatial N₂O Distributions to Each Measurement Height During a Precipitation Event (December 7th, 2007)

N₂O Spatial Distribution

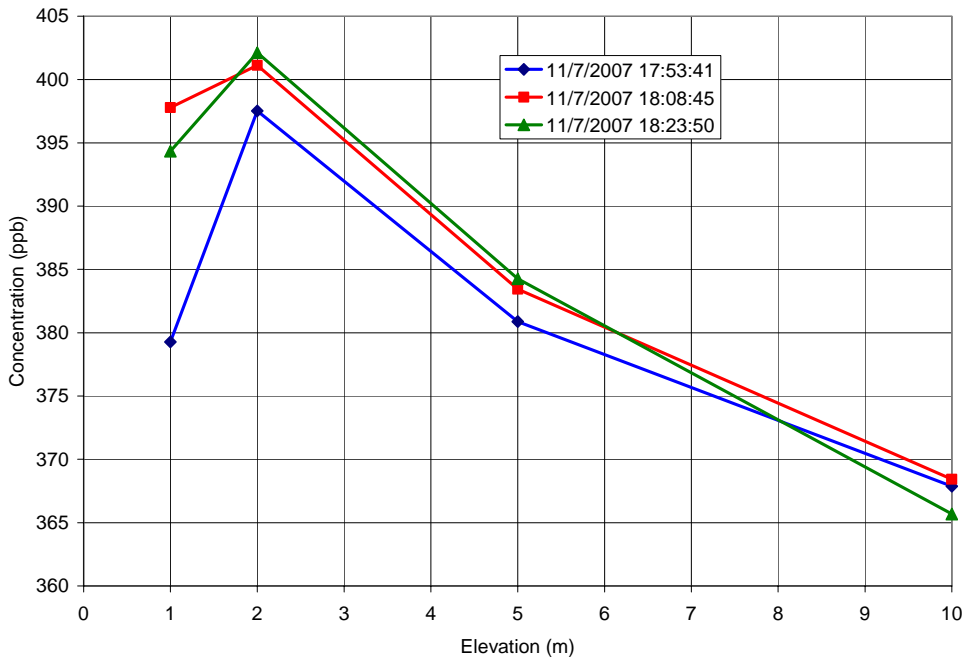


Figure 43: Representative Spatial N₂O Distributions to Each

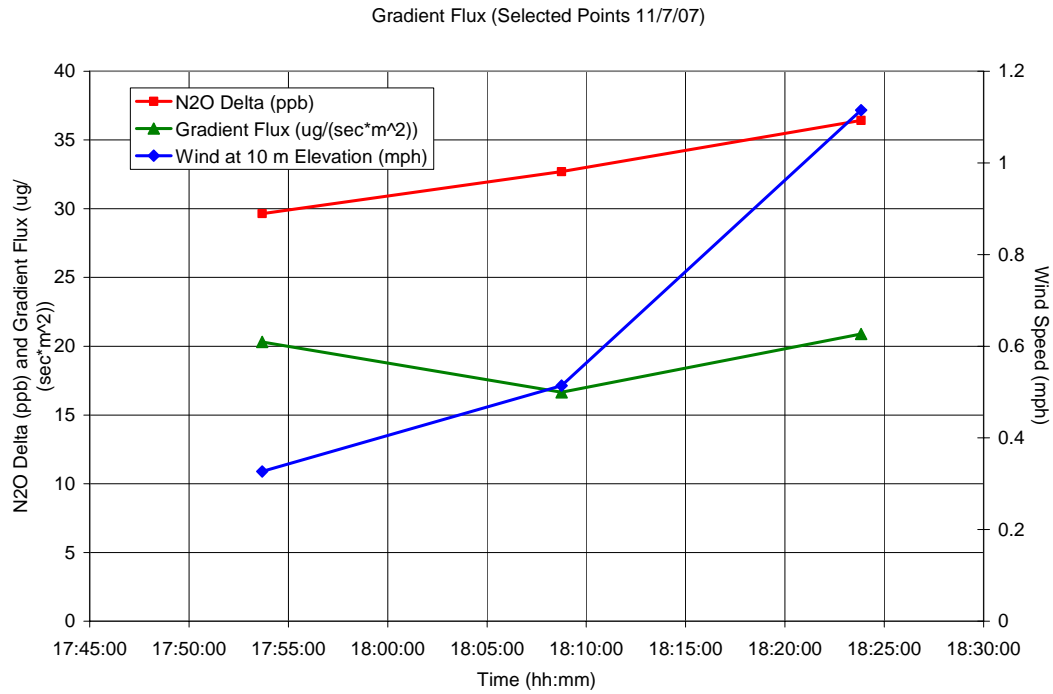


Figure 44: Gradient Flux Calculation for Representative Spatial N₂O Distributions t During a Period with Nominal Wind Conditions (November 7th, 2007)



Figure 45: Instrumentation Trailer (left) with Sensor Tower (2/8/08) over the compost pile



Figure 46: Instrumentation Trailer (left) with Sensor Tower (2/9/08) over the disturbed compost pile, notice backhoe in rear of figure

Compost - All Data Points (Feb 9 2008)

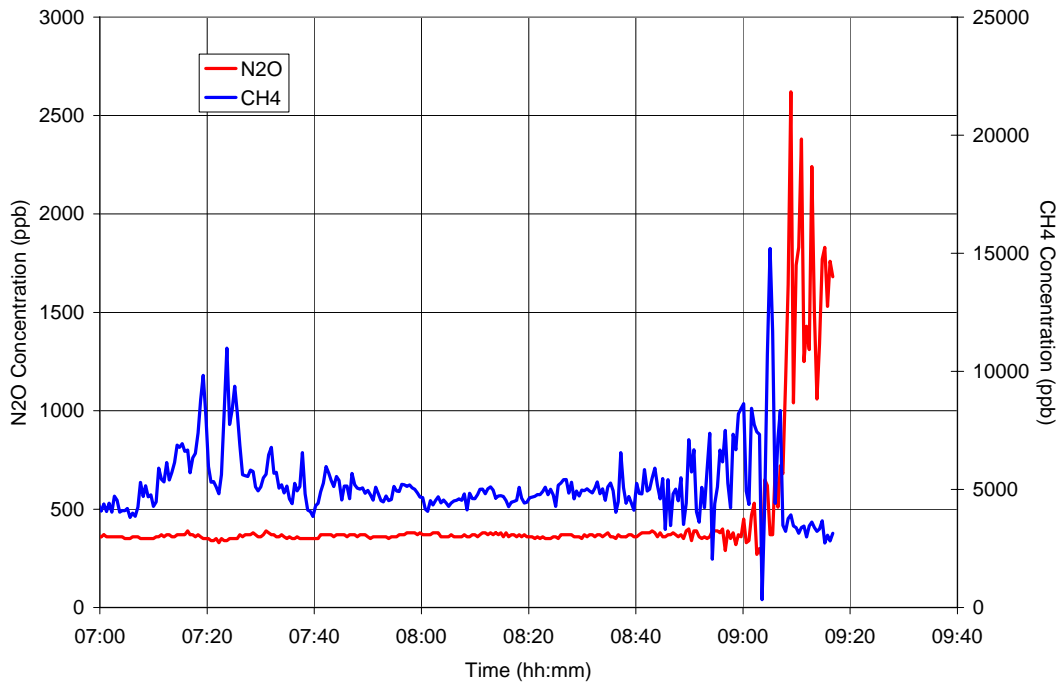


Figure 47: Response of N₂O and CH₄ Concentrations to Compost Disruption

Tables for Component 2

Table 7: UCR/CE-CERT FTIR Specifications

Supplier:	IMACC FTIR
Model:	B-ZME20-C
S/N:	B001001D
Date purchased:	April, 2001
Resolution:	0.5 cm ⁻¹
Wavenumber:	650 to 4000 cm ⁻¹ (400 to 4000 cm ⁻¹)
Max Scan Rate:	one scan per 1.4 seconds
Cell Accessory	
Model:	E-1000-C
S/N:	E001201D
Date purchased:	April 2001
Volume:	approx 2.0 liters
Path:	8.28 meter
Software:Nicolet	OMNIC E.S.P. 5.2a
Quantification Method: Classical Least Squares (CLS)	

Table 8: Interferometer parameters

Interferometer:	
Resolution:	0.5 cm ⁻¹
Mirror Velocity:	1.899 cm/sec
Aperture:	10
Gain:	1.0
Zero filling:	None
Apodization:	Happ-Genzel
Sample Spacing:	2 (yields spacing of 0.241 cm ⁻¹)
Spectral Range:	650 to 4000 cm ⁻¹

Table 9: Gas Cell parameters

Gas Cell:	
Temperature:	30 °C
Pressure:	720 torr
Optical Pathlength:	8.3 meters

Table 10: Standards Information

Component		Conc.	Temp.	Press.	Path.
Abbr. Code	File Name	(ppm)	(C)	(Torr)	(m)
H2O	H2O c:\omnic\spectra\ref5\h2oc1s.spa	1.0	23.0	750.0	8.3
CO2	CO2 c:\omnic\spectra\ref5\co2-400.spa	400.0	25.0	760.0	8.3
CO	CO c:\omnic\spectra\ref5\ref5002b.spa	10.5	25.0	735.0	8.3
N2O	N2O c:\omnic\spectra\ref5\ref5006.spa	25.0	20.0	740.0	8.3
CH4	CH4 c:\omnic\spectra\ref5\ref5009.spa	175.0	20.0	740.0	8.3
NH3	NH3 c:\omnic\spectra\ref5\ref5007.spa	543.0	20.0	740.0	8.3
HCONT	HCONT c:\omnic\spectra\ref5\hcont.spa	30.0	25.0	650.0	8.3

Table 11: Analysis Frequency ranges (note all regions are in wavenumbers)

Regions		Windows	
#	Start End	#	Start End
1	723.30 767.00	1	723.30 739.90
		2	746.20 753.50
		3	755.30 767.00
2	780.50 815.40	4	780.50 783.40
		5	786.00 797.00
		6	800.30 815.40
3	926.30 994.90	7	926.30 934.00
		8	960.40 970.70
		9	990.10 994.90

4	2109.90	2177.70	10	2109.90	2112.50
			11	2118.50	2120.50
			12	2153.50	2159.00
			13	2164.00	2170.00
			14	2174.00	2177.70
5	2187.90	2219.90	15	2187.90	2199.30
			16	2201.40	2204.20
			17	2206.10	2211.00
			18	2212.10	2219.90

Table 11 (continued): Analysis Frequency ranges (note all regions are in wavenumbers) continued from previous page

6	2850.00	2972.00	19	2850.00	2892.00
			20	2895.30	2925.30
			21	2939.00	2945.00
			22	2949.60	2952.60
			23	2962.90	2965.00
			24	2970.30	2972.00
7	2860.00	2950.10	25	2860.00	2888.00
			26	2894.20	2898.00
			27	2904.90	2908.10
			28	2914.80	2928.60
			29	2936.40	2938.80
			30	2946.80	2950.10

Table 12: Analysis Frequency ranges (note all regions are in wavenumbers). The components in region are defined as: **S**, where the primary standard is applied to the subject species; **I** where the component

identified is a possible interferent to the subject species and – where the component is not a known interferent to the subject species investigated.

