Dairy Operations: An Evaluation and Comparison of Baseline and Potential Mitigation Practices for Emissions Reductions In the San Joaquin Valley

FINAL REPORT

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Disclaimer

The statements and conclusions in this report are those of the Contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material herein is not to be construed as actual or implied endorsement of such products.

NOTE: This project was proposed in response to a request by the California Air Resources Board for a monitoring study to determine the sources and species of ROG emissions from dairy operations. A data set was to be collected that would serve to validate processes that might reduce emissions and provide a broader base of data for facility and regional modeling. After the study was approved and began the initial stages of selecting sites and sampling methods; there were requests from other agencies and researchers to cooperate and add support to make the project larger in scope and extend the time to increase the amount and value of the data collected. One of the secondary objectives of the CARB proposal was to solicit just such augmentation to the original work. The net result of these additions to the project was positive in all respects but one. The additional, related projects are not scheduled to be completed until 2009 or 2010. The terms of the CARB research contract require a draft final report for review by January, 2009 and a final version of the report by May, 2009. A considerable amount of field work remains to be completed and much more data has yet to be analyzed from these related projects. Consequently, only data and results from the original CARB contract work will be reported here. That data comes from the analysis done by Dr. Blake at UC Irvine. The related projects have added air samples analyzed at CSU Fresno, analysis of alcohols, N compounds and greenhouse gasses, sampling and analysis of feed, silage, manure, soils and other materials to correlate with flux rates monitored at the dairy sites. This additional data is not yet complete and cannot be reported here. In several instances, UC Irvine data cannot be completely evaluated until those related projects are complete. A comprehensive report will be prepared by the end of 2009 to include all the data reported here along with the additional results from the related projects.

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The Dairy Sub-committee, formed by CARB and CDFA in 2002 and reconstituted by the SJVAPCD in 2005 became the advisory group for this project. The original proposal and all subsequent revisions described below were suggested and approved by this advisory group. The Dairy Sub-committee members directly and actively involved in this project were:

Public Agency members:
California Air Resources Board: Patrick Gaffney, Michael FitzGibbon and Dale Shimp
California Department of Food and Agriculture: Matt Summers and Rolf Frankenbach
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Table of Contents **Page**

List of Figures Page

List of Tables Page

Glossary of terms, abbreviations, symbols and units

General terms

CARB – California Air Resources Board
CDFA – California Department of Food and Agriculture
CSU Fresno – California State University at Fresno
Dairy sub-committee – A group formed jointly by CARB and CDFA in 2002 that subsequently became the advisory group for this project.
DPAG – Dairy Permitting Advisory Group formed by the SJVAPCD in 2004. Members of the Dairy Sub-committee also participated in this activity.
SJVAPCD – San Joaquin Valley Air Pollution Control District
UC Davis – University of California at Davis
UC Irvine – University of California at Irvine
UNH – University of New Hampshire

Dairy terms

Commodities - Purchased components of the TMR such as cottonseed meal, rolled corn, almond hulls, distillers grain, citrus pulp and other materials to add energy and nutrition to the feed.
Flush lanes – long sloping, hard-surfaced lanes upon which the cows stand when feeding. The lanes are washed with a large volume of water or scraped several times each day to flush manure into various collection and storage areas.
Lagoons – Ponds containing the water from the flush lanes, generally after separation of coarse manure material. Flush water is recycled from the lagoon.
Manure - The combination of urine and feces eliminated by the dairy cows.
Open lots – Corrals, exercise pens and other fenced areas available for the cows adjacent to the barns. Most dairies restrict access to open lots in wet weather.
Silage – Chopped and compressed plant material harvested and stored for use in making the TMR. Silage is usually the largest component of the TMR. Typically made from field corn, it is also made from alfalfa and various small grains and referred to as “grass” or “winter” silage.
TMR - Total mixed ration is the term for the feed mixture made from silage, alfalfa hay and various commodities. TMR is usually mixed at the dairy and delivered from a truck or wagon into a feed bunker. TMR is fed 2-4 times each day. Most dairies employ a nutrition consultant to recommend the specific components of TMR to achieve the desired level of energy and nutrition for the cows as it relates to their condition, the season and the various commodity prices.

Research terms and units

Alcohols – Ethanol, Methanol and Propanol analyzed by UC Irvine and reported as components of ROG in this report
DMS – Di-Methyl Sulfide, a significant component of ROG from some dairy sources.
DMDS – Di-Methyl Di-Sulfide, a significant component of ROG from some dairy sources.

Emissions – In this report, “emissions” is a term used in a general sense to describe the volatile flux of a gas or combination of gasses such as ROG from a surface. The term is not intended to imply an emission rate or emission factor when used in this report.

Flux – In this report, “flux” is the term used to describe volatile transfer across the interface between a surface and an atmosphere. This interface can be either surface to ambient atmosphere or surface to flux chamber atmosphere.

Flux rate – In this report, “flux rate” refers to the quantitative volume of a flux in units of mass per unit area per unit time.

Flux chamber – In this report, “flux chamber” is the field sampling device described in the US-EPA Isolation Flux Chamber Methodology (Appendix D). Flux Chambers used in this study covered an area of 0.1924 m^2 and were flushed with zero air at a rate of 10 liters/minute. Flux chambers used in this project were manufactured by Odotech of Toronto, Canada.

GC-MS – Gas Chromatography with Mass Spectrometry detection. This is the general term for the method of analysis used by UC Irvine to speciate and quantify the components of the air samples collected at the dairy sites.

$\mu g/m^2$/minute – The unit of flux rate used in this study. Micro-grams per square meter per minute.

$\mu g/m^3$ - The unit of mass per unit volume of air. Micro-grams per cubic meter. This is the intermediate step in the conversion of proportional volume such as pptV reported in the UC Irvine analysis to mass per unit of air before the calculation of flux rate.

ROG – In this report, “Reactive Organic Gas” is the sum of volatile organic compounds reported from the UC Irvine analysis that are sufficiently reactive to be considered ozone precursors. In this study, 60 of the 64 gasses in the UC Irvine analyses were summed and reported as ROG. Methane, CO, CO_2 and acetone were excluded from the ROG total though they were reported by UC Irvine. The gasses included in the total of ROG are not equally reactive. Some may result in much more ozone than others. No distinction was made in this study with respect to relative reactivity among the ROG gasses but other contemporary studies are evaluating reactivity with respect to dairy ROG emissions. A complete evaluation of dairy ROG emissions will require the application of the relative reactivity of these components of ROG once it has been determined in future research.

VOC – Volatile Organic Compounds. In this report, “VOC” is used to indicate the total of all volatile organic gas from which ROG is the sub-set of gasses that are considered precursors of ozone.

Zero air – Bottled, compressed gas made up of 80% N_2 and 20% O_2. It is the flush gas for the flux chamber method that eliminates contamination of an air sample by ambient air above the surface being sampled.

Abstract

Dairy operations in California were assumed in 2004 to be major sources of Reactive Organic Gas (ROG) and therefore, ozone formation in the Central Valley. In 2005 this project was proposed to determine the specific sources and components of ROG in emissions from dairies. An advisory group of public agency, industry and academic members was formed to develop the initial plan and supervise revisions in accordance with initial results. Six dairies were selected to be sampled three times each year to evaluate facility and seasonal differences. Ambient air samples were collected initially to identify specific ROG components and develop analytical methods for dairy air samples. The initial data indicated the predominance of alcohols in feed components of dairy ROG emissions and a sampling program was designed to focus on those while also monitoring other dairy ROG sources. The sampling program was conducted by Dr. Charles Krauter at CSU Fresno. The corresponding analytical program was administered by Dr. Donald Blake at UC Irvine. After review of the initial data, in 2006, the advisory group revised the sampling program to reflect the discovery that alcohols from the feeding operations, rather than manure management appeared to be the most significant ROG source. The six dairies were sampled three times from June, 2007 through July, 2008. The highest flux rates were for silage and feed with an average flux rate of 4,229 $\mu g/m^2$/minute from the vertical silage pile face and 19,170 $\mu g/m^2$/minute for loose, disturbed silage used for mixing feed. Fluxes from feed were 15,022 $\mu g/m^2$/min when first placed in the feed bunker, though the rate decreased to 2,929 $\mu g/m^2$/min as it was consumed. Flux rates for the flush lanes were considerably lower with a rate of 353 $\mu g/m^2$/min prior to the flushing operation that decreased further to 21 $\mu g/m^2$/min after the flush. Open lots and exercise corrals were similar to the flush lanes. Areas of the corrals where the manure pack was relatively deep had flux rates of 243 $\mu g/m^2$/min. while the shallow manure pack in the open lots averaged 102 $\mu g/m^2$/min. The anticipated seasonal effects appear to be less significant than expected. Only emissions from the open lots correlate with surface temperatures, increasing in the summer and declining in winter. When the areas represented by each of these operations were applied to the flux values, it became apparent that feed was the dominant (60%) ROG source, followed by the open lots (25%), flush lanes (8%) and silage piles (7%). These proportions were calculated as an example of a fictitious dairy that was a composite of the six sampled facilities. These percentages would vary when calculated from actual fluxes and facility dimensions but feed would probably remain the dominant source of ROG.

After this California Air Resources Board (CARB) supported project began, several related projects were added to the sampling program at the six dairies. Additional sampling and analytical systems were added as well as the collection of data related to nitrogen compounds, lagoon emissions, land application emissions, silage, feed, manure, soil and compost materials. These related projects are still in progress. Only data related to the CARB contract is complete and reported here. A comprehensive report of all projects related to sampling at these six dairies and other sites will be prepared at the end of 2009.

Executive Summary

Background

In 2002, a study group made up of members from state agencies, academic institutions and the diary industry was formed by the California Air Resources Board (CARB) and the California Department of Food and Agriculture (CDFA). This group was known as the Dairy Sub-Committee. Their primary goal was to evaluate existing research to estimate the impact of dairy operations on air quality in California. In 2004, the San Joaquin Valley Air Pollution Control District (SJVAPCD) began the process of permitting dairies in their jurisdiction. Many of the Dairy Sub-Committee members became part of the Dairy Permitting Advisory Group (DPAG) of the SJVAPCD. The primary issue addressed by the DPAG process was the uncertainty regarding dairy emissions of the ozone precursors known as Reactive Organic Gas (ROG). ROG was defined as those Volatile Organic Compounds (VOC) that are active in the atmospheric reaction that forms ozone. The Dairy Sub-Committee, noting the lack of current research in California related to this issue, advocated funding and solicitation of proposals to address the problem. This project is one of the responses to that advocacy. The project proposal mandated an advisory group of industry, public agency and research representatives to oversee the study and suggest changes to increase the relevance of the project. The Dairy Sub-committee remained in that role throughout the project.

Methods

The original, primary objective of this study was to evaluate the potential emission reductions from various methods for handling and managing dairy manure. During the initial year, however, research by Dr. Frank Mitloehner at UC Davis suggested ROG emissions from feeding operations were more significant than those from the manure management processes. This was confirmed by the first flux chamber sampling by CSU Fresno and subsequent analysis by Dr. Blake at UC Irvine. The advisory group reviewed the initial data and recommended revisions to the sampling program. The focus was shifted from ambient samples and dispersion modeling of the whole dairy to more site-specific, flux chamber sampling methods that concentrated on feed and the feeding operations. Flush-lanes, corrals, lagoons and alternative manure management operations continued to be monitored and proved, as suggested by the UCD research, to have significantly lower ROG flux rates compared to the feed and feeding operations.

This CARB funded project was the initial support for what became a much larger study with additional objectives beyond the monitoring of ROG emissions from dairy operations. The additional funding allowed expansion of the regular sampling program from five to six dairies. The focus on ROG by the project advisory group was at the expense of the ammonia, methane and other air quality issues that were included as possible constituents to be sampled in the original proposal. These added, related projects include these other constituents along with more ROG monitoring of additional sources. The initial CARB funding is the only part of the study that has reached the end of its term. Most of the additional projects will be completed in 2009. Consequently, only the data and conclusions from this first ROG study can be reported here. Some supporting data from the other projects will be included as it applies to the CARB project. A comprehensive report will be prepared upon the completion of the related projects that will include the data and results from this project compiled with the additional data from the other studies. That final report will be completed in 2009.

Results

Results from this CARB funded project are primarily from the flux chamber monitoring program developed and conducted by CSU Fresno to provide the analytical program at UC Irvine with air samples. The results of the UCI analysis were correlated with site data to meet the primary objective of characterizing the ROG flux rates from dairy operations and evaluating the variability of those fluxes. Total ROG flux rates were highest for silage. Undisturbed silage had a flux rate average of 4,229 $\mu g/m^2$/minute. The disturbed silage pulled from the pile had an even higher rate, averaging 19,170 $\mu g/m^2$/min. The composition of these ROG fluxes was about 85% alcohols, predominantly ethanol. Feed mixed and delivered to the animals produced similar results. Immediately after placement in the feed bunkers, the flux rate averaged 15,022 $\mu g/m^2$/min but decreased to 2,929 $\mu g/m^2$/min over a period of 6 – 8 hours as it was consumed. Disturbing the feed by sweeping partially consumed material closer to the animal's reach appeared to cause a spike in flux rate. ROG flux rates for manure management procedures were much lower than for feed. The flush-lane rates averaged 353 $\mu g/m^2$/min, prior to the flushing operation, and 21 $\mu g/m^2$/min after the flush. Open lot areas where manure not left in the flush lanes is deposited had flux rates that averaged 102 $\mu g/m^2$/min where the layer of manure was shallow and 243 $\mu g/m^2$/min for the deeper manure pack areas. Variability with respect to season was not apparent except for ROG fluxes from the open lots where there appears to be some correlation with surface temperature. No seasonal differences in the emissions from feed or flush lane operations can be shown with the data from this study.

Conclusions

The monitoring procedures used in this project produced calculated flux rates for a unit area of the process being sampled. While those values can show the ranking of the flux rates for the ROG sources, the calculated flux rate must be multiplied by the area at the dairy represented by the particular operation to determine its actual proportion of the facility's ROG emissions. The areas of each source vary among the facilities as do the flux rates for each, as measured by this study. However, an estimate of the percentages that each of these four sources contributes to the total ROG emissions can be calculated from a composite of the six diaries sampled and the average flux rates from the study. When these flux rates are applied to the dimensions of the composite dairy, the highest flux rate for silage produces the lowest proportion (7%) of the dairy's emissions. Flush lanes are 8%, open lots are 25% and feed is the major source at 60% of emissions. Differences in dairies and the variation in flux rates monitored in this study will produce different percentages for specific facilities but it is likely that the feed material will always be the major component of ROG emissions. Additional data from related projects will be evaluated to include smaller emission sources such as lagoons and solids separation processes as well as better characterization of the variability among different dairies.

INTRODUCTION

This project was conceived from the findings of two different study groups formed to evaluate air quality problems associated with dairy operations in California. The first of these groups was the Dairy Sub-committee organized in 2002 by the California Air Resources Board (CARB) and the California Department of Food and Agriculture (CDFA) and chaired by Dr. Matt Summers of CDFA. The sub-committee was made up of representatives from public agencies (CDFA, CARB, USDA, EPA and SJVAPCD) academic researchers from UC Davis and CSU Fresno, and dairy industry organizations (Western United Dairymen, Dairy CARES, Hilmar Cheese and California Dairy Campaign). The primary goal of the Dairy Sub-committee was to evaluate existing air quality research related to diary operations and recommend new projects needed by the agencies to develop science based regulations. At the same time the Dairy Sub-committee was developing its recommendations, the San Joaquin Valley Air Pollution Control District was beginning to develop a permitting process for dairies in their jurisdiction. A Dairy Permitting Advisory Group (DPAG) was formed and included most of the agency and industry members of the Dairy Sub-committee. The primary issue addressed by DPAG was ozone formation and the role of dairy emissions in the level of ozone precursors known as Reactive Organic Gas (ROG). ROG was defined as volatile organic compounds (VOC) that were reactive in the atmospheric production of ozone. In practice, ROG was all measured VOC with the exclusion of methane, carbon monoxide, carbon dioxide and acetone. This project proposal was initially developed from the findings of the Dairy Sub-committee. As the DPAG process indicated the priority of ROG emissions, the original, blanket proposal that also included ammonia, hydrogen sulfide and other air quality issues was revised by the Dairy Sub-committee to focus on ROG. The original proposal to CARB for this project mentioned those other constituents but the project advisory group mandated the emphasis on ROG sampling/analysis with the others relegated to monitoring that could be done without interference with the ROG work. Additional funding from other sources became available over the course of the project to monitor these other constituents. That data will be reported in a later, more comprehensive report.

This CARB funded project was conducted over the past 36 months though the execution of six specific tasks, described below. Six dairies with different manure management practices and feeding procedures were evaluated over the course of the project. Nearly 600 ROG samples were collected and analyzed at UC Irvine for VOC species over the course of the project. CSU Fresno researchers, under the direction of Dr. Krauter, were responsible for the field work portion of the project including collecting all samples, delivering samples to the IC Irvine laboratory, collecting relevant field data, and conducting additional field work to support the related projects. UC Irvine research group, under the direction of Dr. Blake, analyzed the samples for organic gases and assisted in the analysis and speciation of the collected emissions data.

The related projects, from the additional funding, will continue through 2009 and, in some cases, beyond to collect and analyze additional samples for alcohols, N compounds, silage and feed emissions, alternative lagoon emissions, compost emissions, and land application emissions. Data related to these additional projects from UCI analysis as well as interpretation, correlation and conclusions related to those issues cannot occur until those projects are completed.

MATERIALS and METHODS

Objectives

There was a primary and three secondary objectives in the original proposal, adopted by the Dairy sub-committee. These objectives and their subsequent revisions by the sub-committee in their role as the project advisory group are described below.

Primary Objective:

The primary objective as stated in the project proposal was to monitor and model ROG flux rates at baseline dairies and dairies with alternative manure handling systems to evaluate the potential for emissions reduction. While that objective remained significant, contemporary research at UC Davis by Dr. Frank Mitloehner found higher flux rates from feeding operations than the manure handling processes that were to be studied in this project. Dr. Mitloehner and other members of the advisory group suggested at the end of the initial year that the focus be shifted to feed and feeding operations while continuing to monitor manure management practices. The air samples collected by CSU Fresno and analyzed by UC Irvine were used to calculate flux rates from sources associated with both feeding and manure handling operations. These flux rates are summarized in the results section and the individual samples are listed in Appendix A.

Secondary Objectives:

1. A secondary objective, as stated in the project proposal was to monitor and model ammonia emissions from the tested dairies to evaluate the effect of the alternative practices on ammonia emissions and to improve baseline emission estimates. The GC-MS analytical program at UC Irvine, funded by this CARB project, was not the most efficient or cost effective method for ammonia monitoring, particularly with the emphasis on the feed sources. The advisory group recommended the ammonia sampling and analysis be assigned to a related project with the University of New Hampshire (UNH) to preserve CARB budget resources for the ROG analysis at UCI. A photo-acoustic gas analyzer was suggested by an advisory group member and was evaluated against the ammonia denuder method used by the CSU Fresno research group in a previous fertilizer emissions study. The INNOVA analyzer proved to be equivalent in accuracy to the denuder method for ammonia and had the additional advantage of providing real-time results. The INNOVA subsequently proved to be a useful secondary method of analysis for alcohols and other gases in the related projects. This first related study, funded by Dr. William Salas of UNH from his USDA CSREES grant, enabled INNOVA monitoring of ammonia and several other N compounds from additional sampling at the six regular dairy sites. Results

from that study will be included in the comprehensive report to be completed in 2009.

2. Another secondary objective, as stated in the project proposal was to use the CARB project award to obtain matching funding from the California State University Agricultural Research Initiative (CSU/ARI). The CSU-ARI funding is from a program that requires initial support from an external source which can then be matched. No CSU-ARI support would have been available without this CARB funding. A CSU/ARI project was proposed in 2006 to expand the regular sampling sites from five in the original proposal to six and add other sites to be monitored periodically. The addition of the feed sources was included in this and a subsequent CSU/ARI proposal that funded most of the additional equipment and staff required for those sources. These CSU/ARI projects are scheduled to be completed in 2009 and 2010.

3. The final, secondary objective, as stated in the project proposal was to provide additional data from these dairies to cooperating researchers conducting projects related to ammonia, methane, N_2O, PM, and other factors related to dairy operations. The relevant portions of the budgets for these cooperating projects shared the common field sampling and other costs with the CARB project. In addition to Dr. Salas at UNH, related monitoring projects at these dairy sites were funded by UC Riverside, Dr. Mitloehner at UC Davis, Sustainable Conservation, Engineered Composting Services, and the California Dairy Campaign. This additional funding was also used as match for the CSU/ARI projects described in objective 2. A considerable body of data is being developed by these related studies and part of each agreement is a commitment to share all information from all projects with all cooperating agencies. The complete data set will be made available on a website and the results included in the comprehensive report at the end of 2009.

The objectives of the project were to be met through the specific tasks, listed in the proposal and outlined below in their original form.
Modifications and additions to each of the original tasks, as revised by the project advisory group, are shown in italics below each task.

Task 1. Select at least five dairies to monitor in cooperation with ARB and district staff. Ensure selected dairies are representative of typical conditions and operations.

The additional projects and funding enabled a sixth dairy to be added to those to be sampled on a regular basis for comparison of their different methods of feeding and manure management. The six dairies were chosen with the assistance of several members of the advisory group and the approval of the entire group prior to the beginning of the sampling program. A list and description of each dairy can be found below.

Task 2. Determine and evaluate specific field sampling procedures to accommodate the unique features at each dairy. Prepare field test plan including quality assurance objectives and data handling protocols and sample custody.

The initial year of field work was designed to evaluate alternative sampling methods as well as determine the initial speciation of the dairy ROG emissions. The discovery of the significant alcohol emissions from feeding operations showed the value of this strategy. The downwind-upwind ambient samples proved to be unsuitable for separating emissions from discrete operations. The substitution of flux chamber sampling proved to be a much more viable method.

Task 3. Conduct initial field sampling at each dairy, analyze collected samples and model emissions. Provide summary of results for review by the advisory group.

The regular sampling of six dairies began in early 2006 and continued through summer of 2007. Various sampling methods were tested and refined. In the spring of 2007, a summary of the Year-1 results was prepared and discussed at a series of advisory group meeting. That Year-1 report is attached as Appendix B.

Task 4. Adjust sampling and analytical procedures based on results from the initial sampling periods at each dairy. Revise field test plan.

After discussion of the Year-1 results, a revised sampling plan was submitted to the advisory group. That Year-2 program included not only the CARB sampling but also the complete field program for all the related projects that involved monitoring at the six regular sites. That field plan is described in the following section and in Appendix B.

Task 5. Continue sampling and modeling at each dairy in the second year using consistent procedures on a regular basis to determine the effect of climate, crop season and seasonal dairy practices on emissions.

The Year-2 program was approved by the advisory group in September, 2007 and was implemented in October, 2007. Most of the procedures were included in the spring and summer sampling in 2007 as well and are included in the data where appropriate. The final sampling period for the six regular dairies was completed in July, 2008. Analysis of UC Irvine samples was completed and reported to CSU Fresno in November, 2008.

Task 6. Compare emissions from each dairy operation in the second year of the project to begin to determine differences between potential mitigation practices related to dairy operations. Prepare report on results.

The analysis of the samples taken at the six dairies and analyzed at UCI in Year-2 have been converted from concentrations to unit surface fluxes and are reported in the results section. A great deal of additional flux chamber data will be added to the body of data reported here when the related projects are completed. Correlations between calculated fluxes and other data will be more valid at that time and will be included in the comprehensive report at the end of 2009.

Task 7. If, as anticipated, co-funding is available from CSU-Agricultural Research Initiative or other sources, select additional sites and waste mitigation processes to continue the work started with the initial ARB funding.

Additional funding for related field work and analysis at these six sites and others was secured from CSU/ARI, CEC through UC-Riverside, USDA-CSREES through UNH and UCD, California Dairy Campaign, Engineered Compost Systems and Sustainable Conservation. The data set for all these related projects will be available on a project website beginning in April, 2009. The data will be summarized in the comprehensive report to be prepared upon completion of most of the related projects in December, 2009.

Field Sampling Overview

The original project field sampling plan, developed by the advisory group, relied on collection of ambient upwind and downwind air samples to be analyzed at UCI. Dairy ROG emissions were to be quantified through downwind-upwind measurements from ambient air sample concentration data collected for the various lagoons, corrals, and other dairy emission sources to be evaluated under the project. Samples were collected in standard 6-liter evacuated summa canisters outfitted with regulators to allow time-integrated samples to be collected. Upwind samples were collected at a height of 1 to 2 meters, and downwind samples taken at heights of 1, 2, 5, and 10 meters for dispersion modeling. Sampling periods were to be selected to ensure a high likelihood of consistent wind speed and direction necessary for effective emission flux estimates using the Industrial Source Complex Short Term version 3 (ISC-STv3) steady state Gaussian plume model. Each dairy sampling event was to include a minimum of two sampling periods per day for at least two days. Following sample collection, all canisters were to be immediately shipped to Dr. Blake at UC Irvine for sample analysis and quantification.