Components in Regions								
H C C N C N H								
2 O O 2 H H C								
O 2 O 4 3 O								
Region							N	
#	Start	End	T					
1	723.30	767.00	I	S	-	-	-	
2	780.50	815.40	S	-	-	-	-	
3	926.30	994.90	I	I	-	-	S	
4	2109.90	2177.70	I	I	S	-	-	
5	2187.90	2219.90	I	I	I	S	-	
6	2850.00	2972.00	I	-	-	-	I	
7	2860.00	2950.10	I	-	-	-	S	

Table 13 Air Sampling Setup Data:

Sample heights:	1 m, 2 m, 5m, 10 m, inside trailer
Sample line length	100 ft, 100 ft, 100 ft, 100 ft, 0 ft
Nominal flow rate	7.1 LPM
Cell flow rate	7.6 LPM
Ambient flow rater	6.7 LPM
Sample line transit	8.6 sec
Cell residence time	16 sec

Table 14 FTIR Setup Data:

Resolution	0.5 cm ⁻¹
Wavenumber range:	650 to 4000 5 cm ⁻¹
Scans per sample:	20
Time per sample	~30 sec
Path length	8.28 m
Sample pressure	~ 660 torr
Sample temperature	35 °C
Sample cell volume	2 liter

Table 15 Sampling Time Periods

1) Week of Oct 26, 2007
2) Week of Nov 2, 2007
3) Week of Nov 9, 2007
4) Week of Nov 16, 2007 (Note data taken 11/22 to 11/24 is included for completeness but not used in any calculations as the FTIR suffered a malfunction)
5) Nov 27-30, 2007
6) Week of Nov 30, 2007
7) Week of Dec 8 2007
8) Feb 8 – 9, 2007

Table 16 Data Plots for each Time Period

1) Meteorological Data 1
2) Meteorological Data 3
3) H2O Concentration
4) CO2 Concentration
5) CO Concentration
6) N2O Concentration
7) CH4 Concentration
8) NH3 Concentration
9) Hydrocarbon Concentration
10) Total N2O Flux at each elevation

Component 3: Development of Manure-DNDC Model

Approach

This section of the report presents our efforts toward building a detailed, process-based biogeochemical model for simulation air emissions from California dairies.

Scientific basis for modeling manure life cycle

From the biogeochemical view, manure is nothing but a complex mainly consisting of organic compounds including lipids, proteins, hydrocarbons, cellulose, semi-cellulose, lignin, and living microorganisms. As soon as the manure is produced from animal excretion, it will undergo a series of biochemical or geochemical reactions, namely decomposition, hydrolysis, ammonium/ammonia equilibrium, ammonia volatilization, nitrification, denitrification and fermentation, no matter the manure is located in the feeding lot, the storage, the treatment facility or the field soil. The rates of these biogeochemical processes occurring with the manure are controlled by two groups of factors, the internal factors consisting of quantity and quality of the manure and the external factors including temperature, moisture, pH, Eh and relevant substrate concentrations in the environment. The mission of modeling is to (1) determine the manure quantity/quality, (2) track variation of the environmental factors and (3) predict rates of the biogeochemical processes based on the modeled internal and external factors for each of the farm components, which usually include feeding lots, storages, treatment facilities and the field receiving the manure applications. As intermediate or byproducts of the biogeochemical processes, NH₃, N₂O, NO, CH₄, CO₂ and nitrate fluxes will be quantified during the process modeling.

The quantity and quality of manure are determined by the animal type, population, and feed material (e.g., rate and nutrients content). For example, under current feeding practices in the US, 20-30% of the crude protein (CP) fed to dairy cows is secreted in milk, and the rest nitrogen (N) goes to feces and urine about equally. The fecal N exists in two pools: endogenous N and undigested feed N. Any change in the feed rate or CP content will alter the manure production as well composition. The amount of manure produced by an animal can be calculated based on the energy balance between the total intake and the milk and meat production. The quality of manure can be defined by its C/N ratio. The N content in urine and feces is calculated based on total N intake, which is related to total protein intake, and the N secreted in milk and meat. The feed rates and CP contents can be adopted from the standards regulated for different animals (e.g., lactating cow, dry cow, heifer, beef cow, veal cow etc.) or defined based on the farmers' specific feeding records.

As soon as the quantity and quality of manure are obtained, the environmental factors will become crucial to determine rates of the biogeochemical processes. At farm scale, the life cycle of manure could go through several farm components including the feeding/resting lots, the storages, the treatment facilities, and finally the field receiving the manure applications. These stops of the manure life cycle usually have different environmental conditions, which drive the temperature, moisture, pH, Eh and substrate concentration with different rules. One of the major tasks for modeling is to track the variations of the environmental factors for each of the farm components based on its specific characteristics. For example, a feeding/resting lot could be a house or an open corral. The house is sheltered and hence its temperature or moisture can be adjusted by ventilation or heating. In contrast, the open corral is exposed to the mother nature and its temperature and moisture are totally controlled by the air temperature, radiation, wind speed and precipitation. If the environmental factors be correctly modeled for the two feeding lot conditions, then the biogeochemical processes occurring with the manure in between the two lots will be differentiated. The same is true for storage and treatment. The environmental conditions in compost, lagoon, tank or digester are controlled by the facility specifications as well the processes occurring in the facilities.

When the information of manure quantity/quality and environmental factors is available, the biogeochemical reactions (e.g., decomposition, hydrolysis, ammonium/ammonia equilibrium, ammonia volatilization, nitrification, denitrification, fermentation etc.) are ready to be calculated. Most of the above-listed reactions have been well documented to text books or research publications. As chemical reactions are mediated by bio- or abio-agents, these processes are commonly regulated by a limited number of environmental factors such as temperature, moisture, pH, Eh and substrate concentration. By using these environmental variables as input data, the directions and rates of the reactions can be quantified across the farm components. Classical equations in physics, chemistry and biology as well empirical functions from laboratory experiments have been utilized to link the environmental drivers to the biogeochemical processes. The details of the reactions have been described in former publications and parameterized in a biogeochemistry model, DNDC (Li et al., 1992; Li, 2000; Li, 2007). During the development of Manure-DNDC, these algorithms generalized for the biogeochemical reactions have been adopted and linked to the algorithms specified for manure production, treatment and application under animal farm conditions.

Outcome:

The outcome of this component of the project is a detailed process-based biogeochemical model called Manure-DNDC.

Framework of Manure-DNDC

A virtual farm was constructed in Manure-DNDC to generalize or represent a wide range of animal farms in California or other parts of the world. The virtual farm consists of seven components namely house, outdoor pen, grazing plot, lagoon, compost, digester and field where the manure is produced, stored, treated or applied, respectively. These components are integrated into an entity through the manure life cycle (Figure 48).

The components housing, outdoor corral and grazing plot are the locations where the animals are fed and rest. The herd characteristics (e.g., animal types and population) are required as input information for the three feeding/resting lots. Feeding data (feed rates and CP contents in feed) are required as input for the house and outdoor pen components. In addition, data on floor, bedding, ventilation and manure removal method are required for housing; data of ground surface, bedding and manure removal are required for outdoor pen. For the herd grazing in pasture, its type, population and grazing timing and duration need to be specified. The input data will be used to calculate the manure production and turnover within the feeding/resting lots, and partition the manure to compost, lagoon or digester if applicable.

Lagoon receives the manure liquids discharged from housing or outdoor corrals. The temperature, pH, Eh and substrates concentration in the lagoon slurry will be tracked by incorporating the weather data, lagoon capacity and surface conditions, and the slurry characteristics. Anaerobic decomposition, ammonia volatilization, nitrification, denitrification and fermentation take place in lagoon to quantify NH₃, CH₄ and N₂O emissions from and the manure turnover in the storage.

Compost receives the manure solids transported from house or outdoor pen. The temperature, oxygen consumption, Eh and substrates concentration in the compost will be calculated based on the activity of microbial decomposers in the decomposing manure, which are subject to the size, additives, aeration of the manure pit. CO₂, NH₃, CH₄ and N₂O emissions from the compost is quantified based on the rates of decomposition, ammonia volatilization, nitrification, denitrification and fermentation controlled by the compost climate.

Anaerobic digester is characterized by its capacity, CH₄ productivity, additives, treatment temperature and duration. The CH₄ produced from the digester will be utilized as an energy source and will not count for greenhouse gas flux. Based on mass balance, the residue from the digester is defined for its dry matter, organic C and C/N ratio.

The outputs from lagoon, compost and digester are applied to the field in the farm based on user-defined timing and amount. Manure-DNDC will handle the quantity and quality of the residue manure from each of the storage/treatment. As soon as the manure is applied to the field, the manure will be partitioned into the soil organic matter (SOM) pools based on quality (i.e., C/N ratio) of the manure. And, hence, the manure partitioned into the SOM pools will merge in the SOM processes, which are also regulated by the decomposition, ammonia volatilization, nitrification, denitrification and fermentation processes although under totally the field conditions that have been well developed in the DNDC model.

The Manure-DNDC model runs at daily or hourly time step. Daily fluxes of NH₃, CH₄, N₂O and CO₂ as well nitrate leaching are calculated for each of the seven farm components. The sum of the fluxes from all the seven components constitutes the farm emissions. Table 17 summarizes the input parameters, modeled processes and output parameters for the seven components.

The relationship among the inputs, outputs and processes is shown in Figure 49.

Sensitivity tests with Manure-DNDC

As a process-based model, Manure-DNDC was developed based on theoretical analyses and observed data from field or laboratory experiments. The modeling framework will need to be calibrated and validated although the principles on mass balance and biogeochemical dynamics have been embedded in the model. So far, we are still in the stage of calibrating and validating the model. However, some simple tests have been conducted to observe the basic behaviors of the model. A series of sensitivity tests were conducted to check the mass balance and reaction dynamics for Manure-DNDC.

An assumed farm was simulated with Manure-DNDC. The farm represented a typical dairy farm in California. The farm was located in the Central Valley having 500 cows with milk production 10 kg/head and weight gain 0.8 kg/head per day; feed rate was 6.8 kg dry matter (DM) with crude protein 0.43 kg/head per day; after secretion, feces and urine were separated and immediately moved to compost and lagoon, respectively; compost had litter addition 2000 kg DM with C/N ratio 45; lagoon capacity was 2000 cubic meter with a surface area 200 m²; no anaerobic digester was utilized; 50 ha of pasture land received the manure released from compost and lagoon.

Figure 50 shows the modeled annual N mass balance for the dairy farm where 70% of the total N intake 42 tons N went to the animal waste including 23 tons N in urine and 6 tons N in feces. About 13 tons of the manure N was lost as gases during the compost and lagoon treatments, and 7 tons of manure N was taken by the crop in the 50 ha of corn field. A small portion, about 1 ton N, was leached. The rest part (6 tons N) remained in organic forms in the field soil. The N mass balance was well kept through the farm scale simulation.

Figures 51, 52 and 53 show the different spatial and temporal patterns of three major pollutant gases (i.e., methane, ammonia and nitrous oxide) emitted from the dairy farm. The methane (CH₄) fluxes from the enteric source were constant and dominated the farm CH₄ emissions. Lagoon CH₄ was the second source fluctuating with accumulation from slurry inputs and draining events from the lagoon (Figure 51). Under the simulated management scenario with neither urine nor feces remaining in house after secretion, the major source of ammonia (NH₃) emissions took place when the manure was applied in the field. Lagoon was a stable but weak source of NH₃. NH₃ fluxes varied periodically following the composting cycles (Figure 52). N₂O emissions were highly episodic mainly from compost and field application (Figure 53). The modeled results are basically in agreement with observations.

To test the model's response to management changes, we reduced the intake protein rate from 0.43 to 0.40 kg/animal per day. The modeled results indicated that the emissions of all the three major pollutant gases decreased with the reduced protein intake rate. CH₄ reduction mainly driven by the decreased enteric CH₄ production (Figure 54). Lower protein intake led to lower N concentrations in the manure (urine and feces), and hence reduced NH₃ volatilization rate from the lagoon as well the field soil (Figure 55). The same reason is also applicable for the reduction of N₂O emissions (Figure 56). This sensitivity test indicates that any management alternatives taking place in the upper stream of the manure life cycle would have a thorough impact on the gas emissions across all the components of the farm.

A test was conducted to observe the effect of change in the storage/treatment facilities on gas emissions. Keeping the lagoon capacity constant, we changed the lagoon surface area from 200 to 1000 m². The change significantly increased NH₃ emissions from the lagoon and reduced NH₃ fluxes from the field due to the N mass balance (Figure 57). The lagoon NH₃ emission can be reduced with an impermeable cover. Since this management alternative was adopted for a mid-stream location (i.e., lagoon), the impacts were limited to only the downstream fluxes.

Conclusions and Recommendations:

The framework of Manure-DNDC was accomplished through this effort including field measurements, information/data collection, algorithm development and code integration. The preliminary tests proved the model had a healthy framework to handle the mass balance and biogeochemical dynamics across the entire components of animal farms. However, for a complex, process-based model such as Manure-DNDC, setting up of framework is only the first step of the model development. Calibration and validation with the data observed at each of the farm components are crucial to make the model reliable and applicable. Unfortunately, so far, we have only obtained very limited amount of field data to fulfill the unavoidable stage of the model development. The recent completion of the FTIR data acquisition will provide new data for model validation. In addition, our collaboration with Dr. Charlie Krauter's group at SCUF will provide additional flux measurements of N₂O and NH₃ from flux chambers studies at 6 commercial dairies in 2007 and 2008. Fortunately, this modeling effort is attracting more interest and support. We expect Manure-DNDC will become a useful tool for livestock industry in a few years following rigorous calibration and validation. Additional investment I validation efforts are needed to shift the tool from basic research tool to a decision support system for inventories and mitigation analyses of greenhouse gas emissions from animal feeding operations.

Figures for Component 3.

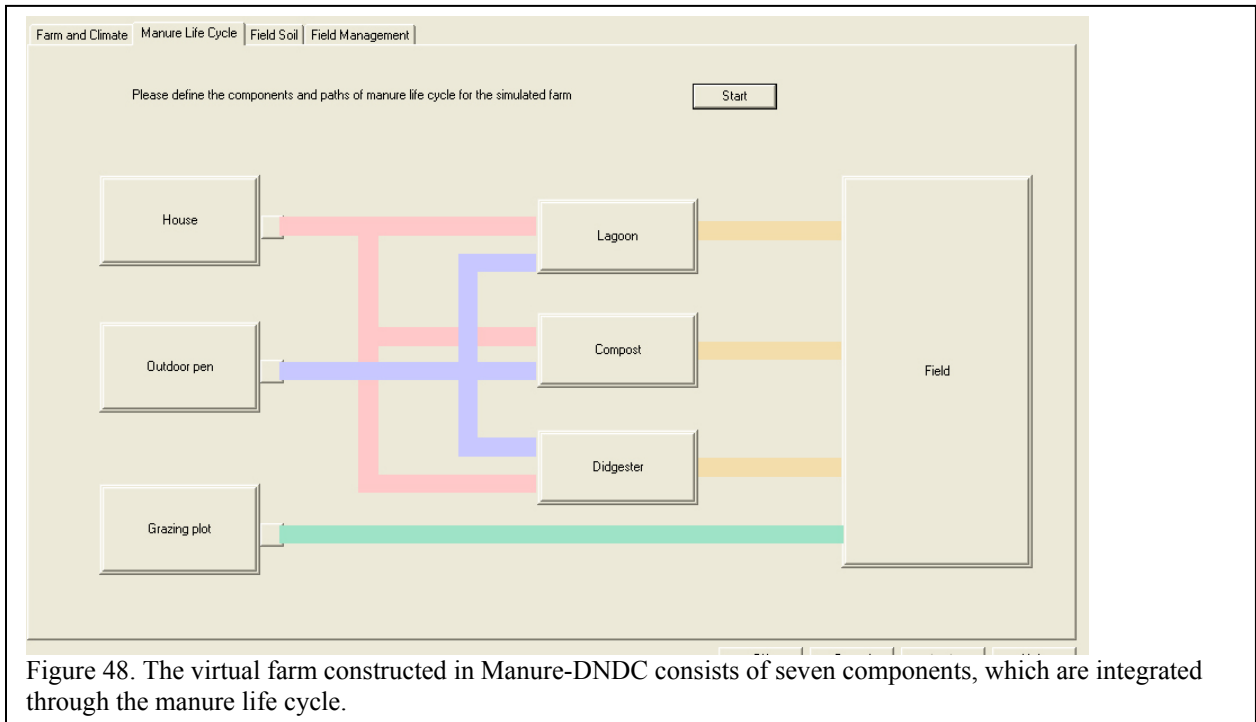


Figure 48. The virtual farm constructed in Manure-DNDC consists of seven components, which are integrated through the manure life cycle.

Manure life cycle in a virtual farm constructed in Manure-DNDC

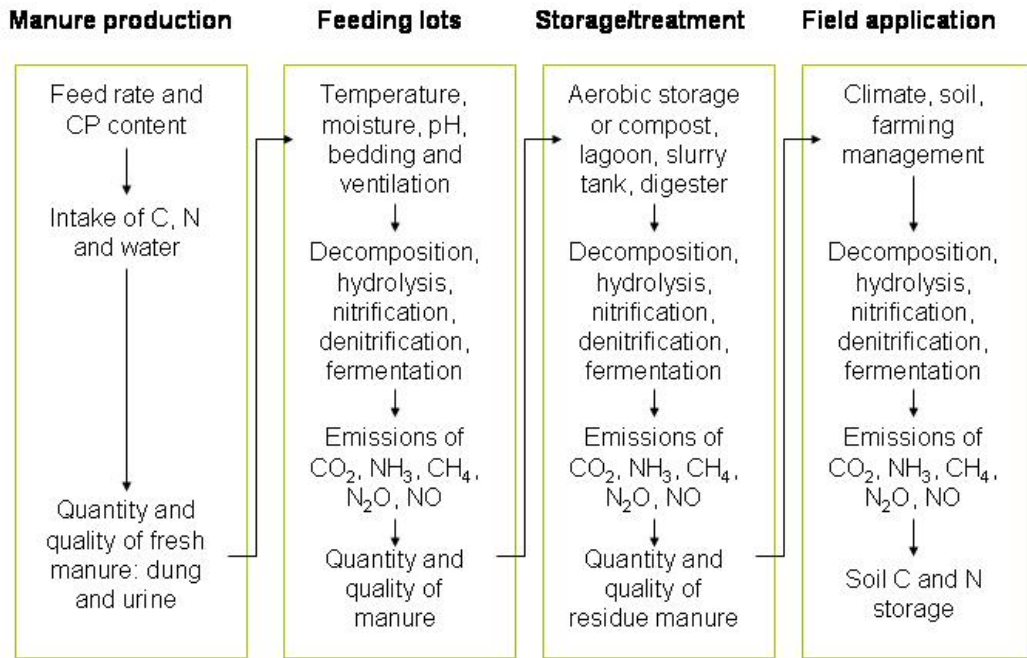


Figure 49. Manure life cycle simulated in Manure-DNDC

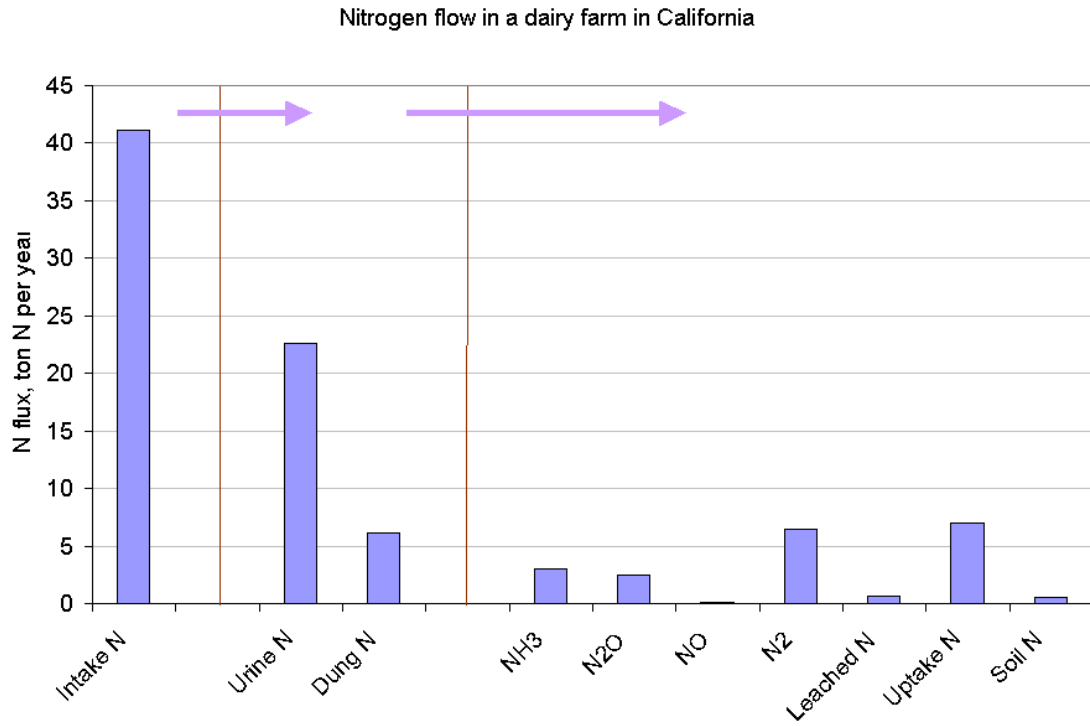


Figure 50. Modeled nitrogen mass balance in the simulated dairy farm in California