This original plan proved to be unsuitable for a variety of reasons:

1. *Wind speed and direction parameters for the ISC model were never achieved in 12 sampling events and several other failed sampling attempts.*
2. *Excessive requirements for the limited amount of GC-MS analysis available in the budget for UC Irvine precluded more intensive sampling at each facility.*

After the evaluation of the unsatisfactory ambient sampling, a number of alternatives were considered and a Year-2 sampling program emphasizing flux chamber sampling was developed and approved by the advisory group.

Quality Assurance Objectives

Under Task 2 of the project, all field sampling, data collection, analysis, and reporting will be designed within a comprehensive Quality Assurance/Quality Control (QA/QC) program. The objectives of the QA/QC program will ensure and document the precision, accuracy, completeness, representativeness, and comparability of collected data.

The QA/QC procedures for the field sampling are included in the Year-2 plan, (Appendix B). The QA/QC program for the UCI analysis was included in the original proposal and is attached in Appendix C.

Sample Coordination and Recording
All samples were to be accounted for from the time of collection until results are verified and reported. Sample custody procedures provide a mechanism for clearly documenting field records, sample labels, a sample master logbook, sample shipment and receipt chain-of-custody, sample handling procedures, and sample preservation protocols.

A series of field log sheets were developed, specific to each sampling operation. These sheets were designed to combine data for the ambient conditions, location details, sampling parameters and all other sampling related to the specific location and date on a single, master sheet. Examples of these log sheets are shown in Appendix D. The primary use of these sample logs will be to coordinate the data from the UC Irvine analysis reported here with other data for the same locations related to the other projects for the comprehensive report.

Calibration Procedures and Frequency
All sampling equipment, sampling canister cleaning equipment, laboratory analytical equipment, instrumentation, and other analytical devices was to be maintained and calibrated according to manufacturer's specifications. All key equipment was regularly calibrated to ensure full and accurate operation. Calibration results will be properly documented and retained. Detailed standard operating procedures for key processes will be provided as part of project reporting.

Calibration procedures for this CARB portion of the overall study are all related to the UC Irvine analytical procedures found in Appendix C. Calibration of field analytical equipment and CSU Fresno procedures for the related projects are detailed in the Year-2 program in Appendix D.

Data Reduction, Validation, and Reporting
All key project field, laboratory, and analysis data was to be stored in appropriate databases or spreadsheets for analysis and documentation. Blank sample analysis, QA analysis, out of range data analysis with qualifiers, and all other relevant data descriptors and qualifiers will be fully documented.

Analyses of the canister samples at UC Irvine were reported in proportional volumetric units, pptV (parts per trillion by Volume). Calculation of ROG flux from this data was a two step operation:

1. Each constituent in the UC Irvine data had to be converted from a volume proportion to a mass in order to accurately sum them for an ROG total.

$$\text{pptV X molecular weight X } 0.0000409 = \mu g/m^3$$

This formula gave a mass value for each constituent per unit volume of air so the sum of the gasses identified as ROG could be expressed as mass for the calculation of flux.

2. Each constituent and the sum, in $\mu g/m^3$ of air, could then be converted to a flux rate by a formula described in the US-EPA Isolation Flux Chamber methodology (Appendix D). The area covered by the particular flux chamber (0.1924 m^2) and the rate of flow of the zero-air flushing gas (10 liters/minute = 0.01 m^3/minute) were required for this calculation.

$$\mu g/m^3 \text{ X } (0.1924\ m^2\ /\ 0.01\ m^3/\text{minute}) = \text{flux rate } \mu g/m^2/\text{minute}$$

All flux rates in tables 3-10 in the results section as well as the individual samples shown in Appendix A were calculated in this manner.

The analytical results from UCI along with conversion steps from the reported concentrations to the flux values reported here will be available on a website to be set up as part of the comprehensive data set for the entire project. The data for the CARB study along with feed, silage, manure, soil and ambient conditions will be available to all participating agencies and researchers on this project website by April, 2009. Additional data will be added to that website as it is developed. A final report of the comprehensive project will be prepared at the end of 2009.

Sampling Sites

The original proposal called for five dairies to be selected for a regular sampling program over the term of the project. The addition of the related projects enabled the regular sampling program to be expanded to six dairies. The sampling periods were chosen by the advisory group to reflect three different times during the season when both the climate and the operations at the diaries would be different from the other two sampling periods of the Year-2 program.

The regular sampling periods were selected as:
Winter = January – March
Early Summer = May – July
Fall = September – November

The dairies were originally selected to have different manure handling systems. As discussed above, ROG from the feeding operations was shown to be more significant and so the focus of the study was altered to emphasize feed and silage while still monitoring emissions from the manure management systems. Fortunately, the six dairies were sufficiently different with respect to silage, commodities, feeding schedule and feed management to be a representative sample of feeding practices across the dairy industry. Characterization of the feed and feeding practices involves more sampling and records with regard to the materials and ration. Most of this characterization is still being done as part of the continuing projects and will be documented in detail in the report at the end of 2009.

One of the first suggestions from the industry representatives in the advisory group was to preserve the privacy of the cooperating dairies. Approximately a dozen dairymen were contacted and considered for the regular sampling program. Each was reluctant until anonymity was promised. Several questioned the ability of the research group to maintain their privacy. Each cooperating dairy operation was given the following assurance:

1. The name of the dairy would not appear in any reports or published documents related to the project.
2. The address or location of the dairy would not appear in any reports or publications beyond identifying all six as being in the San Joaquin Valley.
3. All records such as feed rations, lab reports and other documents obtained from the dairy for the purpose of supporting the project would be redacted to remove identifying information.
4. Each dairy would be identified by a letter (A – F)
5. The published reports would state that the dairies were located from Tulare County north to Stanislaus County.
6. Each dairy operator would be furnished with all data collected from that particular operation and would be given a draft of the final report to review prior to publishing. (This will apply to the final, comprehensive report to be published at completion of all related projects rather than this CARB report).

Dairy Descriptions

The six dairies selected for the regular sampling, designated by letter, and their operational characteristics are these:

A. A free-stall, flush-lane dairy milking 2000 cows with 350 dry cows and 500 heifers. The manure is flushed into a processing pit, over a sloping screen and into one of two treatment lagoons. Effluent flows from the treatment lagoon to a large storage lagoon where it is mixed with fresh water and applied to surrounding cropland. The separated solids are used for bedding in the free-stalls. Lane flushing, corral scraping and other maintenance operations are more frequent than at the average dairy. The feed storage and mixing operations are carried out on site.

B. A 3000 cow dairy with 500 dry cows and no heifers. The manure is flushed into small pits at the end of the barns, pumped over a sloping screen and into a single large lagoon. The barns are a free-stall system with cow mats for bedding instead of composted manure. Effluent from the lagoon is pumped into the irrigation pipeline system where it mixes with irrigation water and is applied to surrounding cropland. Also, lagoon effluent is separated from solids via the liquid-solid separator. Corrals are scraped infrequently. Feed storage and mixing operations are done at another location approximately 1km from the site.

C. A free-stall, flush-lane dairy milking 525 cows with 150 dry cows and heifers. The manure is flushed into a small processing pit, over a sloping screen and into a series of four treatment lagoons. The volume of the lagoons is very large for the animal population and the organic loading of the lagoons is very low. Each lagoon has several circulators that operate continuously. The lagoon environment is such that photosynthetic microbes are prevalent, giving the lagoon a purple/red color. The effluent from the final lagoon in the series is used as irrigation on 130 acres of pasture for the dry cows and heifers and is also delivered to a neighboring farm for production of forage and other crops. The feed storage and mixing operations are carried out on site.

D. A free-stall, flush-lane dairy milking 3700 cows with no dry cows or heifers on site. The manure is flushed into a large processing pit, over a series of sloping screens, through two treatment lagoons and finally into a large storage lagoon. The lagoon system is doubled so that half the effluent from the separation screens is processed in each of two series of treatment lagoons. Both sets of treatment lagoons feed into the large storage lagoon. All treatment lagoons and the storage lagoon have several circulators that run continuously. The separated solids are used for bedding in the free-stalls. The effluent from the storage lagoon is pumped onto cropland when needed for fertilization of the 880 acres of forage. A nutrient management consultant monitors the soil, crop and lagoon effluent to determine the optimum use of effluent for crop nutrition and to avoid N leaching problems. The feed storage and mixing operations are carried out on site.

E. A free-stall dairy that utilizes a vacuum truck to collect the undiluted manure slurry from lanes twice each day. The dairy milks 1000 cows with 200 dry cows and heifers. The manure slurry is pumped from the truck to a plug-flow digester with a residence time of approximately 21 days. The gas from the digester is used to power a 100 kW generator. Effluent and solids from the digester are separated using a screw press with the solids used for bedding and the liquid stored in a lagoon for use on surrounding orchards and cropland. In 2007, the free-stall beds were converted to cow mats as opposed to composted manure beds. The feed storage and mixing operations are carried out on site.

F. A free-stall dairy with lanes similar to a flush-lane system. The dairy milks 2500 cows with no dry cows and no heifers on site. The cows are kept in the free-stalls with very small open lots. This dairy utilizes water mattresses in the free-stall barn as opposed to composted manure bedding. The lanes are not flushed as is the usual practice in similar operations. Undiluted manure slurry in the lanes is scraped into small pits at the center and end of the free-stall barns. The slurry then drains to large holding pits in between the free-stall barns without being flushed with a large volume of water. The dairy is surrounded by extensive cropland. The manure slurry from the storage pit is pumped into a large tank-trailer, hauled to a field and the slurry is injected 20cm below the surface of the soil. The feed storage and mixing operations are carried out on site.

Regular Sampling Program (Year-2)

Tasks 2 and 3 of the proposal established the first year's (Year-1) sampling program once the six dairies were selected. That program was primarily to collect initial data for speciation of dairy ROG and to evaluate various sampling and analytical methods to be validated and used in the final year (Year-2) of the study. A Year-1 report was prepared in the spring of 2007 and submitted to CARB in July. That report is attached as Appendix B. Prior to submission, a draft was provided to the advisory group for discussion of the changes in the sampling program for Year-2 as required for Task 4.

After several meetings, the following modified sampling program was approved by the advisory group and implemented for the fall, 2007 sampling period.

Note: This plan includes all sampling for all related projects. Only samples designated "UC Irvine" pertain to this CARB project and the data reported below. Data from the other sources listed will be added to the CARB/UC Irvine data in the comprehensive report at the end of 2009.

The Year-2 monitoring plan proposed in the Annual Report submitted to the ARB Research Division in May, 2007 was modified after discussions with the ARB staff, the local air district staff and the advisory group at the July 12, 2007 meeting. After input from the advisory group and further discussions with the ARB staff, several changes to the original monitoring plan were adopted. There were three significant areas where the plan was modified:

1. The ambient sampling that requires specific wind conditions and consumes at least six canisters and subsequent GC-MS analysis at both UC Irvine and CSU Fresno was eliminated from the regular sampling program. It was found to be impossible to obtain the required wind conditions at each dairy for each of the sampling periods. Under the best conditions, this monitoring/modeling only differentiates between emissions from animal housing vs. lagoons. These results, from uncertain modeling conditions, consumed nearly half of the canisters and analytical activity for results of limited value. The unexpectedly significant emissions of alcohols from feed and fresh manure (see item 2 below) will require additional canisters and GC-MS analysis for documentation. The elimination of the regular ambient sampling will enable the re-direction of those resources to the more critical feed and silage monitoring. Ambient downwind-upwind sampling will be added, when wind conditions warrant, to the special sampling program discussed below in item 3.

2. The most significant new information from the Year-1 data is the documentation of significant emissions of alcohols, particularly from feed and silage but also from fresh manure. In some instances, the two dominant alcohols, ethanol and methanol, comprise well over 90% of the total monitored ROG emissions. The original monitoring plan did not include sufficient sampling to adequately document the emissions from those sources, particularly with regard to their spatial and temporal variability. After discussion in the Dairy Sub-committee and consultation with the ARB staff, the focus of the sampling plan has been shifted to these sources of alcohols. Additional canisters and analysis at UCI and CSU Fresno will be devoted to silage and Total Mixed Ration.

3. The regular monitoring of the six dairies as described in the original proposal will be supplemented by additional sampling between the scheduled sampling periods. More intensive sampling of alcohol sources to better characterize variability, additional feed components and ambient sampling when wind conditions are suitable will be done on two of the six dairies as the opportunities

are presented. Additional monitoring of emissions from lagoons and land applications of lagoon effluent will also be done when possible, primarily for N compounds but the full suite of ROG's will also be monitored.