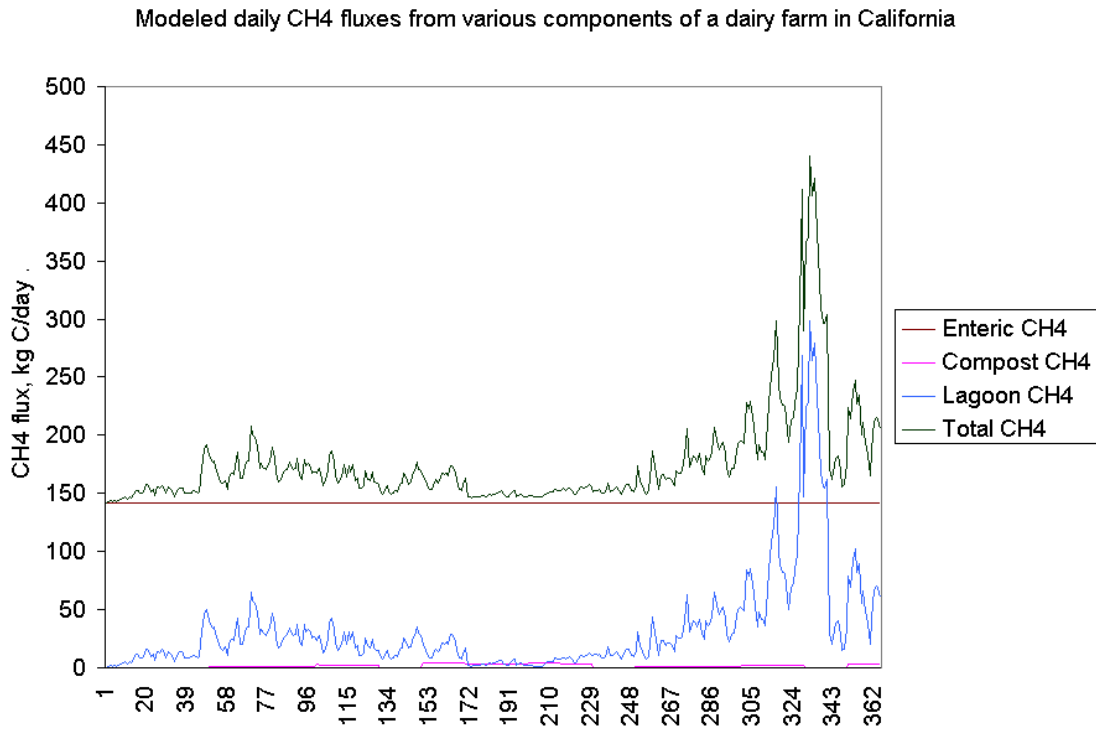


Figure 51. Modeled daily methane fluxes from enteric source, compost and lagoon in the simulated dairy farm in California

Modeled daily NH3 fluxes from various components of a dairy farm in California

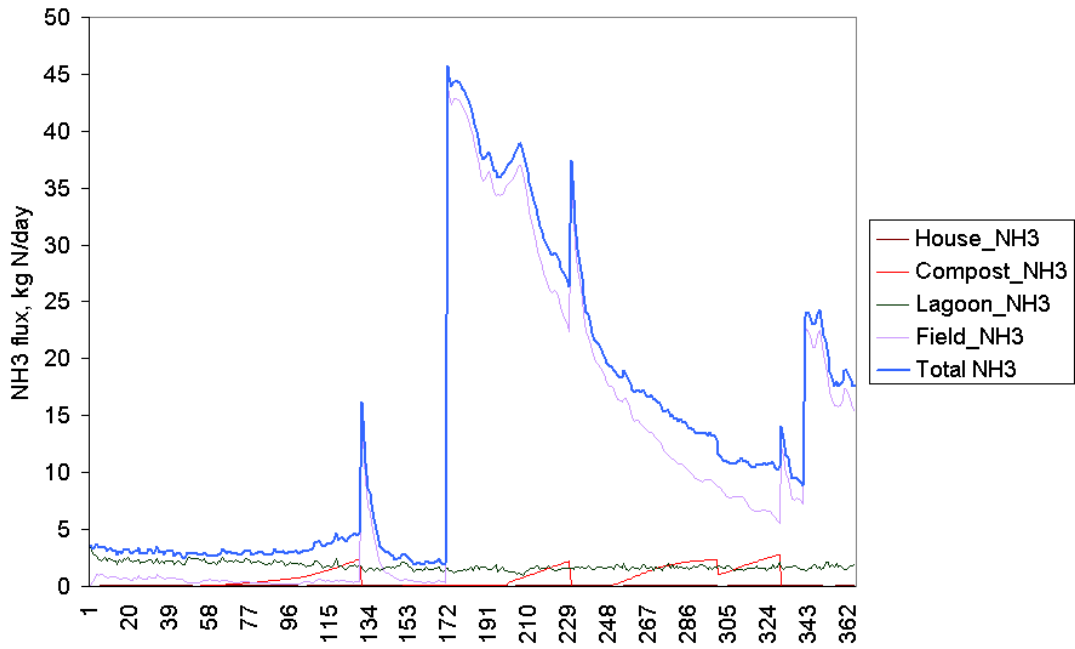


Figure 52. Modeled daily ammonia volatilization fluxes from house, compost, lagoon and field in the simulated dairy farm in California

Modeled daily N2O fluxes from various components of a dairy farm in California

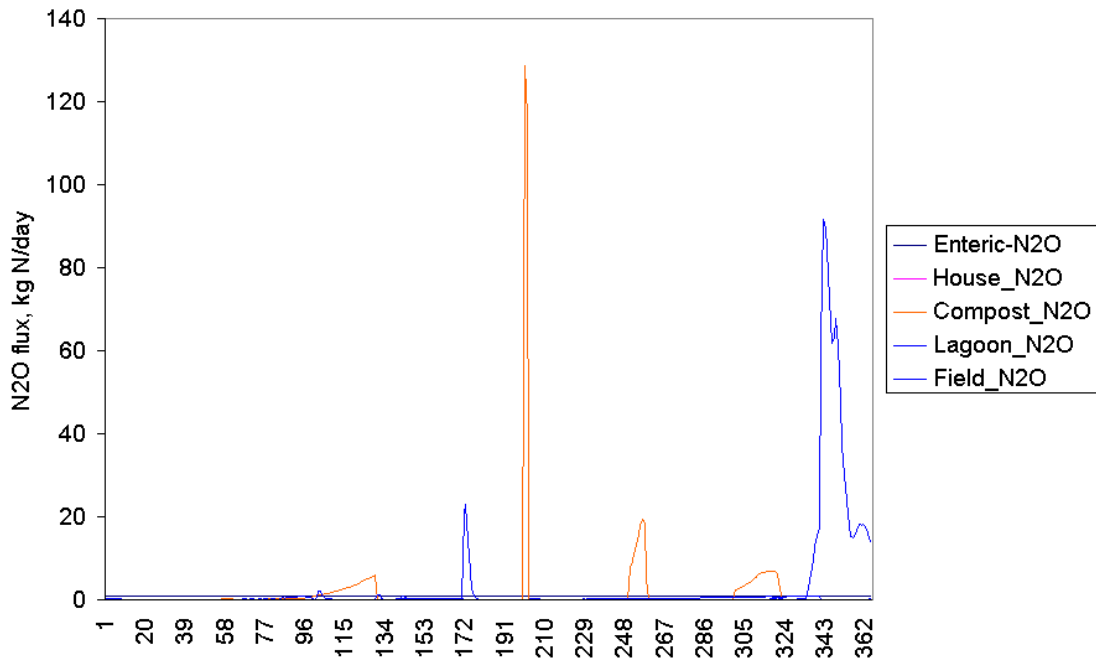


Figure 53. Modeled daily nitrous oxide (N2O) fluxes from enteric source, house, compost, lagoon and field in the simulated dairy farm in California

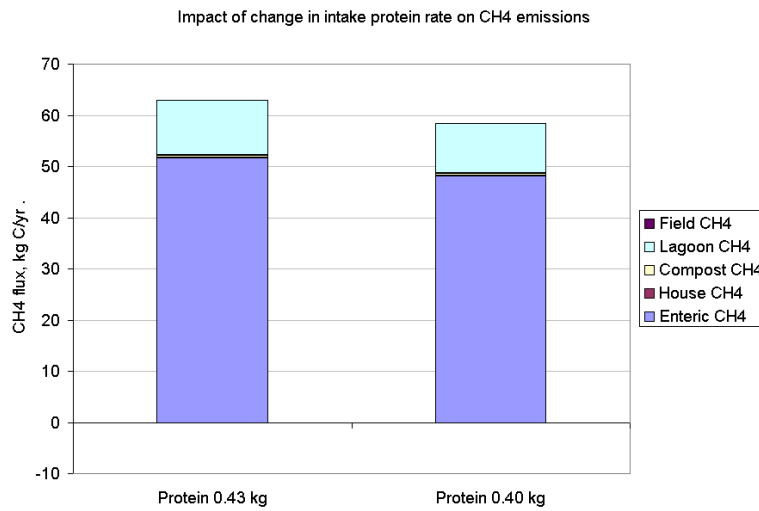


Figure 54. Impacts of change in intake protein on CH4 emissions at farm scale

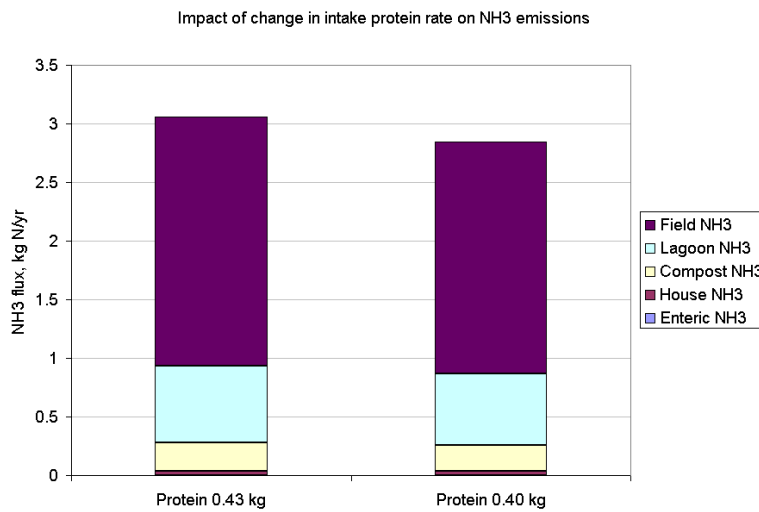


Figure 55. Impacts of change in intake protein on NH3 emissions at farm scale

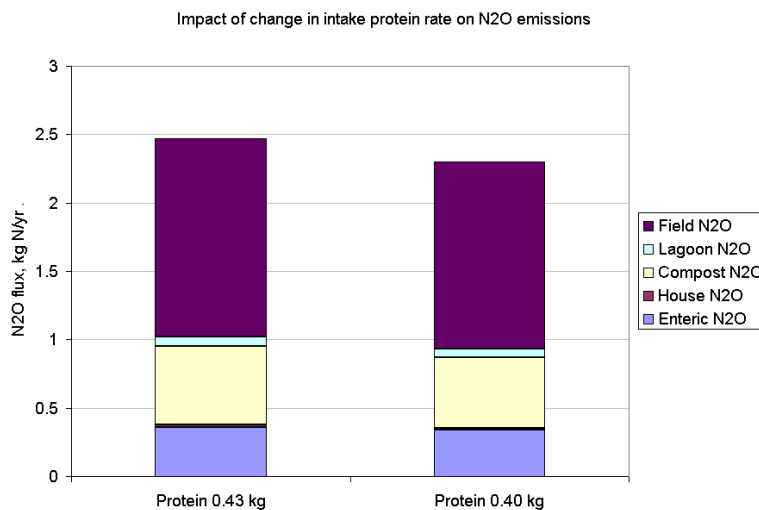


Figure 56. Impacts of change in intake protein on N2O emissions at farm scale

Impact of lagoon surface area and coverage on NH3 emissions from a dairy farm in California (lagoon capacity: 2000 cubic meter)

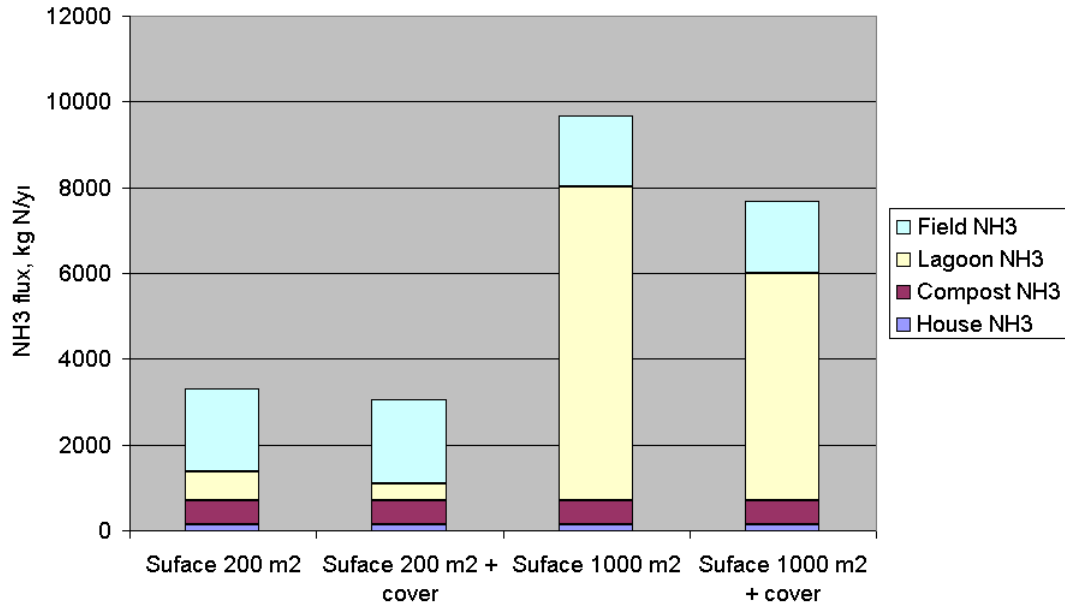


Figure 57. Impacts of change in lagoon surface area and coverage on NH3 emissions at farm scale The above described sensitivity tests indicated that (1) the mass balance and biogeochemical dynamics simulated by Manure-DNDC were acceptable and basically in agreement with observations reported in publications, and (2) Manure-DNDC was sensitive to changes in the farming management practices.

Tables for Component 3:

Table 17. Input/output parameters and modeled processes for seven components of the virtual farm constructed in Manure-DNDC

Farm component	Input parameters	Modeled processes	Output parameters
House	Air temperature; Wind speed; Animal type and heads; Feed rate; Crude protein content; Floor area; Floor surface properties; Bedding material type, amount, C/N ratio and timing; Ventilation type and rate; Frequency and method of animal wastes removal; Fractions of animal wastes partitioned to compost, lagoon, digester and remaining in house.	Indoor temperature and air flow rate; Conversion of feeding materials to productions of milk, meat, urine and feces; Manure accumulation on floor or in gutter; Manure temperature, moisture, pH and Eh dynamics; Biogeochemical processes* in manure.	Quantity and quality (C/N ratio) of manure released from house; Partitioning of liquid and solid manure to compost, lagoon and/or digester; Enteric CH4 and N2O fluxes; Fluxes of NH3, CH4, N2O, NO, N2, CO2 emitted from floor or gutter.
Outdoor pen	Air temperature; Precipitation; Wind speed; Animal type and heads; Feed rate; Crude protein content; Ground area; Ground surface properties; Bedding material type, amount, C/N ratio and timing; Frequency and method of animal wastes removal; Fractions of animal wastes partitioned to compost, lagoon, digester and remaining in pen.	Conversion of feeding materials to productions of milk, meat, urine and feces; Manure accumulation on ground; Manure temperature, moisture, pH and Eh dynamics driven by weather data; Biogeochemical processes* in manure.	Quantity and quality (C/N ratio) of manure released from outdoor pen; Partitioning of liquid and solid manure to compost, lagoon and/or digester; Enteric CH4 and N2O fluxes; Fluxes of NH3, CH4, N2O, NO, N2 and CO2 emitted from ground.
Grazing plot	Field area for grazing; Grazing application periods; Start and end dates for each grazing period; Hours per day for the animals stay in the grazing field; Animal type and heads; Frequency and method of animal wastes removal;	Production of urine and feces driven by grass quantity and quality available in the field; Manure accumulation on and incorporation in soil; Biogeochemical processes* in manure; Nitrate leaching.	Quantity and quality (C/N ratio) of manure removed from field; Partitioning of removed manure to compost, lagoon and/or digester; Enteric CH4 and N2O fluxes; Fluxes of NH3, CH4, N2O, NO, N2 and CO2 emitted from manure accumulated on soil;

	Fractions of animal wastes partitioned to compost, lagoon, digester and remaining in the field.		Nitrate leached to soil.
Aerobic compost	Quantity and quality (C/N ratio) of manure received from house, outdoor pen and/or grazing plot; Compost storage size and density; Storage duration; Additional litter amount and C/N ratio; Fractions of mature compost partitioned to field application, market selling and remaining in compost.	Temperature, moisture, pH and Eh dynamics within compost; Biogeochemical processes* in compost.	Quantity and quality (C/N ratio) of manure removed from compost; Partitioning of removed manure to field application; Fluxes of NH ₃ , CH ₄ , N ₂ O, NO, N ₂ and CO ₂ produced during composting.
Anaerobic lagoon or tank	Quantity and quality (C/N ratio) of manure received from house, outdoor pen and/or grazing plot; Capacity; Surface area; Surface coverage; Rain water intake; Slurry drain frequency; Fractions of slurry partitioned to field application, market selling and remaining in lagoon.	Temperature, moisture, pH and Eh dynamics in lagoon or tank; Biogeochemical processes* in lagoon or tank.	Quantity and quality (C/N ratio) of slurry removed from lagoon or tank; Partitioning of removed slurry to field application; Fluxes of NH ₃ , CH ₄ , N ₂ O, NO, N ₂ and CO ₂ emitted from lagoon or tank.
Anaerobic digester	Quantity and quality (C/N ratio) of manure received from house, outdoor pen and/or grazing plot; Digester capacity; Methane production; Processing temperature; Processing duration; Fractions of digester residue partitioned to field application, market selling and remaining in digester.	Temperature, moisture, pH and Eh dynamics in anaerobic digester; Biogeochemical processes* in digester.	Quantity and quality (C/N ratio) of digested residue removed from digester; Partitioning of removed residue to field application; Fluxes of CH ₄ and CO ₂ produced in digester.
Field	Quantity and quality (C/N ratio) of manure received from compost, lagoon and/or digester; Soil properties; Cropping management practices: crop type and rotation, tillage,	Crop growth; Soil climate; Applications of cropping management practices including manure/slurry amendment; Soil water hydrology;	Fluxes of NH ₃ , CH ₄ , N ₂ O, NO, N ₂ and CO ₂ emitted from soil; Soil carbon sequestration; Nitrate leaching; Crop yield.

	fertilization, manure application timing and method, flooding and drainage, irrigation and grass cutting.	Biogeochemical processes* in soil.	
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* Biogeochemical processes include decomposition, hydrolysis, nitrification, ammonium-ammonia equilibrium, ammonia volatilization, denitrification and fermentation, which have been parameterized in the agricultural version of DNDC.

Component 4: GIS Database Development

Cropland and Dairy Extent Database

Contemporary cropland areas were defined principally using the California Department of Water Resources (DWR) land use survey database. The California DWR supports ongoing efforts to conduct county land use surveys on a frequent basis. Since 1950 the DWR has conducted over 250 land use surveys for all or part of California's counties. The main emphasis and detail of the surveys is agricultural land with the results of the surveys used to determine agricultural area for the survey year. Potentially, over 70 different crop types can be mapped in the survey.

The DWR land use database contains a spatial distribution of land use and cropland polygons for 42 of the 53 counties with irrigated cropland in California. The database includes descriptions of crop type, animal feeding operations (including dairies), and irrigation practices. The distribution of dairies for this study was derived from these county land use survey GIS databases for all major crop areas in California. The county data were obtained through the DWR website (<http://www.landwateruse.water.ca.gov/>). We created a spatial map showing locations of dairies by extracting all dairy polygons from the DWR tiles and stitching them together to create a basemap coverage of dairy locations. Our DWR dairy database contains 2300 polygons, covering an area of approximately 25,500 hectares. These dairy polygons do not include surrounding cropland areas that are owned and used by the dairies for crop production and land application of manure. The polygons represent the physical location of the dairies, including housing, dry lots, milking parlors, manure storage and treatment areas and feed production and feed bunk areas. The CDFA California Agricultural Resources Directory (2006) reported that there were 2,107 dairy operations in California. Figure 58 shows the density of dairies in California, expressed as the total area of dairies within 5 kilometer grid cells. It is clear that the majority of dairies are located on the central valley, with a few pockets of dairies in Riverside and San Bernardino Counties in southern California.

Climate Data

The Manure-DNDC model requires daily climate data on precipitation, temperature, solar radiation and wind speed. We developed software scripts to automatically request and retrieve California Irrigation Management Information System (CIMIS) station data and reformat the data to run with Manure-DNDC model. CIMIS provides data access to their database via following two ways –

1. Free ftp access. This dataset provides access to partial data covering only last few years. In addition single station data is subdivided to multiple files in multiple directories with inconsistent data formats. In addition some files are compressed and some not. Scripting of data

retrieval tools from this free ftp site is straight forward, but some complicated due to complex data organization and very limited to available data range (dates).

2. Membership access. While this one provides full access to CIMIS database, it requires registration and user/password login.

Since membership login provides access to full dataset we focused on this direction and developed the following set of tools that allow complete, automated data retrieval from CIMIS:

"*cimis_download_daily.pl*" - Universal code for manual or automatic scheduled data downloads and daily updates of CIMIS DAILY data for one or given list of stations. The downloaded data is stored in a local file depository in DNDC daily data format.

"*cimis_download_hourly.pl*" - Universal code for manual or automatic scheduled data downloads and daily updates of CIMIS HOURLY data for one or given list of stations. The downloaded data is stored in a local file depository in DNDC hourly data format.

"*cimis_coord_2_station.pl*" - Supporting code to find a list of nearest CIMIS stations to given LON/LAT coordinates. The code give also distance and azimuth to those stations so that a user can choose which one is more appropriate for data retrieval and analysis.

The code has been tested to run on both Linux/Unix and MS Windows family of operating systems. We used these scripts to download climate data from all the CIMIS stations in the dairy production regions of California.

County Dairy Cow Statistics

Annual statistics listing inventory of total cattle and milk cows were downloaded for all counties in California from the NASS website at <http://www.nass.usda.gov>. Inventories on head of total cattle, beef cows and milk cows were extracted for years 1975 through 2005. A cursory review of the database revealed missing data for several years for a number of the California Counties.

We identified 2004 as the target date for our modeling analysis. As an initial step in validating the database we identified counties with no milk cow entries for 2004. Thirty-one counties were identified as having a blank field for milk cow inventory in 2004. Historical milk cow inventory trends in the NASS database were then reviewed for the 31 counties to determine the extent and potential trajectory of dairy

activity over the 30 year database time period. In addition, the California Department of Water Resources (DWR) irrigated areas GIS database was consulted to identify any dairy polygons in the 31 counties no milk cow inventory for 2004. Seventeen of the 31 counties had very low numbers of milk cows reported throughout the NASS census and most only reported through the early 1990's. Also, most of these counties did not have any dairy polygons in the DWR GIS database. Based on historical information and trends it was assumed that these 17 counties had negligible or no dairies in 2004.