The modified Year-2 monitoring program for the regular sampling of the six dairies is shown in Table 1 and the special sampling program is shown in Table 2. These were approved by the CARB staff and the project advisory group for the monitoring period scheduled for September/October, 2007, continued through January/February, 2008 and May/July, 2008.

Table 1. Modified Year-2 monitoring program adopted for Fall-07. This monitoring program, after approval by ARB and the project advisory group was used at the six dairies for the regular sampling and analysis from September/October, 2007, through January/February, 2008 and May/June, 2008.

CSUF Dairy Flux Chamber Sampling Sources and Analytical Methods- Year 2

Proposed Sampling Program at Each Dairy- Routine Sampling (6 Dairies) (Number of Samples)								
Source	**Location #**	**Analytical Method**				**Additional Tests**		
		Innova 1412	**UCI Can**	**CSUF Can**	**TO-17 Tube**	**Lab Samples**	**Silage Density**	**Silage Aerobic Stability**
Feed Sources								
Total Mixed Ration (0.5 h Post Placement- Not Consumed)	1 & 2	2	1	1	1	2	-	-
Total Mixed Ration (~6 h Post Placement- Consumed)	3 & 4	2	1	1	1	2	-	-
Total Mixed Ration (~6 h Post Placement- Not Consumed)	5 & 6	2	1	1	1	2	-	-
Silage Pile Disturbed Face	7 & 8	2	1	1	1	2	-	-
Silage Pile Vertical Undisturbed Face	9 & 10	2	1	1	1	2	4	2
Field Blank	11	1	1	1	1	-	-	-
Media Blank	-	1	1	1	-	-	-	-
Total Feed Sources (Each Dairy)		**12**	**7**	**7**	**6**	**10**	**4**	**2**
TOTAL Feed Sources (6 Dairies)		**72**	**42**	**42**	**36**	**60**	**24**	**12**
Manure Sources								
Open Lot/Corral (Deep Manure Pack)	1 & 2	2	1	1	1	2	-	-
Open Lot/Corral (Shallow Manure Pack)	3 & 4	2	1	1	1	2	-	-
Flush Lane (Pre-Flush)	5 & 6	2	1	1	1	2	-	-
Flush Lane (Post-Flush)	7 & 8	2	-	1	-	2	-	-
Bedding	9 & 10	2	-	1	-	2	-	-
Field Blank	11	1	1	1	1	-	-	-
Media Blank	-	1	1	1	-	-	-	-
Total Manure Sources (Each Dairy)		**12**	**5**	**7**	**4**	**10**	**0**	**0**
TOTAL Manure Sources (6 Dairies)		**72**	**30**	**42**	**24**	**60**	**0**	**0**
Total Feed & Manure Sources (Each Dairy)		**24**	**12**	**14**	**10**	**20**	**4**	**2**
TOTAL Feed & Manure Sources (6 Dairies)		**144**	**72**	**84**	**60**	**120**	**24**	**12**

Table 2. Special Sampling program proposed for Year-2. This monitoring program was conducted at two of the six dairies between the scheduled sampling periods. Most of this activity was conducted for the related projects but the UCI data is shown in the Results section of this report.

CSU Fresno Dairy Flux Chamber Sampling Sources and Analytical Methods- Year 2

Proposed Sampling Program at 2 Dairies- Special Sampling (Number of Samples)							
Feed Source	**Analytical Method**				**Additional Tests**		
	Innova 1412	**UCI Can**	**CSUF Can**	**TO-17 Tube**	**Lab Samples**	**Silage Density**	**Silage Aerobic Stability**
Silage Pile							
Silage Pile Disturbed Face	2	2	2	1	2	-	-
Silage Pile Vertical Undisturbed Face	2	2	2	1	2	4	2
Main Commodities							
1-	2	1	1	1	1	-	-
2-	2	1	1	1	1	-	-
3-	2	1	1	1	1	-	-
Total Mixed Ration (TMR)							
TMR +0.5 h Post Placement (Not Consumed)	2	2	2	1	-	-	-
TMR +1.0 h Post Placement (Consumed)	2	2	2	1	-	-	-
TMR +2.0 h Post Placement (Consumed)	2	2	2	1	-	-	-
TMR +3.0 h Post Placement (Consumed)	2	2	2	1	-	-	-
TMR +4.0 h Post Placement (Consumed)	2	2	2	1	-	-	-
TMR +5.0 h Post Placement (Consumed)	2	2	2	1	-	-	-
TMR +6.0 h Post Placement (Consumed)	2	2	2	1	-	-	-
Total (Each Dairy)	**24**	**21**	**21**	**12**	**7**	**4**	**2**
TOTAL (2 Dairies)	**48**	**42**	**42**	**24**	**14**	**8**	**4**

In addition to comments and suggestions from the advisory group that generated the modified programs described above, there were a number of questions related to the documentation of the sampling and the dairy operations. A summary of the flux chamber procedures as applied to the sampling locations at these dairies follows this section. These photos and descriptions illustrate the application of the US-EPA Isolation Flux Chamber methodology to these specific monitoring sites. More detailed descriptions of the flux chamber methodology as well as examples of the forms used to document the sampling locations are attached as Appendix D.

Figure 1. Flux chamber sampling of an open lot area at Dairy B. The canister sampling the chamber on the left was analyzed by GC/MS for data reported below. The gas analyzer in the cart and the ammonia denuder on the top of the chamber on the right are sampling for data to be included later in the comprehensive report.

The flux chamber is placed on the surface to be monitored with care to disturb the surface material as little as possible. A tight seal is not required because of the continuous flow (10 L/minute) of sweep air into the chamber, resulting in a positive flow out of the chamber through both 1 cm vents in the top and gaps at the bottom of the chamber. The sweep air is commercially available “zero-air” (80% N_2 plus 20% O_2) in the cylinder at the center of Figure 1. The chamber is flushed for 30 minutes prior to any sampling to eliminate ambient air trapped as the chamber was placed on the surface. After the 30 minute conditioning period, various samples can be taken for another 30 minutes before significant changes in the surface conditions could occur due to the enclosed atmosphere. Initial temperature measurements are recorded for the ambient air and surface as well as the air and surface inside the chamber. The ambient and chamber temperatures are recorded again at the time of sampling. Flux sampling of the open lots was done in this manner; followed by manure/soil samples collected where the chambers were placed.

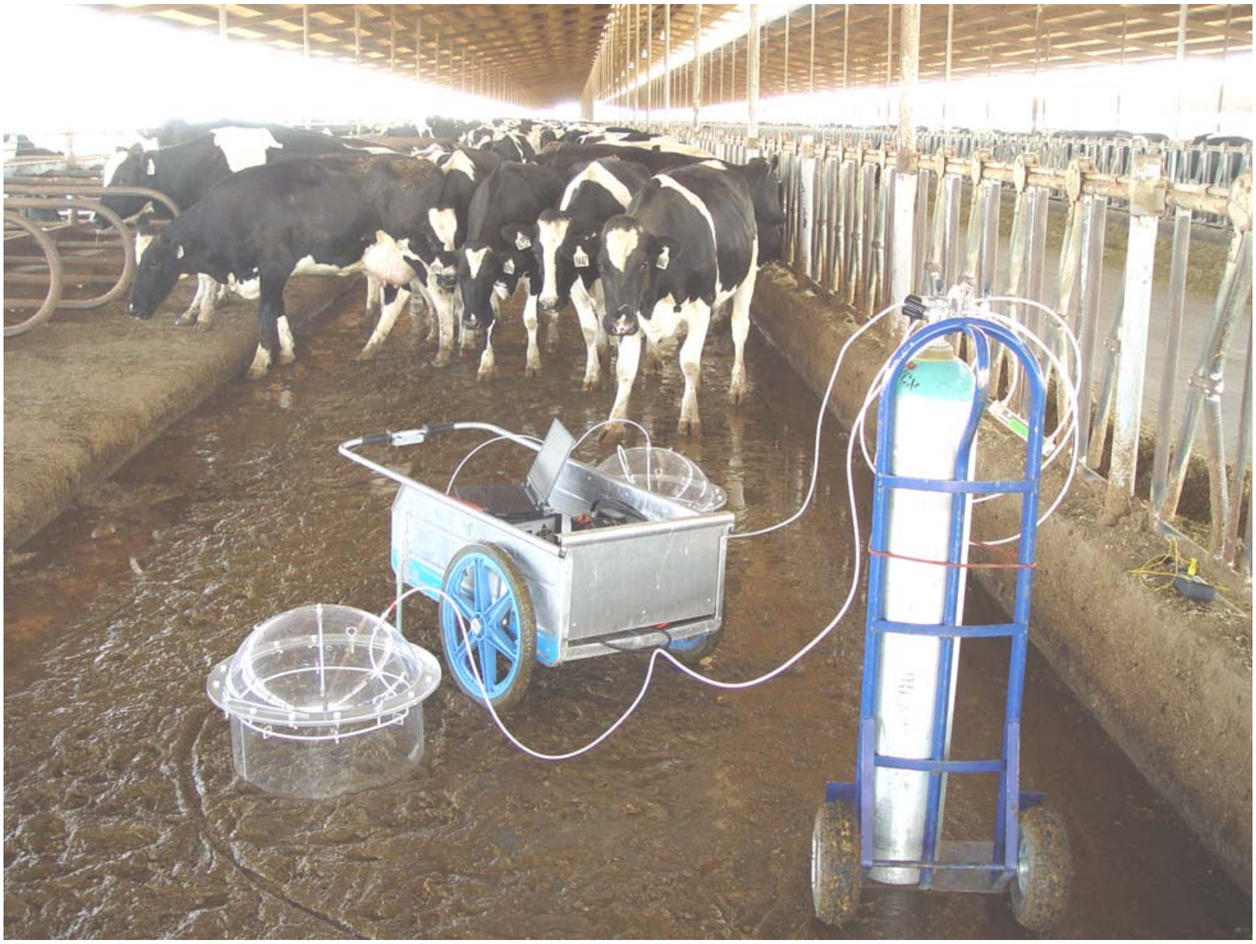


Figure 2. Flux chambers during the conditioning period prior to sampling on a flush lane at Dairy B.

Sampling of the flush lanes began when the cows were feeding and ruminating prior to flushing so that the manure/urine slurry was relatively thick in the lane as shown in Figure 2. The one-hour monitoring period was timed to occur just prior to a flush so the exclusion of the cows from the sampling area would not reduce the amount of manure to be sampled below what would normally be found there in the 3 hours prior to the flush. Once the Pre-Flush samples were collected, the lane was flushed and the chambers were set up at the same location. That often coincided with the cows being milked so the barn was empty and no manure was deposited in the lane during the one-hour sampling period. The flushing cycles were from 6 to 12 hours apart so it appeared this monitoring program was appropriate to determine the beginning and ending conditions of the cycle. Deposition of manure was continuous once the cows returned from milking so an average of the Pre-flush and Post-flush emissions should give a reasonably accurate picture of the flush lane emissions during the cycle.

Figure 3. Flux chambers sampling Total Mixed Ration at Dairy A. This is an intermediate sample, a few hours after placement of the feed, as shown by the absence of nearly half of the TMR and the disturbed top of the pile of feed.

Monitoring the TMR with the flux chambers required considerable care and method development. The feed is delivered from a large truck or wagon 2 – 4 times each day. It was apparent from the initial sampling that the TMR was both a significant and variable source. Chambers were placed on the TMR just after it was delivered to the bunker. The conditioning period for the chambers precluded any sampling prior to 30 minutes post-placement so this first sample is considered the initial value. It was apparent that the emission rate decreased as the TMR was both consumed and exposed to the air over the period of about 6 hours that it was in the bunker. Sampling for UCI analysis took place at the beginning and on the residue remaining after 6 hours. Sampling was also done on the surface of the bunker after the TMR had been consumed or swept up prior to the subsequent feeding operation. Some TMR sampling was done between 30 minutes and 6 hours for the special sampling to be reported in the comprehensive report. Portions of that intermediate data are shown in Figures 6 and 7 to illustrate the decrease in emissions over time from the TMR.

Figure 4. Flux chamber sampling of silage at Dairy C. Initial sampling of “disturbed” silage pulled down from the pile, shown by the two chambers on the right of the photo, indicated very high emissions of alcohols from that source, under these conditions. Sampling the relatively larger surface of the “undisturbed” silage of the pile face required a frame to hold the chamber against the vertical face shown by the two chambers on the left. Canisters for GC/MS analysis are on the ground at the right-center, near the Zero-air cylinder and flux chambers on the small pile of disturbed silage.

Silage as described in the results section below needed to be monitored in two forms. The compacted, vertical face of the silage pile was very dense and required the chambers to be held against the surface by a rack constructed for that purpose. There was also an amount of silage pulled loose from the face by the equipment used to mix the TMR. That disturbed silage had a lower density and appeared to be more biologically active. Chambers could be placed on this loose silage at the base of the pile face to determine the differences in emission rates from the two forms of silage. Core samples were taken from the face at the location of the undisturbed samples and analyzed for composition and density.

Figure 5. Flux chamber field blank at Dairy F. The flux chamber is placed on a clean, Teflon sheet on the floor of the equipment trailer; then conditioned and sampled by the same procedures used to collect samples from dairy sources. Here the chamber is being conditioned to determine a field blank immediately after sampling TMR at Dairy F.

A field blank was collected at least once each day, following the sampling procedures described above. A Teflon sheet was cleaned with distilled water, wiped dry and placed on the bed of the truck or equipment trailer while parked in the location of the most recent sampling procedure. The chamber was conditioned with sweep air and then sampled by a UCI canister as well as the other methods used for that day's data collection. In addition to the field blanks, a media blank was also prepared by filling the canister with the zero-air used for sweeping the chamber and sent to the lab for analysis. The media blanks were prepared at the same time the field blanks were collected. Field blank and media blank data can be found on the project website. Data reported in Tables 2 – 10 of this report have been corrected by subtraction of the appropriate blank.

RESULTS

Over the period from June, 2006 through the end of the regular sampling period in July, 2008, a total of 556 air samples were collected in 2 liter canisters and analyzed by Dr. Donald Blake at UC Irvine. The first 57 of these were ambient air samples to be used for speciation of dairy ROG emissions and eventually downwind-upwind differences for dispersion modeling. These ambient samples were successful in confirming the contemporary research at UC Davis showing the predominance of alcohols, particularly ethanol, in dairy emissions. Modeling downwind-upwind samples to calculate flux rates requires consistent wind direction and a minimum wind speed of 1 m/sec. The consistent wind direction could sometimes be obtained with some difficulty but the consistent minimum wind speed was never achieved in 12 attempts.

The advisory group's recommendation to focus on feeding operations required a method of monitoring that was more specific than downwind-upwind sampling could provide, even with appropriate wind conditions. The EPA Isolation Flux Chamber method (described in Appendix D) proved to be much more suitable in obtaining emission fluxes for specific locations and surfaces at the dairies. A number of flux chamber samples were collected in Year-1 and summarized for the advisory group in April, 2007. After comparing the flux chamber results with the unsatisfactory downwind-upwind data, the advisory committee decided to change the major sampling effort to flux chamber measurements and increase the emphasis on operations related to feeding while still monitoring manure management in Year-2.

In the Year-2 program, the sampling for the CARB portion of the project is designated as the UCI Can samples in Table 1. A more detailed evaluation of feed and silage also used UCI Can samples to study silage variability and the feeding operation in more detail. The special sampling is described in Table 2 and the data from the UCI Can samples is reported below. Comprehensive evaluation will not be possible until the completion of related projects later in 2009.

The regular sampling program, designated as the Year-2 program, began in the fall of 2007 and was completed in summer of 2008. The UC Irvine/CARB portion of that program included 78 samples from silage, 144 samples of feed (TMR), 91 samples from flush lanes, 64 samples from open lots or corrals, and 102 samples for field and media blanks. Results reported below, with the exception of the ambient samples in Appendix A, Table A6 are corrected by the subtraction of an appropriate field blank for that day. Some samples taken prior to the beginning of the Year-2 program did not have UC Irvine field blanks for corrections and are not reported here. Data from the related projects may provide adequate QC for these samples so they can be reported later.

The average flux rates for each of the four dairy operations that made up the regular sampling program during the Year-2 period of summer, 2007 through summer, 2008 are shown in Tables 3 through 8 and summarized in Table 10. These are the average flux rates for all dairies and dates. Table 10 indicates the relative differences among the four dairy sources of feed, the Total Mixed Ration, flush lanes and open lots. The individual analyses averaged for the tables in this section are shown in Appendix A. While each sample taken was analyzed for all identified gasses by UC Irvine, most samples included only a few components in significant quantities. The alcohols mentioned above made up the major portion of nearly all samples from each operation. A few others such as acetaldehyde, di-methyl sulfide, (DMS) and di-methyl-disulfide were sometimes as much as 1% - 15% of some samples. Two of the dairies (A and D) included cull citrus pulp in their TMR with the result that significant amounts of limonene were found in their TMR and manure samples. In order to reduce complexity in the tables, only the significant components of the fluxes, the alcohols, acetaldehyde, DMS and limonene are shown in the results tables. The remaining ROG components analyzed by UC Irvine were nearly always in trace concentrations, at most and contributed less than 1% to the total ROG flux. The complete analysis of each UC Irvine sample including the trace components will be reported on the project website.

Silage Flux Rates

The highest flux rates monitored in the study were from the compressed and fermented forage known as silage. Silage is generally the largest component of the Total Mixed Ration that is made up at the dairy and fed to the animals. It is 40% - 65% of the TMR and provides both energy and nutrition. Silage is most often made from corn grown near the dairy. It is harvested in early fall by chopping the entire plant just as it reaches maturity. The chopped plant material is piled at the dairy, compacted and covered. The material ferments and, if compacted sufficiently, the interior of the pile will be anaerobic to the point that lactic acid fermentation will lower the pH until no further microbial activity can occur. In this form the silage can be stored for several months to provide feed for the cows through the winter and spring when their energy and nutrition requirements are highest.

The silage emissions monitored in this study were from both the compressed, undisturbed silage at the “face” of the covered pile, Table 4, and the loose silage pulled down from the face to be used for making up the next TMR to be fed. The disturbed silage data is shown in Table 3. The flux rates for disturbed material are higher than the undisturbed silage piles by a factor of 5. This is most likely due to the rapid fermentation and other microbial activity that would be stimulated when the compressed, anaerobic material is pulled loose and exposed to air. The very high percentage of ethanol from fermentation may be an indication that this is occurring. The variability seen in emissions from disturbed material, compared to the more consistent emissions from the undisturbed silage in Table 4 is an indication of differences in both silage composition and quality. A less compacted silage pile will be less anaerobic and may degenerate more rapidly when exposed to air. This variability will occur in both disturbed and undisturbed silage but is likely to most prevalent when the material is aerated by the feeding equipment. The high levels of DMS are possibly indications of spoilage related to high protein silage. Ammonia and other N compound emissions as well as silage composition and density were monitored for a related study and those results should provide considerably more detailed evaluation of silage quality vs. flux rates in the later report.

There is considerable variation among the six dairies with regard to silage flux rates shown in Tables 3 and 4. Corn silage is most common but dairies B and F also made silage from small grains such as wheat and barley. This “winter silage” has a different protein and energy content and would produce different emissions of alcohol and other constituents. It is also a more coarse material and more difficult to compress so it may degrade more rapidly. Emissions from the different types of silage will be separated in more detail when the data from the related projects is complete and reported.

Potential for emission reductions related to silage management might include minimizing the disturbance of the silage by only pulling sufficient material from the pile to make up the current feed mix. In spite of the high flux rates from silage, it is a relatively small area compared to the rest of the dairy and complicated changes in silage management may not have as much potential to contribute to the overall emissions of ROG from a dairy.

Table 3. Average flux rates for “disturbed silage” material pulled loose from the pile face for use in the next mixed ration. Individual data averaged for this table can be found in Appendix A, Table A1. Values are in $\mu g/m^2$/minute and are corrected by the subtraction of Field Blank values.

	Ambient Temperature (degrees C)										
Dairy Averages	Surface	Air	**Total ROG**	Ethanol	Methanol	**Total Alcohols**	**Total Alcohols**	Acetaldehyde	d-Limonene	DMDS	DMS
A	25.7	22.5	19,018	13,001	1,383	14,407	80%	480	287	1	3,776
B	22.1	15.4	2,961	2,558	325	2,892	98%	32	3	1	34
C	24.6	18.8	36,192	34,828	555	35,401	93%	303	9	1	451
D	27.5	20.5	18,620	8,810	459	9,283	84%	41	4	2	9,266
E	27.1	18.4	13,789	10,440	555	11,004	78%	76	1	1	2,636
F	19.4	19.5	20,252	7,111	513	7,637	75%	321	0	1	12,287

Table 4. Average flux rates for "undisturbed silage" material still compacted in the exposed face of the pile. Individual data averaged for this table can be found in Appendix A, Table A2. Values are in μg/m^2/minute and are corrected by the subtraction of Field Blank values.

Dairy Averages	Ambient Temperature (degrees C) Surface	Air	**Total ROG**	Ethanol	Methanol	**Total Alcohols**	**Total Alcohols**	Acetaldehyde	d-Limonene	DMDS	DMS
A	27.0	21.4	4,848	3,575	573	4,167	88%	192	11	1	471
B	22.2	17.5	5,577	4,540	282	4,823	86%	16	1	1	738
C	23.8	17.2	5,368	3,605	496	4,107	79%	152	5	1	1,095
D	26.2	16.7	6,124	4,439	697	5,198	85%	665	18	0	239
E	21.5	16.8	2,636	1,798	294	2,094	84%	24	2	0	513
F	19.9	20.7	1,905	1,542	203	1,745	91%	53	0	1	106

Total Mixed Ration and Feed Materials Flux Rates

The general term for the material fed to the dairy herd is "Total Mixed Ration" referred to here as TMR. The TMR is usually made up from components at the dairy though some may truck it in from another facility as is done at Dairy B. The TMR is mixed from silage and alfalfa hay with various commodities such as distiller's grain from ethanol production, cotton seed meal, almond hulls and other commodities that can provide energy and nutrition. Most dairies employ a consulting nutritionist to recommend the most economical components available to provide the energy and nutrition needed for the cows. The TMR is mixed and fed generally twice each day in a bunker or trough so the cows can eat when they choose. TMR is usually consumed in 6-8 hours. Dairies scrape or sweep the remaining feed after about 5 hours so the cows can reach it more easily from the flush lane. This practice may affect ROG emissions as seen in the data below.

ROG emissions were monitored by flux chambers on the TMR immediately after it was placed in the bunker. The flux chamber procedure requires 30 minutes before sampling can take place (see Appendix D) so the flux rates could not be measured until that time. As the cows consumed the feed, the amount decreased and the TMR appeared to change as it dried. As was observed with silage, disturbing the material appeared to stimulate emission of ROG. The mixing and delivery of TMR with its large percentage of silage would be expected to produce a spike of emissions. The advisory committee anticipated this and included further sampling of the TMR at 6 hours post-placement for the Year-2 program. When possible, a sample was taken of the bunker surface after the TMR was completely consumed. This was often done 6 hours post placement when most of the dairies would sweep the remaining TMR to a small pile nearer the flush lane. The 6 hour TMR sample and the "6 hour consumed" sample could be taken simultaneously.

The Year-2 TMR flux rates for the post-placement time periods are shown in Table 5 and the averages for each dairy monitored are in Table 6. The magnitude and variability of TMR flux rates are the most significant features of these tables. The rates are highest just after feed placement as anticipated and show a significant decrease at 1.5 hours. The flux rates at 6 hours increase to about twice the level at 1.5 hours though the bunker surface when the feed is consumed is decreased. The increase in ROG flux rates at 6 hours occurred primarily at Dairies A, B, C, and D while Dairies E and F show a continuing reduction in emissions over time (see Table A3 in Appendix A). Those first four dairies scrape and sweep the TMR more frequently and it may be that disturbing the feed stimulates ROG emissions as it appears to do with silage.

The special sampling described in the Year-2 program added more frequent monitoring of TMR at Dairies A and B in addition to the regular sampling reported here. Flux chambers were used to continuously monitor the feed from placement until it was consumed. Data from the special sampling of this related project will be included in the comprehensive report and should better characterize the relationship between TMR management and flux rate. Some UC Irvine samples and analysis was included in this special sampling program. While the related project is not yet completed, the UC Irvine analysis is finished and the results of five monitoring periods are graphed in Figure 6 for total ROG and Figure 7 for alcohols. The comprehensive report will include this data along with other sampling and supporting information to better characterized the changes in TMR fluxes with time.

Table 5. Average TMR flux rates for all dairies sampled compared to elapsed time from placement in the feed bunker. The 1.5 hour values were only taken in spring, 2007 and do not correspond to all of the 0.5 and 6 hour post-placement values. The 6 hour post-placement values may, in many cases include sweeping or scraping of the TMR about 4-6 hours after placement, the 1.5 hour samples do not. Values labeled “consumed” are the feed bunker surface after the TMR was consumed. Individual data averaged for this table can be found in Appendix A, Table A3. Values are in μg/m^2/minute and are corrected by the subtraction of Field Blank values.