Fourteen of the 31 counties reported higher milk cow inventories through the end of the 1990's and in many cases also have dairy polygons in the DWR dataset. It was assumed that these counties represent areas where dairies were once active but have since been converted to other agricultural and/or land uses.

The two exceptions to this assumption were Imperial and Del Norte Counties. Both Imperial and Del Norte Counties have milk cow inventories listed for year 2005 but lack information for years 2001-2004. We assumed that dairy cows were present in 2004 but this information was not available to be entered in the NASS census. An estimate of milk cows for 2004 was derived for each county by scaling the 2005 milk cow inventory by total cattle (i.e., 2004 milk cows = 2005 milk cows/ 2005 total cattle * 2004 total cattle).

Dairy Soils

Soil data on organic carbon content, pH, bulk density and soil texture, which are required for running the Manure-DNDC model, were compiled using the USDA's The Natural Resources Conservation Service (NRCS) - National Cartography and Geospatial Center (NCGC) Soil Survey Geographic (SSURGO) database. The SSURGO database represents the highest detail of geographic soil data developed by the NRCS-NCGC. The dataset was developed from digitizing soil survey maps revised as needed using aerial photos and other available information. The database is designed to be used for broad planning and management uses covering state, regional, and multi-state areas. The SSURGO attribute database based on the National Soil Information System national database gives the proportionate extent of the component soils and their properties for each map unit and includes over 25 physical and chemical soil properties, interpretations, and productivity. The SSURGO dataset was used to obtain the minimum and maximum ranges for the soil attributes required by DNDC (pH, clay content, bulk density, soil organic matter) for each of the Manure-DNDC spatial modeling units.

The SSURGO database is arranged in a multi-layer format, where each polygon (referred to as 'map unit' by SSURGO) can have multiple components and each component can have multiple layers. A soil component is a set of properties that is used to describe a certain soil type. The percent areas that each soil

component occupies within the SSURGO polygons are provided ('*COMPPCT_R*' variable), however there is no information provided as to the actual spatial distribution of each component within the polygons.

It is evident that each SSURGO polygon has the potential for dozens of scenarios based on multiple soil components and layers; however the Manure-DNDC model requires a single set of input ranges for the soil input variables. In order to take advantage of the detail that is available in the SSURGO database, an area-weighted approach was used. First, all soil layers except the top layer were eliminated, since this layer is typically deeper than the rooting depth for most crops which is the depth used for Manure-DNDC simulations. Second, based on the *COMPPCT_R* variable, soil components greater than 10% (of the surface layer) were area-weighted to be used as Manure-DNDC soil inputs.

Several soil texture categories in the SSURGO dataset were identified that have 'no data' for the DNDC variables. These soil texture categories include: cemented, fragmented, ice, indurated, mucky-peat, muck, peat, unweathered bedrock, weathered bedrock, and variable. It was assumed that cropland would not occur on any of these soil texture types; thus data from these soil texture categories were excluded.

To generate our modeling database of soil input variables, area-weighted Manure-DNDC soil variables (clay fraction, bulk density, organic carbon, and pH) were calculated for each of the 2300 dairy polygons from the DWR dataset.

Dairy Manure Management Practices

As part of our effort to build a process-based modeling system for estimating greenhouse gas emissions from California dairies, we collected data on manure management systems. A database of dairy manure management practices has been compiled from hard copy dairy permit applications provided by the San Joaquin Valley Air Pollution Control District (SJVAPCD) and the South Coast Air Quality Management District (SCAQMD). These permits contain general data on livestock inventory and management practices for 293 large dairies in the SJVAPCD (282 dairies) and SCAQMD (11 dairies) regions required to submit a permit application. A description of the data with general statistics on manure management practices is provided in a separate report (see Appendix C). It is important to note that these statistics represent the management practices found on larger (typically >800 head) California dairies in general because permit are not required for smaller dairies. According to CDFA California Agricultural Resources Directory (2006), in 2004 there were approximately 1,100 dairies in California with at least

500 head. So, our permit pool represents approximately a 27% sample of the dairies. The dairies represented by these permits contain just over 1,000,000 of the 1, 800,000 dairy cows in 2004 (CDFFA).

Dairy cow permit data were assigned to the DWR dairy polygons using the inventory values provided in the manure management system dairy permit database based on the GIS addressing for each permit. Some manual assignment and reassignment of permits to individual DWR dairy polygons was required. Two permits near the towns of Bakersfield and Buttonwillow were not assigned to DWR polygons because there were no available dairy polygons within a 20 mile radius of these towns (i.e., all proximal polygons were already assigned to larger dairies). All remaining dairy polygons were assigned inventory based on a livestock density ratio derived from county level dairy statistics and dairy polygon area from the DWR database. Where needed the livestock density ratio was adjusted to account for existing inventory from the permit data. A comparison of livestock density by county for those counties containing polygons with assigned permit data yielded density values similar to county estimated values from the NASS dataset. By linking the permit database to the DWR GIS databases we are able to assign local soils and climate information to each of the individual permits. This enables us to model emission from each permit facility.

Model Simulations

While the current version of Manure-DNDC requires more validation before its emissions estimates can be considered with a known level of accuracy and uncertainty, the current version of Manure-DNDC was used for demonstration purposes to compile an estimate of CH₄ and N₂O emissions from California dairies. The simulations were performed for each of the dairies where we had permit data describing manure management practices (e.g. frequency of dry lot scraping, land application, type and size of manure storage/treatment facilities, etc), type of dairy (freestall, corral, etc), number of cows (lactating, dry and heifers). There were 265 dairies for this analysis. These dairies had just over 1 million milking cows, which is approximately 56% of the total 1.8 million milking cows in the state. CIMIS climate data and SUSRGO soils data were used for the simulation. Without specific information on housing size, feed regimes, bedding, water used for flushing freestalls, size of corrals, etc, we had to make some simplifying assumptions. Table 18 provides a list of our assumptions and the basis for making each assumption.

Since lactating and dry cows receive very different feed regimes and often have different manure management practices, we ran Manure-DNDC twice, once for lactating cows and once for dry cows, for each of the permit dairies. The 530 simulations (265 permits, with 2 simulations per facility) were then compiled in a spatial database to examine spatial and temporal variability in emissions and to facilitate

scaling emissions estimates up to the county and state level. We used the 2004 climate year for this simulation.

Based on the results from the permit dairy simulations, we scaled up the emissions to the statewide level by using average emissions at the county scale from our permit based model runs. For those counties that had dairies, but did not have dairies in our permit database, we used an average value from all the permit simulations. The Manure-DNDC based emission factors were then applied to each of our DWR dairy polygons throughout the state. Figure 59 shows the distribution of dairy cows (milking and replacement stock) from our databases (figure presents total number of cows – milking and replacement stock - across California in a 5km grid.

Methane Emissions

Our model results indicate that total methane emissions from dairies in 2004 was approximately 485,000 Metric Tons (MT). Following the IPCC Second Assessment Report guidance (SAR, 1996 vintage) using a GWP factor of 21 for CH₄, the methane emissions were 10.2 MMT (Million MT) CO₂eq. There were 3 main sources of methane emissions: enteric fermentation, lagoon/storage ponds, and compost piles. Enteric fermentation was the largest source of CH₄ emissions, accounting for approximately 83% (or 8.5 MMT CO₂eq.) of the total emissions. Lagoons/storage ponds accounted for 15%, or 1.6 MMT CO₂eq. Compost piles made a small contribution of approximately 1% (0.1 MMTCO₂eq.) of the total emissions. Our model estimate of total methane emissions is quite close to the 2004 CEC emission inventory estimate of 10.4 MMT CO₂eq. (CEC 2006). However, the estimates differ in the contributions from enteric and manure management. CEC (2006) estimates were 4.7 MMT CO₂eq and 5.7 MMT CO₂eq for enteric and manure management emissions, respectively.

Nitrous Oxide Emissions

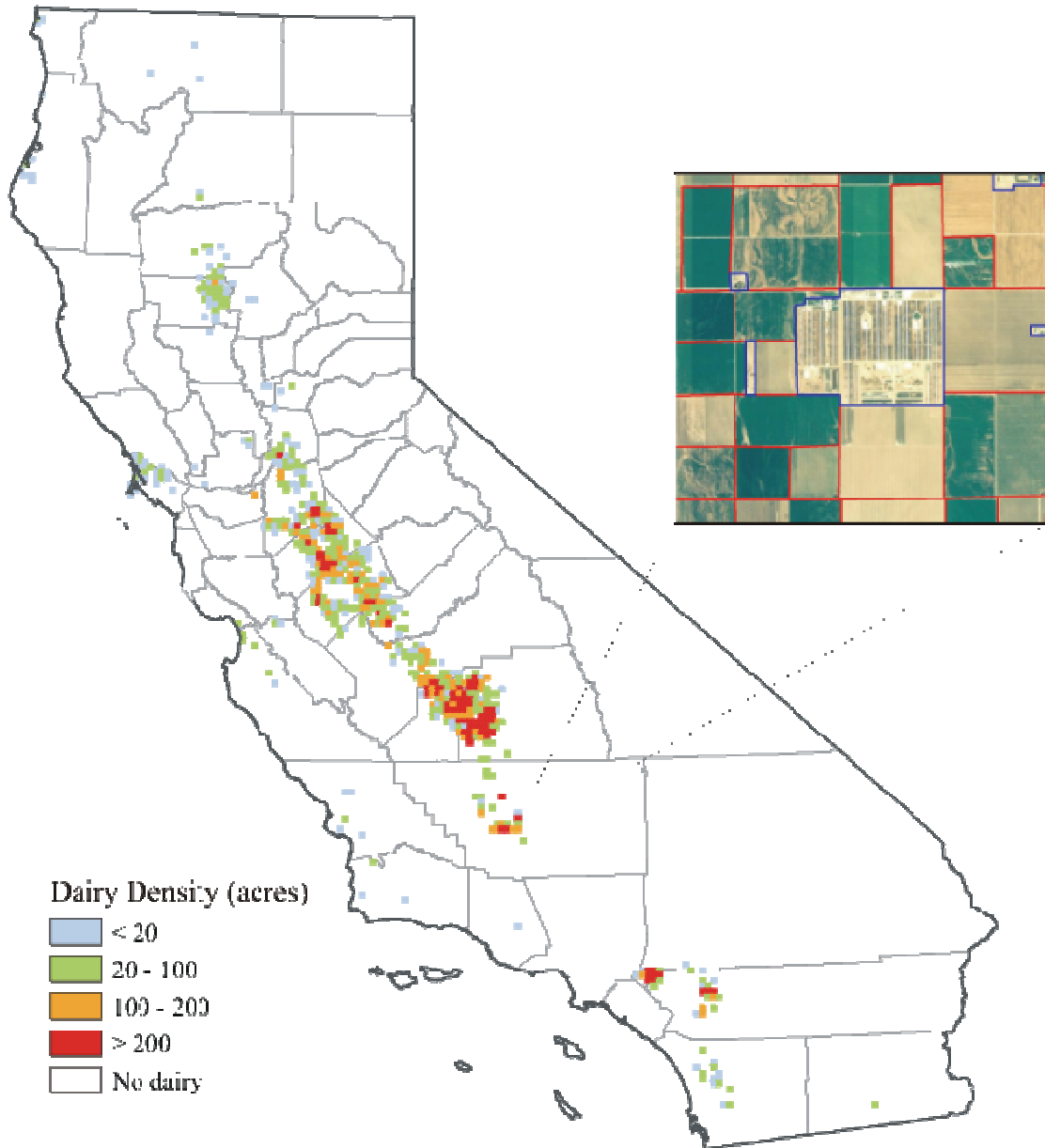
Our model results indicate that total nitrous oxide emissions from dairy manure management (includes emission from animals, housing, and manure storage/treatment) in 2004 was approximately 7,400 Metric Tons (MT). Following the IPCC Second Assessment Report guidance (SAR, 1996 vintage) using a GWP factor of 310 for N₂O, the nitrous oxide emissions were 2.3 MMT CO₂eq. Enteric (directly from the cows) and compost/solid stacks were the main sources of N₂O emissions. The existence of direct N₂O emissions from the cows themselves is a source of emissions that has not been accounted for in emission inventories. Our model estimates of enteric N₂O emissions are based on the chamber work described above (Component 1). Our model estimate of total enteric N₂O emissions is 2.0 MMT CO₂eq. If our estimates of direct emissions of N₂O from dairy cows is accurate, then this is an important finding and needs to be addressed further. It is important to note that due to inconsistent calibration of the