	Total ROG	Ethanol	Methanol	**Total Alcohols**	**Total Alcohols**	Acetaldehyde	d-Limonene	DMDS	DMS
Total Mixed Ration (0.5 h Post Placement)	15,022	11,668	1,460	13,141	86%	336	584	26	831
Total Mixed Ration (6 h Post Placement)	10,582	7,747	1,591	9,350	87%	469	557	9	152
Total Mixed Ration (6+h Post: consumed)	2,929	2,289	389	2,683	89%	106	102	3	32
Total Mixed Ration (1.5 h Post Placement)*	4,507	3,394	547	3,941	90%	15	459	34	12

*sampled spring, 2007 only- see comments in text

Table 6. Average TMR flux rates for each dairy sampled. Values are averages of all samples taken over the feeding period when TMR was present. Individual data averaged for this table can be found in Appendix A, Table A3. Values are in $\mu g/m^2$/minute and are corrected by the subtraction of Field Blank values.

Dairy	Ambient Temperature (degrees C) Surface	Air	**Total ROG**	Ethanol	Methanol	**Total Alcohols**	**Total Alcohols**	Acetaldehyde	d-Limonene	DMDS	DMS
A	13.9	13.7	9,674	5,356	2,074	7,440	76%	275	1,772	12	85
B	19.9	18.7	7,445	5,127	1,257	6,391	90%	304	2	28	679
C	24.0	17.1	15,549	14,376	602	14,983	95%	314	26	6	187
D	22.9	20.2	10,487	8,165	1,078	9,256	87%	326	641	8	169
E	19.4	20.1	5,781	4,778	432	5,214	90%	142	2	20	368
F	21.1	22.7	3,383	2,591	550	3,150	93%	103	1	27	96

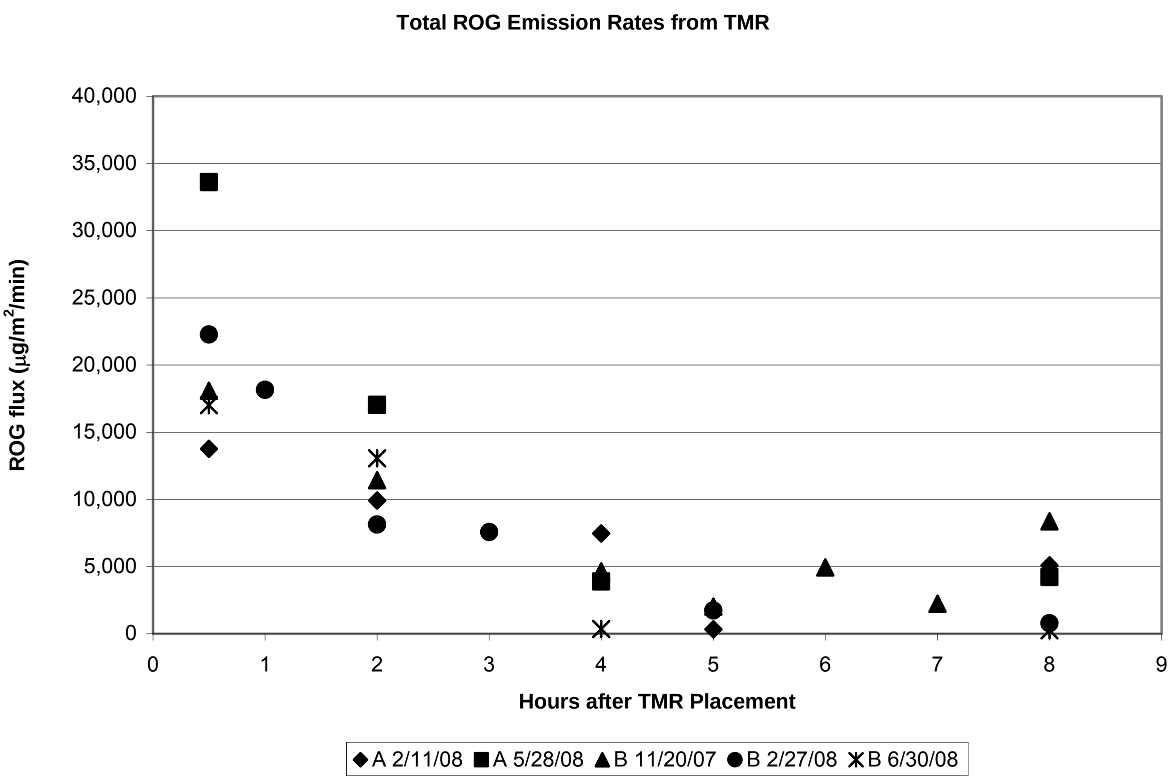


Figure 6. Total ROG fluxes related to time after feed placement from additional TMR flux data sampled as part of a related project.

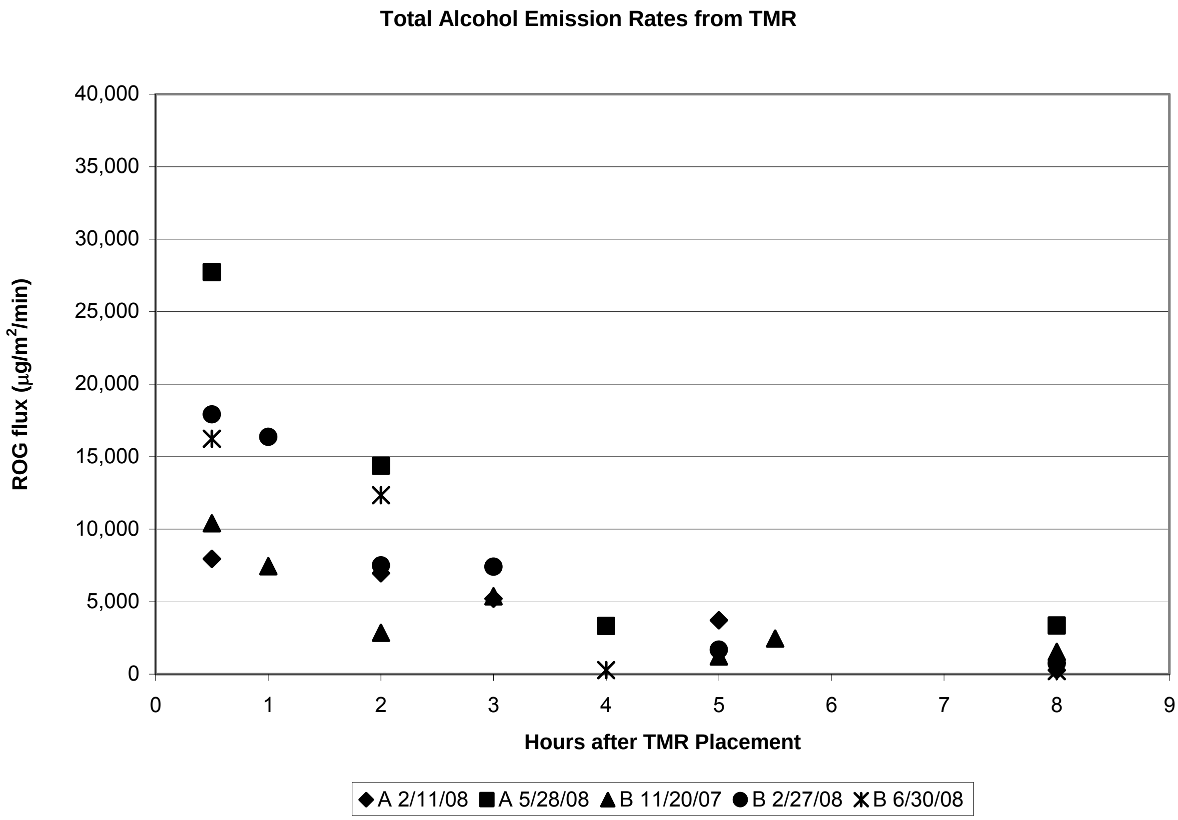


Figure 7. Total Alcohol (Methanol, Ethanol and Propanol) fluxes related to time after feed placement from additional TMR flux data sampled as part of a related project.

Flush Lane Flux Rates

Flush lanes are the concrete surfaced areas between the feed bunkers and the bedding stalls in a free stall dairy barn. The cows stand in a flush lane while eating the TMR and much of their manure is deposited in the lanes at that time. Most dairies construct the lanes with a slope so that a large volume of water can be used to flush the lane and remove the manure several times each day. The flush water drains to a collection and separation facility where the soil particles and coarse fiber in the manure are separated before the water and fine solids are stored in a lagoon. Water from the lagoon recycles for subsequent flushing operations. A few dairies remove the manure with a vacuum truck (Dairy E) or scrape it into pits (Dairy F) to eliminate the need for the large volume of flush water.

The largest components of ROG identified in the silage and feed monitoring are alcohols that are very soluble in water and would, therefore, not be expected to be as volatile from an aqueous medium compared to a soil or concrete surface. The emissions from the lane after flushing are low as is shown by the Post-flush averages in Table 7. The fresh manure also has a significant water content and might also produce lower emissions of alcohols and other soluble ROG species. The flux rates for flush lanes are generally much lower than those of feed or feed components. The exceptionally high ROG total for Dairy A on 2/15/08 appears to be an anomaly. The total ROG for that sample exceeds the next highest by a factor of 4 and is more than 10 times the average flux rate. Though the alcohols and DMS are higher than other samples, the high rate is due primarily to CFC-12, a refrigerant gas that was not found in other samples at more than trace concentrations. It remains to be determined whether this is an error or an example of a sporadic phenomenon. Other samples were taken on that date that may help explain these anomalous values in the comprehensive report. In the event that this one sample is not representative, the flush lane averages were recalculated without Dairy A on that date and are shown in Table 8.

In general, the pre-flush flux rates are about 10% or less compared to those from TMR and silage. The post-flush flux rates are about 1% of those from feed. The rates from the individual dairies were fairly consistent and the differences between the flush dairies (A, B, C, and D) compared to vacuum (E) and scraping (F) were less than expected. The two dairies that did not use flush water were lower than the average of the flush dairies but only slightly so and the differences may not be statistically significant. Additional data from the related projects may result in more definitive evaluation of emissions from flush vs. scraped or vacuumed manure management.

Table 7. Average flush lane flux rates for ROG. Values are averages for each dairy from samples taken prior to flushing unless specified as “Post-flush”. The significantly higher values for Dairy A are from one sampling event on 2/15/08. See text for further explanation. Individual data averaged for this table can be found in Appendix A, Table A4. Values are in $\mu g/m^2$/minute and are corrected by subtraction of Field Blank values.

	Ambient Temperature (degrees C)		**Total ROG**	Ethanol	Methanol	**Total Alcohols**	**Total Alcohols**	Acetaldehyde	d-Limonene	DMDS	DMS
Average of all dairies	Surface	Air									
Flush Lane (Pre-Flush)	17.1	17.9	353	22	9	108	47%	20	7	0	12
Flush Lane (Post-Flush)	12.9	15.8	21	3	1	6	53%	0	0	0	0
A	16.1	14.3	1,402	95	8	374	27%	67	10	0	71
B	16.6	18.0	246	13	9	66	51%	2	4	0	3
C	17.7	18.8	275	9	1	58	38%	38	4	0	5
D	16.1	18.9	116	12	29	83	72%	2	5	0	0
E	15.3	15.8	181	9	5	65	38%	18	17	0	3
F	20.3	20.6	129	12	6	75	58%	4	5	0	2

Table 8. Average flush lane flux rates for ROG. Values are averages for each dairy as in Table 7 with the possibly anomalous data from Dairy A on 2/15/08 deleted. Individual data averaged for this table can be found in Appendix A, Table A4. Values are in $\mu g/m^2$/minute and are corrected by subtraction of Field Blank values.

	Ambient Temperature (degrees C)		**Total ROG**	Ethanol	Methanol	**Total Alcohols**	**Total Alcohols**	Acetaldehyde	d-Limonene	DMDS	DMS
Average of all dairies	Surface	Air									
Flush Lane (Pre-Flush)	17.1	17.9	241	22	9	108	47%	20	7	0	12
Flush Lane (Post-Flush)	12.9	15.8	21	3	1	6	53%	0	0	0	0
A	16.1	14.3	207	12	9	69	27%	13	7	0	3
B	16.6	18.0	246	13	9	66	51%	2	4	0	3
C	17.7	18.8	275	9	1	58	38%	38	4	0	5
D	16.1	18.9	116	12	29	83	72%	2	5	0	0
E	15.3	15.8	181	9	5	65	38%	18	17	0	3
F	20.3	20.6	129	12	6	75	58%	4	5	0	2

Open Lot, Exercise Pen and Corral Flux Rates

Each dairy has some open uncovered areas that the cows can access from the free stalls. Some of the dairies (B and D) have very large open lots, others (C and F) have much smaller corrals. Except in the winter when access may be restricted, most of the manure that is not deposited in the flush lane will fall in the open lot. Animals tend to concentrate in parts of the corral where the manure pack will be relatively deeper than areas they do not frequent. Flux chamber sampling of fluxes in these open lots included both shallow and deep manure pack areas. The flux rates were expected to be different across the open lot and the average flux rate for the deep pack areas was higher than that of the shallow pack locations.