instrumentation, the accuracy of the N₂O measurements from cows in the chamber experiments is not known. Compost was the other significant source of N₂O, contributing 0.3 MMT CO₂eq. Our model estimate of N₂O from manure management is lower than the CEC 2004 estimate of 0.9 MMT CO₂eq.

Manure-DNDC also provides estimates of N₂O from land application phase of manure management. For these model runs we assumed that all manure effluent from lagoons and compost/solid stacks were applied to the surrounding crop areas. The extent of crop areas was taken from the permits (producers were asked how many acres of cropland they had and used for manure application). We also assumed that these surrounding crop areas were planted with a single corn silage crop. While most dairies grow several types of silage and forage crops, we decided to select a single crop for this demonstration. Manure-DNDC can simulate a wide variety of crops and cropping systems (including multi-cropping systems, use of cover crops, and a wide range of tillage, irrigation and fertilizer management systems). Total 2004 emissions from land application of manure and production of the silage corn, which includes the application of ~300 kg N/ha chemical fertilizer, was approximately 40,100 MT N₂O (12.5 MMT CO₂eq.). The 2004 CEC emission inventory estimated total N₂O emissions from agricultural soils was 19.2 MMT CO₂eq. Unfortunately it is not possible to directly compare the CEC emission estimate with our model results because the CEC estimates includes manure and chemical fertilizer applied to all agricultural soils, while our estimate provides emission just from agricultural areas that received dairy manure.

Figure 60 illustrates the spatial pattern and magnitude of total CH₄ and N₂O emissions, expressed as CO₂eq. As expected, high emissions are evident in areas with high density of dairy farms and cows. Figure 60 illustrates the difference between our total enteric emissions (methane and nitrous oxide) and the CEC (2006) estimate for 2004. Since our model of enteric N₂O emissions was developed based on the chamber work discussed in Component 1 of this report, there is a large degree of uncertainty in the actual magnitude of enteric N₂O emission to the point where there may not be any emissions at all. Nevertheless, taking this into account our estimate of total enteric emission is still considerably higher (~81% higher) than the current emission inventory estimate (Figure 61).

Figures Component 4:



Data Source: California Department of Water Resources land use survey database (<http://www.landwateruse.water.ca.gov>)

Figure 58 Density of dairies in California. Outset shows the detail of the DWR land use databases overlay on aerial photo that was used to digitize the land use. A dairy is outlined in blue and surrounding crop fields are outlined in red.

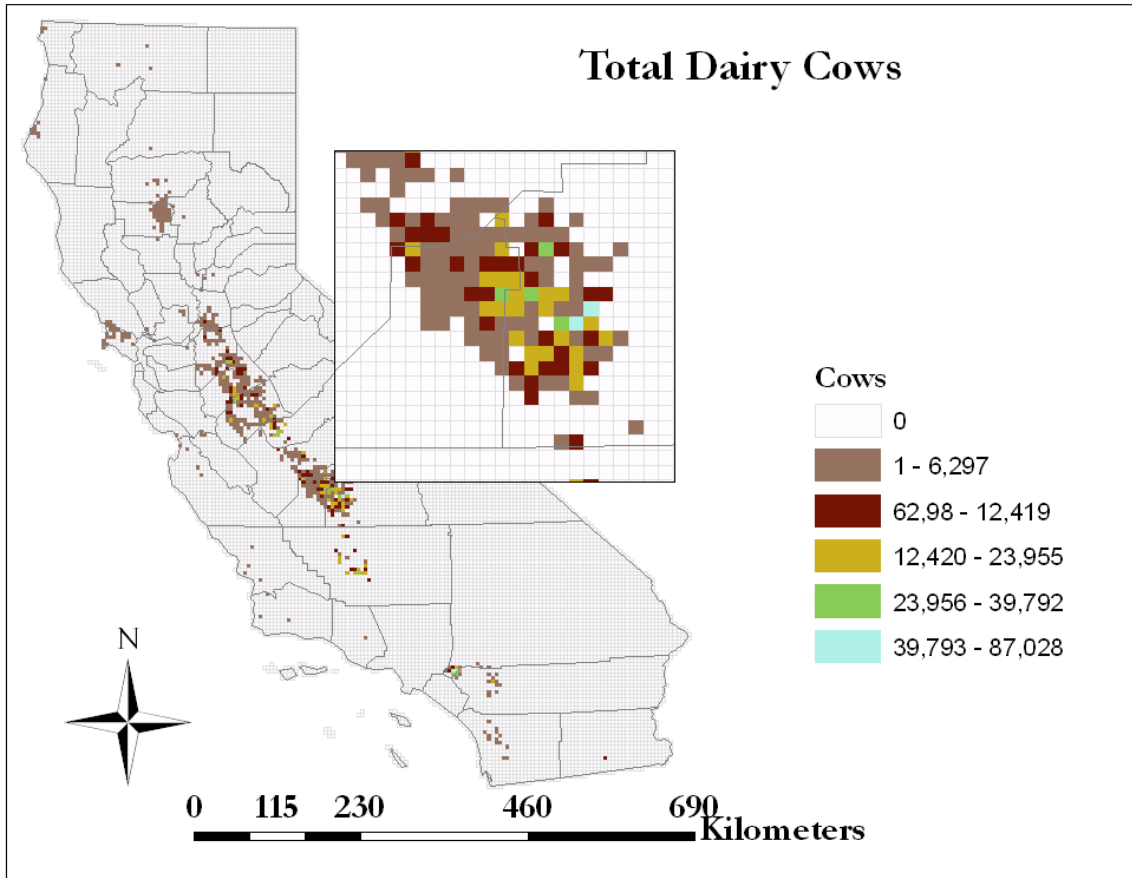


Figure 59: Distribution of dairy cows in California. Our DWR location and cow population assignments were gridded to a 5km grid cell for illustration purposes. The number of cows includes both milking cows and their replacement stock (Heifers and Calves). It is clear that the bulk of dairy cows are in the central valley, with some pockets east of Los Angeles and north of San Francisco.

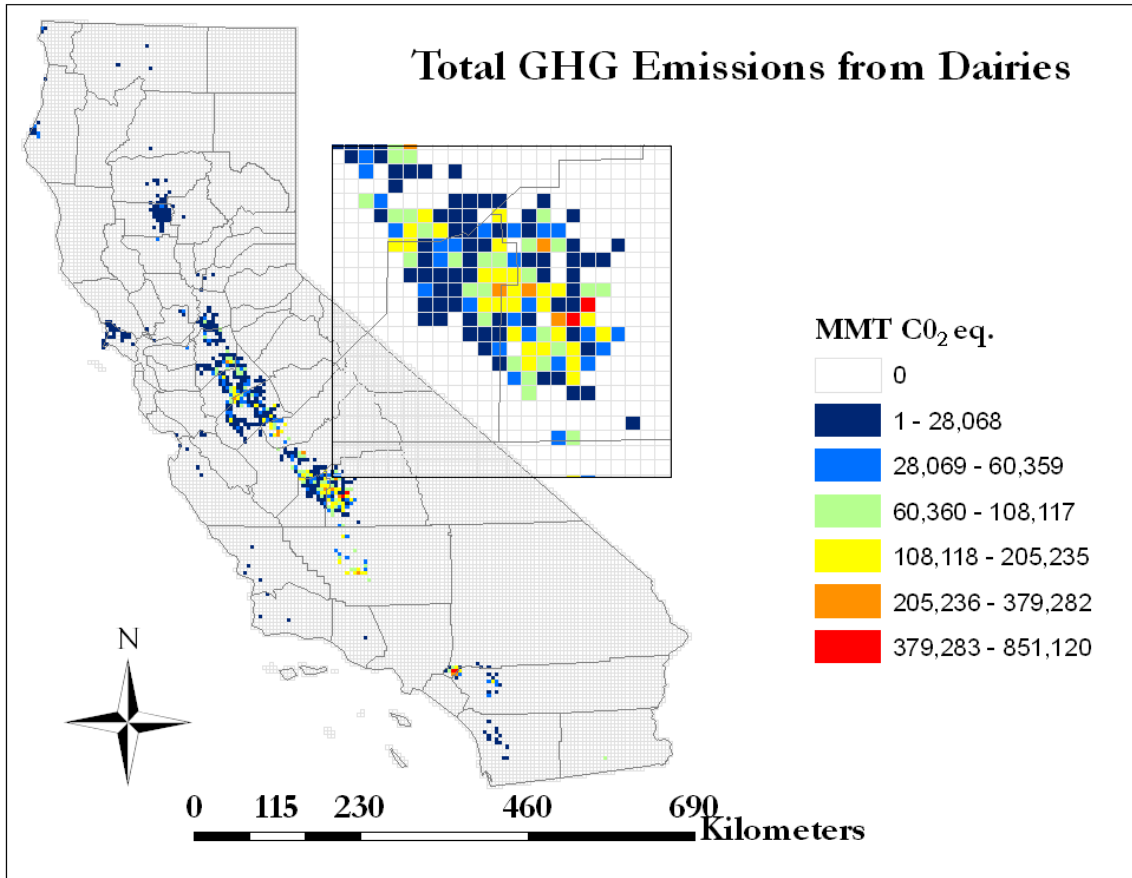


Figure 60: Total methane and nitrous oxide emissions from California dairies. These model estimates include emissions from the dairy cows, manure management systems and land application. Note: the land application emissions also include emissions from cropping areas that received dairy manure. All dairy cropping areas were modeled as silage corn with ~300 kg N/ha of chemical fertilizer.

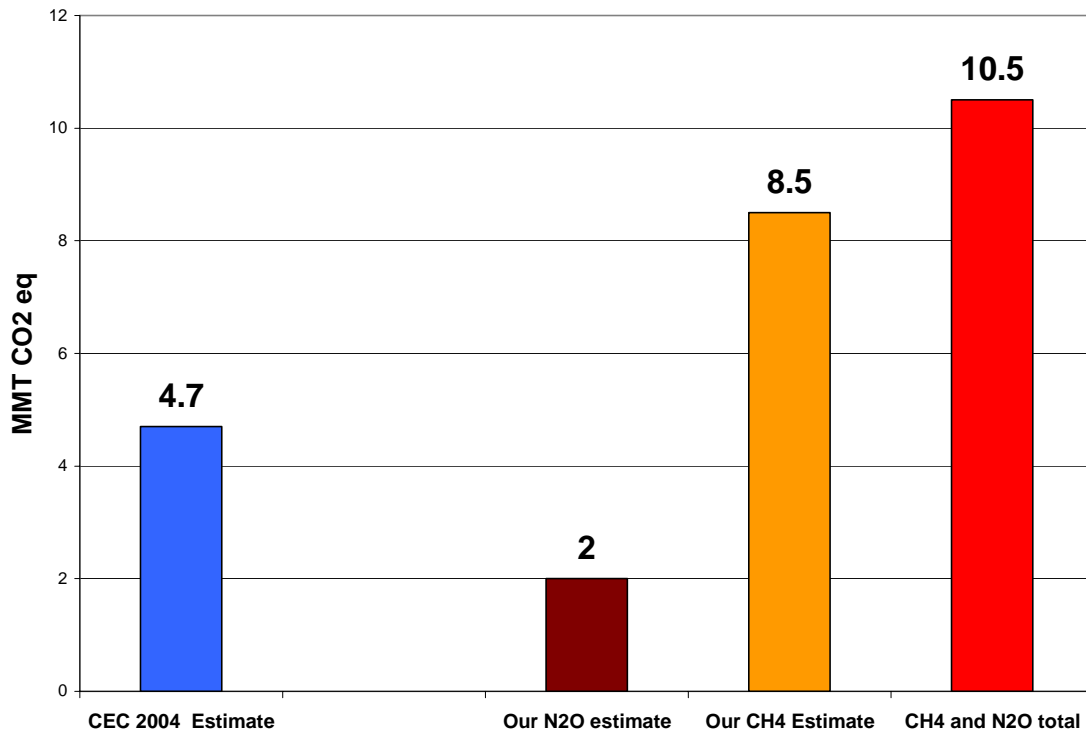


Figure 61: Comparison of 2004 California Emission Inventory estimate of enteric fermentation emissions from dairy cows with our model estimates of enteric sources of methane and nitrous oxide. Our confidence in the nitrous oxide estimate is low at this time due to calibration issues with the measurement source data.

Table 18 Default input parameters for regional runs of Manure-DNDC.

Input	Default Value		Source
Dairy Infrastructure and management			
Free Stall Barn size	9.7 m ² /cow		SMP CA3B (Site Monitoring Plan for California NAEMS site). Free stall housed 600 cows in a 5,797 m ² area, equivalent to 9.7 m ² per cow.
Amount of flush water used per flush.	20 gallons/cow		Assume that lagoon water is recycled as flush water. Therefore, we assume that each time lagoon water is applied to land that an equivalent amount of fresh water will be used as flush water.
Initial bedding in Free Stalls at beginning of simulation	45 kg/cow		Rough estimate based on general volume of bedding material (needs refinement).
Size of corrals for drylot dairies and turnout areas	42 m ² /cow		Based on scale figure in SMP CA3B
Feed			
	Lactating	Dry Cows	
Dry Matter/day	19.35kg	11.61kg	UC DANR Committee of Experts on Dairy Manure Management Report, September 2003.
Carbon Intake/day	7.74kg	4.64	UC DANR Committee of Experts on Dairy Manure Management Report, September 2003.
Nitrogen Intake/day	0.58kg	0.35kg	UC DANR Committee of Experts on Dairy Manure Management Report, September 2003.
Protein Intake/day	0.62kg	0.37kg	UC DANR Committee of Experts on Dairy Manure Management Report, September 2003.
Default Cropping System: Silage Corn			
Planting Date	May 15 th		
Harvest Date	September 25 th		
Type of Fertilizer	6-20-20 (NH ₄ +PO ₄) and Anhydrous		UCCE Silage Corn Cost Return Study (2001)
Fertilizer rates and application dates	121 kg N/ha on May 15 th , 66 kg N/ha on 6/15, 7/5, and 7/20		
Irrigation (amount and dates)	8.21cm on 3/20 5cm on 6/1, 6/15, 7/5, 7/20, 8/1, 8/15, 8/25 and 9/5		UCCE Silage Corn Cost Study for amounts, dates were selected to spread the irrigation events throughout the growing season.
Tillage (dates and type)	Deep rip (20cm) on 4/15; Disc (10cm) on 4/16 and 9/30		UCCE Silage Corn Cost Return Study (2001), gives pre-plant and post harvest estimates of tillage.

Overall Conclusions and Recommendations

Dairy farms may produce high fluxes of alcohol ($>0.25 \text{ g cow}^{-1} \text{ h}^{-1}$) including methanol and ethanol, and CH_4 ($>12 \text{ g cow}^{-1} \text{ h}^{-1}$) from animals and their fresh manure. Both ethanol and methanol were emitted at average flux rates ranged from 0.25 to $0.70 \text{ g cow}^{-1} \text{ h}^{-1}$ from cows' fresh manure. However, flushing of animal housing has a high potential to reduce alcohol emissions due to their high water solubility.

Enteric fermentation was the main process responsible for production of CH_4 , while fresh manure did not produce noticeable fluxes. Lactating cows and their manure produced more CH_4 , methanol and ethanol than dry cows and manure most likely due to the larger amount of fermentable substrate in both feed and feces. Compared with alcohol and methane emissions, the emissions of VFAs and phenol compounds from dairy cows and their manure were very low, and close to the lower detection limit of the assay and instrumentation. Variation in VFA and phenol concentrations across the three cow groups, as well as low concentrations near the lower detection limit of the assay make further interpretation of trends difficult. Current emission inventories in the San Joaquin Valley in California underestimate alcohol emissions and may overestimate VFA emissions from dairy cow housing considerably. Future research needs to address the mitigation of VOC emissions that occur during fermentation of feedstuff and fresh manure as well as CH_4 from cow digestive processes.

The surface acidifier SBS reduces the ozone forming alcohols, ethanol and methanol, from dairies. This may help reduce smog production in areas such as San Joaquin Valley of California that have many dairies and also do not meet federal regulations for ozone. The San Joaquin Valley Air Pollution Control district has recently adopted Rule 4570, which requires large confined animal facilities to select and implement methods of mitigating VOC emissions from their facilities. The results of the present study suggest that application of an acidifier, such as SBS, may be a very effective technique that dairies can use to reduce emissions of alcohols from waste, which have been shown in previous studies to be the most important VOC type from dairies. While SBS may be an effective mitigation technique in reducing VOCs, it may increase greenhouse gases. In the present study, emission rates of the greenhouse gases N_2O and CH_4 were higher in the SBS treatment group.

An FTIR system was developed to measure concurrently N_2O , CO_2 , CO , N_2O , CH_4 , NH_3 , Hydrocarbon Concentrations. The data were used to make estimations of N_2O flux from dairy dry lot using the flux gradient method. Typical N_2O flux values from the dry lot over this study averaged around $25\text{-}30 \text{ ng/sec m}^2$, which is equivalent to an annual emission of 7.9 to $9.5 \text{ kg N}_2\text{O/ha}$. Ambient N_2O concentrations were observed to be elevated ($>10\%$) just after a rain event, indicating the precipitation patterns may lead to significant temporal and spatial variability in dry lot nitrous oxide emissions.

Ambient N₂O concentrations were observed to be slightly higher above a compost pile than the dry lot. Concentration increased dramatically after the compost pile was disturbed.

Note that with such a volume of data from our FTIR analysis, assessment of all the data for all species measured (H₂O, CO₂, CO, N₂O, CH₄, NH₃, Hydrocarbon) is beyond the scale of this project. However, this data is extremely useful and could yield investigations into the other species other than N₂O measured. The original plan was to collect the FTIR data in 2006. However, due to delays the measurements were not completed until early 2008, leaving essentially no time for use in model validation. We will continue to use these N₂O data for model validation during 2008. In addition, through the funding from this CEC project, we were able to get funding through the CSU ARI program to fund additional N₂O emission measurements using flux chambers and an INNOVA Acoustic Analyzer. These data are being collected in 2007 and 2008 and will be used for model validation in 2008. Future research is needed to utilize the extensive FTIR data set collected for this project. In addition, future consideration should be given to a longer term continuous monitoring of N₂O in an open path format would be able to better define annual variability, lead to less variable calculations in the emission rates and factors, better understanding of the spatial and temporal variability of N₂O emission from dry lots and would improve the utility of the data for validating process models.

The modeling component of this project achieved its main goals of designing and building a process-based modeling tool for estimating GHG emissions from individual dairies or regions with dairies, developing and testing FTIR approaches for measuring N₂O emissions from components of dairies, collecting new emissions data in controlled chambers to improve our understanding of enteric sources of GHG emissions, and building spatial databases for regional model simulations. This modeling effort is attracting more interest and support from the dairy industry, which has funded a project to extend the model to dairies throughout the country. We expect Manure-DNDC will become a useful tool for livestock industry in the coming years after the thorough calibration and validation activities planned for 2008. Further research is needed to perform more extensive model validation to improve our understanding of the accuracy and uncertainties of model estimates. We recommend the following next steps:

1. Collect additional GHG emission data specifically for model validation. Data should be collected using automated chambers (to capture the episodic nature of N₂O emissions). Chamber data can be used to assess the efficacy of using open path FTIR technology for area emission estimates.
2. Perform additional studies on N₂O emissions directly from dairy cows, including testing various feed regimes impact on emissions.
3. Transition the modeling and GIS databases from a research tool to an easy to use decision support system for comprehensive assessment of dairy management impacts on local air quality, water quality and greenhouse gas emissions. Manure-DNDC is designed for detailed

biogeochemical modeling with the flexibility to examine and prioritize a suite of management alternatives for mitigating greenhouse gas emissions.

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Glossary

AB = Assembly Bill
ADG = Average Daily Gain
ATV = All-Terrain Vehicle
BGT = Black Globe Temperature
BW = Body Weight
CARB = California Air Resources Board
CDFA = California Department of Food and Agriculture
CH₄ = Methane
CIMIS = California Irrigation Management Information System
CON = Control
CO₂ = Carbon Dioxide
CPE = Cattle Pen Enclosure
DM = Dry Matter
DMI = Dry Matter Intake
DNDC = DeNitrification-DeComposition model
DWR = Depart of Water Resources
GC = Gas Chromatography
GHG = Greenhouse Gas
GWP = Global Warming Potential
HAR = Harrowing
NAAQS = National Ambient Air Quality Standards
NASS = National Agriculture Statistics Service
NH₃ = Ammonia gas
NO_x = Oxides of Nitrogen
N₂O = Nitrous Oxide
OFP = Ozone Forming Potential
PAS = Photoacoustic Spectroscopy
SBS = Sodium Bisulfate
SCR = Scraping
SJV = San Joaquin Valley
SJVAPCD = San Joaquin Valley Air Pollution Control District
TMR = Total Mixed Ration
USDA = United States Department of Agriculture
VFA = Volatile Fatty Acid
VMTH = Veterinary Medical Teaching Hospital
VOC = Volatile Organic Compound

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