Table 9 shows the averages for shallow and deep samples as well as the averages for each dairy. The flux rates for deep pack locations averaged about twice that of the shallow pack areas. It should be noted that most open lots are harrowed or disked for fly and odor control occasionally during dry weather and these practices are very likely to affect flux rates from open lots.

Dairy E had a much higher average flux rate for the deep pack areas. This high average was due to the two deep pack samples taken on 6/21/07 in which the alcohols were similar to other samples but the acetaldehyde and di-methyl sulfide levels exceeded the average flux rates of the other dairies by an order of magnitude. The shallow pack sample for that date was also the highest of all sampled locations. Further analysis of the data from the related projects may be able to explain the high rates for this date.

The average flux rates for open lots are comparable to those of the flush lanes though the larger area represented by open lots at most of the dairies makes them, potentially, a more significant source. Further analysis with the additional data from the related projects should provide more detailed evaluation of the differences between open lot conditions and may suggest management practices that might result in reduced emissions.

Table 9. Open lot, exercise pen and corral flux averages. Fluxes are averaged from the individual samples found in Appendix A, Table A5. Shallow manure pack indicates samples taken from an area where the deposited manure was 0 – 5cm deep. Deep manure pack samples were from areas where the manure was 5-15cm deep. Values are in $\mu g/m^2$/minute and are corrected by the subtraction of Field Blank values.

	Ambient Temperature (degrees C)		**Total ROG**	Ethanol	Methanol	**Total Alcohols**	**Total Alcohols**	Acetaldehyde	d-Limonene	DMDS	DMS
Average of all dairies	Surface	Air									
Open Lot Shallow Manure Pack	25.2	21.0	102	15	17	45	56%	35	1	0	12
Open Lot Deep Manure Pack	24.4	21.1	243	20	28	60	57%	69	1	0	74
Average of each dairy - shallow manure pack											
A	25.9	21.3	109	16	20	55	64%	35	0	0	13
B	23.5	21.0	63	15	12	29	61%	16	0	0	12
C	32.0	26.4	75	11	21	48	60%	17	1	0	5
D	23.9	21.3	150	26	11	75	57%	33	2	0	9
E	25.7	20.6	167	8	30	42	46%	95	1	0	24
F	21.2	15.8	36	8	7	20	44%	4	1	0	7
Average of each dairy - deep manure pack											
A	21.7	18.2	92	17	25	44	61%	30	0	0	6
B	21.9	21.0	211	21	25	52	61%	5	1	0	37
C	36.1	24.8	127	15	19	51	43%	53	2	0	11
D	23.1	19.5	174	31	22	72	60%	27	2	0	17
E	26.6	23.6	616	11	49	75	48%	254	1	0	280
F	22.6	20.6	96	27	18	59	60%	8	1	0	20

Correlations With Ambient Conditions

The first samples collected in 2005-6 were upwind and downwind air samples described in the Year-1 program (Appendix B). This procedure was eliminated for the Year-2 sampling program for reasons described above. There were two specific objectives for the ambient air sampling in Year-1 and the first was achieved while the second was unsuccessful. The use of ambient samples to characterize the range of specific components of dairy ROG emissions was quite useful. The unexpected predominance of alcohols first found in a study at UC Davis was confirmed by these field samples. The initial round of air samples also allowed the UC Irvine lab to calibrate their analytical systems and develop standards for dairy air emissions work. Dr. Blake's lab had not analyzed samples of this type prior to this project and some calibration was needed before quantifiable results could be used with confidence. Table A6 shows the average of 59 ambient samples analyzed in Year-1. The very high values for alcohols may be inflated by some of the first analyses where the lab systems had not yet been properly standardized to the appropriate concentrations. The significance of data in Table A6 is the identification and relative magnitude of the various ROG components. The concentration values were often higher for the upwind or background samples than for the dairy downwind samples due to the variable wind speed and direction discussed previously. These data should not be used as examples of specific dairy emissions but are valuable for the identification of the components of ROG in the ambient atmosphere of the dairy areas of the Central Valley.

DISCUSSION

The four dairy operations sampled for this study were selected by the project's advisory group after consideration of data from the initial year of the study. Though lagoons were originally considered to be a major source of ROG, these four, silage, TMR, flush lanes and open lots, proved to be more significant sources and so were emphasized in the Year-2 monitoring program. Fluxes for the four sources, averaged for all six dairies and each date are shown in Table 10.

Of these four sources, silage has the highest flux rate, closely followed by TMR with flush lanes and open lots at much lower rates. The high flux from silage should be considered in light of the difference between the compressed material in the pile and the disturbed silage pulled from the pile to be used in the next TMR. Silage piles can be hazardous as they are often more than 10m high. The highly compressed material in the pile is generally so consolidated that the pile face, where material is pulled for TMR is usually vertical and may actually overhang the working area below the face. The compaction is never completely uniform and unstable areas of the pile are unavoidable. An unexpected fall of material from high on the face is not uncommon and can be dangerous. Consequently, the silage is usually pulled down in just a few operations each day to minimize the exposure of workers to the danger of a silage avalanche. A large amount of compressed silage is therefore often disturbed to be used over a day or more of TMR mixing. While it is apparent from this data that silage should be left undisturbed as much as possible to minimize ROG emissions, that may be contrary to safe working practices. The emissions from disturbed silage are high; however the amount of material and the area of the emission is small compared to other sources. The average flux rate for undisturbed silage material shown in Table 10 is about 22% of the flux rate from disturbed silage. A typical dairy might have a silage pile with an exposed face of 250 m^2 with a loose pile of disturbed silage at its base of only about 25 m^2. The total ROG flux from the silage operation would therefore be primarily due to the lower flux from the larger area of undisturbed pile face. A considerable amount of additional silage data will be available when the related projects are complete, including more flux data, silage analysis and density as well as pile dimensions for each of the six dairies. More detailed correlations will be possible with that additional data when the comprehensive report is completed.

Table 10. Average flux rates for all dairies, all dates and each dairy operation included in the regular sampling program for Year-2. The 6 major constituents of ROG are reported here with the remaining components grouped as “other”. The UC Irvine analysis included ROG components from a list of 64 gasses identified in the analytical procedure. Values are in $\mu g/m^2$/minute and are corrected by the subtraction of Field Blank values.

	Total ROG	Ethanol	Methanol	**Alcohols**	**Alcohols**	Acetaldehyde	d-Limonene	DMDS	DMS	Other
Open Lot Shallow Manure Pack	102	15	17	45	56%	35	1	0	12	23
Open Lot Deep Manure Pack	243	20	28	60	57%	69	1	0	74	50
Lagoons	36	5	2	7	20%	4	0	0	0	25
Flush Lane (Pre-Flush)	353	22	9	108	47%	20	7	0	12	283
Flush Lane (Post-Flush)	21	3	1	6	53%	0	0	0	0	16
TMR (0.5 h Post Placement)	15,022	11,668	1,460	13,141	86%	336	584	26	831	117
TMR (6 h Post Placement)	10,582	7,747	1,591	9,350	87%	469	557	9	152	55
TMR (6+h Post: consumed)	2,929	2,289	389	2,683	89%	106	102	3	32	9
Silage Pile Undisturbed Face	4,229	3,095	416	3,524	86%	164	6	1	532	16
Silage Pile Disturbed Face	19,170	12,814	632	13,461	84%	214	49	1	5,413	47

A few flux chamber samples were collected from lagoon surfaces for a related project funded by the California Dairy Campaign. These lagoon fluxes do not correspond to the sampling periods reported above but they are shown in Table 10 and Figure 8 to illustrate the relative insignificance of lagoon emission rates compared to other dairy sources of ROG. These lagoon emission rates were monitored at Dairies A and D in May and November, 2007 to compare with lagoons at three other dairies, not included in this CARB study. More complete data related to lagoon emission composition and rates will be included in the comprehensive report.

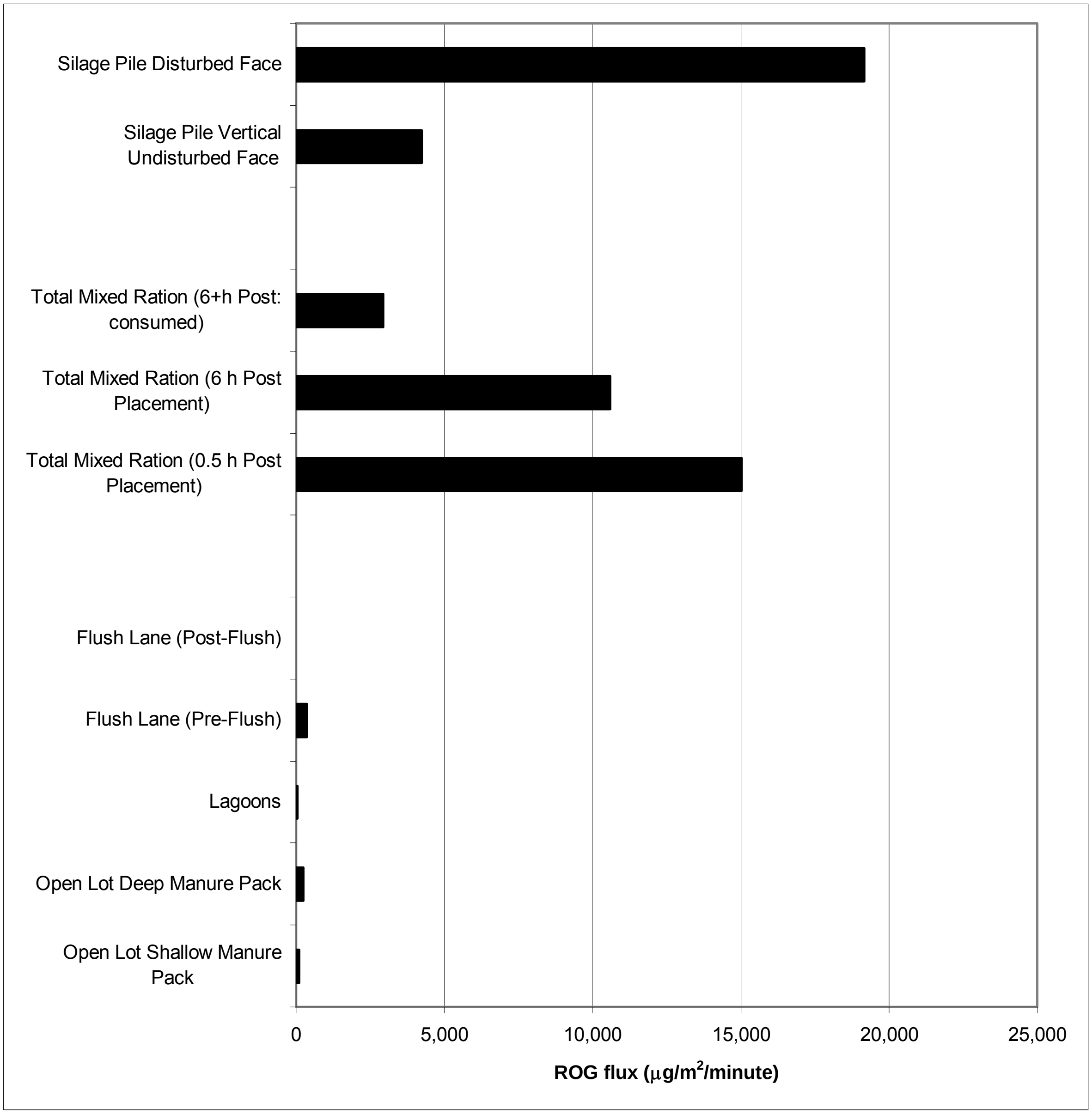


Figure 8. ROG fluxes averaged from each dairy and sampling date. These data are from the Total ROG column of Table 10.

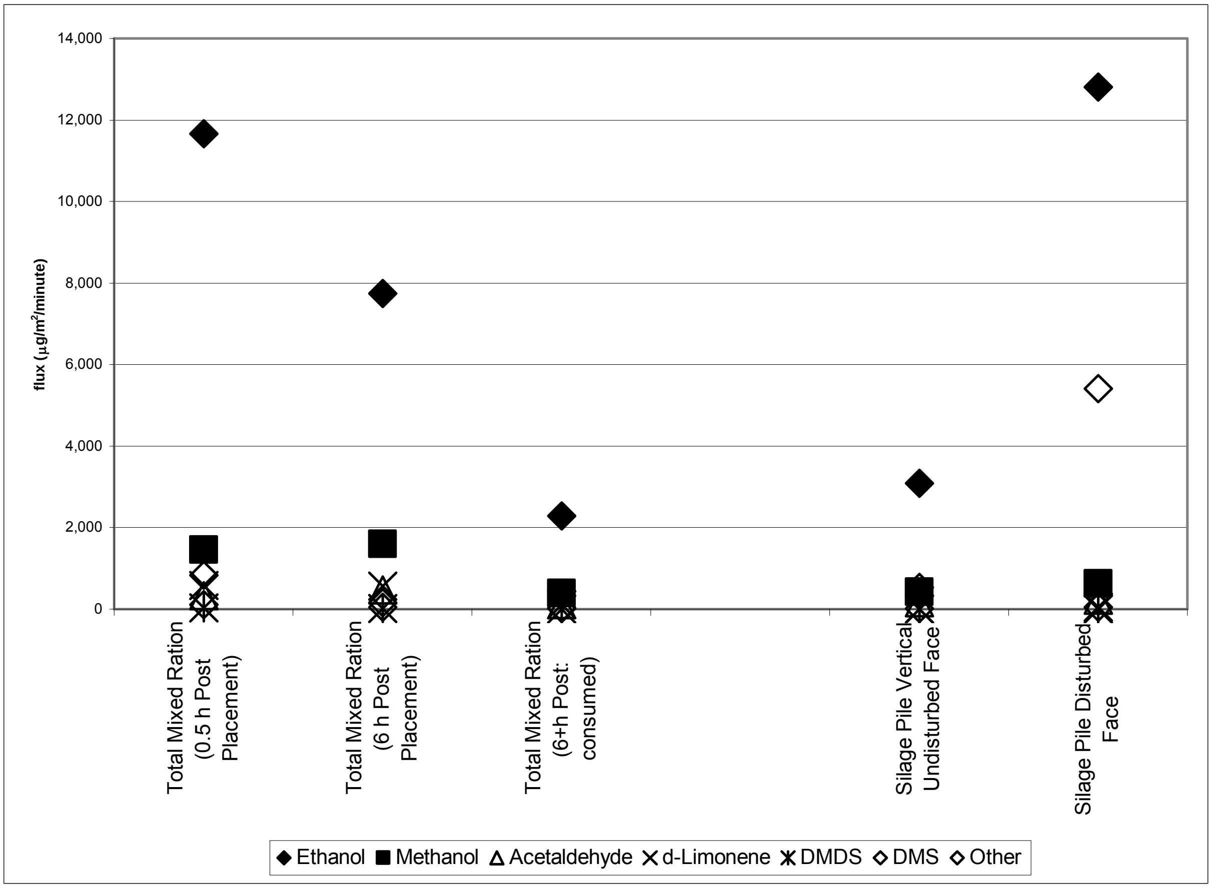


Figure 9. Fluxes of the six prominent, specific ROG components of emissions, compared to the minor components (other) from feed and silage. This data is from the TMR and Silage lines of Table 10.

The feeding operation has fluxes nearly comparable to those from silage, as would be expected from the fact that silage is the major component of the TMR and the mixing process thoroughly disturbs all the components. The data for TMR shown in Table 10 and Figures 8 and 9 reflects the complexity of TMR fluxes of ROG that were not completely understood until the Year-2 program was in progress. It was apparent that fluxes from TMR were high when the material was initially placed in the feed bunker. Consecutive samples in a related project using the real-time INNOVA analyzers showed decreasing flux chamber concentrations for alcohols, minute by minute, over the first monitoring period, 30-60 minutes post-placement. Project staff noted the distinctive odor from the TMR decreased rapidly from the time of placement. Two factors were probably responsible for this decrease in flux. The animals consumed feed and the volatility appeared to decrease rapidly as the TMR was spread out and exposed to the air.

This apparent decrease in flux with time was monitored prior to Year-2 by following the initial, post-placement sample with another at 1.5 hours, post-placement. The flux values for these later samples were lower; about 30% of the initial fluxes. The advisory group, after consideration of this data, requested a more thorough evaluation of the

TMR. The group considered TMR to be, potentially, the largest ROG source, and, perhaps the most complex, variable and manageable. The Year-2 program included samples at each diary for the beginning (0.5 hours) and end (6 hours) of the feeding period and, if possible a flux from the surface after the TMR was consumed. The averages for that portion of the Year-2 program (Table 5) do not appear to match the rapid decrease in flux shown by the earlier 1.5 hour post-placement fluxes. A potential reason for this involves an additional practice in the feeding operation. The large amount of TMR placed initially in the feed bunker is consumed most rapidly in the first hour or two. The cows return to the bunker later to eat the remaining feed. It is a common practice to scrape or sweep the remnants of the TMR into a more accessible pile about 4 – 6 hours after placement. The 1.5 hour samples in Table 5 were taken prior to that sweeping and the 6 hour samples were usually following such a practice. The sweeping operation disturbed the material and exposed previously buried TMR to the air. The odor of the feed was noticeably stronger after sweeping and the fluxes were higher.

This phenomenon became apparent early in the Year-2 program and had, in fact, been anticipated by the advisory group. The emphasis on TMR fluxes included a more detailed sampling program at Dairies A and B, referred to as the "special sampling" described in Appendix B. While that special sampling was done as part of the related projects, some UC Irvine samples were included when there were sufficient canisters. Though much of the data for the special samples is not yet available, the UC Irvine analysis is shown in graphic form in Figures 6 (ROG) and 7 (total alcohols). The continuous sampling from placement to complete consumption of the TMR is shown over an 8 hour span. The fluxes at 8 hours are for the bunker surface after complete consumption. The spike in flux rate at 6 hours seen in the regular sampling is not as apparent in these special samples. Further correlation with additional data may explain the reasons for this.

Flush lane fluxes were originally expected to be the major source of ROG from the animal housing areas. In fact, flux rates from flush lanes are less than 5% of the average TMR flux when the amount of manure is greatest, prior to flushing. When the lanes have been flushed, scraped or vacuumed, the flux rate is less than 0.3% of the average TMR rate. The composition of the ROG flux is also different for the flush lanes. While the alcohols are still the dominant components, they are about half of the ROG from the lanes compared to the 80% - 90%+ alcohols in fluxes from silage and TMR. Propanol was a much greater component of the fresh manure in the pre-flush lane compared to the other sources. The area of flush lanes in the dairy barn is greater than that of the feed bunker by a factor of 5 – 10. The relative fluxes from these two sources are therefore, less different than their flux rates would indicate but the flush lanes are still significantly smaller sources than the TMR.

Fluxes of ROG from the open lots, shown in Table 9, are lowest of the four sources sampled in this project. The open lots are also the most variable in size, composition, pattern of use and management practices. The variability in average flux among the dairies was actually less than expected and was comparable to that of the flush lanes.

The composition of the ROG emission was also similar to the flush lanes with some notable differences. The alcohols made up about half of the ROG emission as with the lanes though ethanol and methanol were responsible for nearly all the alcohols in relatively equal proportions in the manure pack of the open lots. Though the flux rates are comparably low for the open lots, the larger area increases their significance as an ROG source. Some dairies have very large lots (10,000 m^2 or more) and some are quite small (2000 m^2 or less). The differences in size, coupled with different management practices and loading will make estimates of emissions from open lots more difficult than the other sources. Additional data and management information will be included in the comprehensive report.

SUMMARY and CONCLUSIONS

There were three basic questions that led to the original proposal to CARB for this project and the subsequent revisions by the advisory group.

1. What are the components of ROG emissions from dairy operations in California?
2. What are the most significant sources of ROG related to dairy operations?
3. Are there procedural and seasonal effects on ROG from California dairies?

The first question was the first priority since the composition of dairy emissions was unknown and needed to be characterized in order to select the appropriate methods of sampling and analysis for the Year-2 program. The initial downwind-upwind sampling and analysis at UC Irvine was successful in that characterization. The data from those first year samples is shown in Appendix A, Table A6. Once the major components and their relative concentrations were determined, the analytical procedures at UC Irvine could be optimized for dairy air samples and analytical standards could be prepared. While there are certainly other VOC's that might have been present in these samples that could react as ozone precursors, it was assumed that all significant components of ROG were identified and quantified by Dr. Blake at UC Irvine. The identification of alcohols as the major component of ROG emissions from each dairy operation was the first significant conclusion of this project. That led to several related projects to monitor alcohols with additional methods of sampling and analysis.

Once the composition of dairy ROG emissions had been determined, the second question of identifying the relative magnitude of emissions from the various dairy operations could be addressed. The initial downwind-upwind samples that were of such value in characterizing the ROG components could not discriminate between the separate sources within the animal housing areas and so the advisory group directed the sampling program's change to the use of flux chambers. Fluxes measured by this chamber method are specific to the surface and the area on which they are placed for a particular sample. Multiple measurements over both time and area are required to determine the magnitude and variability of the flux from a surface and the limited number of UC Irvine analyses that was available in this project budget was not adequate to accomplish this for every sampling location and period. The other sampling/analysis methods added for the related projects will be important for the further characterization of each location. It is possible, as an academic exercise, to estimate the relative flux magnitudes with the UC Irvine data reported here and that will also serve as an example of the conversion procedures that may be possible with additional data in the comprehensive report.

The flux rate averages in Table 10 can be used to illustrate the calculation of emissions to the degree that the relative magnitude of each source can be compared. In the discussion of the silage source above, an example was given to illustrate the proportion of ROG emissions from disturbed and undisturbed silage. That example can be carried further and used for the other sources as well at a fictitious 2000 cow dairy that might be imagined from a composite of the six facilities sampled in this project. This fictitious dairy has four barns, each 400m long, with a feed bunker, two flush lanes and a large open lot. The areas of those sources, combined with the ROG flux rates from Table 10 can be used to illustrate the relative magnitudes of fluxes from a dairy as well as serve as an example of how fluxes can be combined with specific dairy dimensions to calculate emissions from a specific facility.

Disturbed Silage
Average flux (Table 10) = 19,170 μg/m^2/minute
Estimated area at the fictitious dairy = 25 m^2
Estimated emission = 19,170 μg/m^2/minute X 25 m^2 X 1440 min/day = 0.7 kg/day

Undisturbed Silage
Average flux (Table 10) = 4,229 μg/m^2/minute
Estimated area at the fictitious dairy = 250 m^2
Estimated emission = 4,229 μg/m^2/minute X 250 m^2 X 1440 min/day = 1.5 kg/day

TMR (average of all sample periods)
Average flux (Table 10) = 8,260 μg/m^2/minute
Estimated area at the fictitious dairy = 1600 m^2 (1m wide x 400m long x 4 bunkers)
Estimated emission = 8,260 μg/m^2/minute X 1600 m^2 X 1440 min/day = 19.0 kg/day

Flush lanes (average of pre-flush and post-flush)
Average flux (Table 10) = 187 μg/m^2/minute
Estimated area at the fictitious dairy = 9600 m^2 (3m wide x 400m long x 8 lanes)
Estimated emission = 187 μg/m^2/minute X 9600 m^2 X 1440 min/day = 2.6 kg/day

Open Lots (average of deep and shallow manure pack)
Average flux (Table 10) = 172 μg/m^2/minute
Estimated area at the fictitious dairy = 32,000 m^2 (20m wide x 400m long x 4 lots)
Estimated emission = 172 μg/m^2/minute X 32,000 m^2 X 1440 min/day = 7.9 kg/day

ROG emissions from the fictitious dairy and their relative percentages of the total:
Disturbed Silage…... 0.7 kg/day (2%)
Undisturbed Silage... 1.5 kg/day (5%)
TMR……………….. 19.0 kg/day (60%)
Flush lanes……….. 2.6 kg/day (8%)
Open Lots…………. 7.9 kg/day (25%)
Total ………………..31.8 kg/day (100%)

This estimation does show the fact that the TMR is the largest ROG source at the dairy (60%) followed by the open lots (25%), the flush lanes (8%) and the silage (5% for undisturbed and 2% for disturbed material). While these percentages will change for specific facilities, TMR is likely to remain the dominant source. There is a considerable amount of TMR flux data from the related projects that should produce a more accurate average as well as a better evaluation of the variability and relationship to feed components and other feeding practices. It is clear that reductions in TMR fluxes have the most potential to mitigate dairy emissions of ROG.

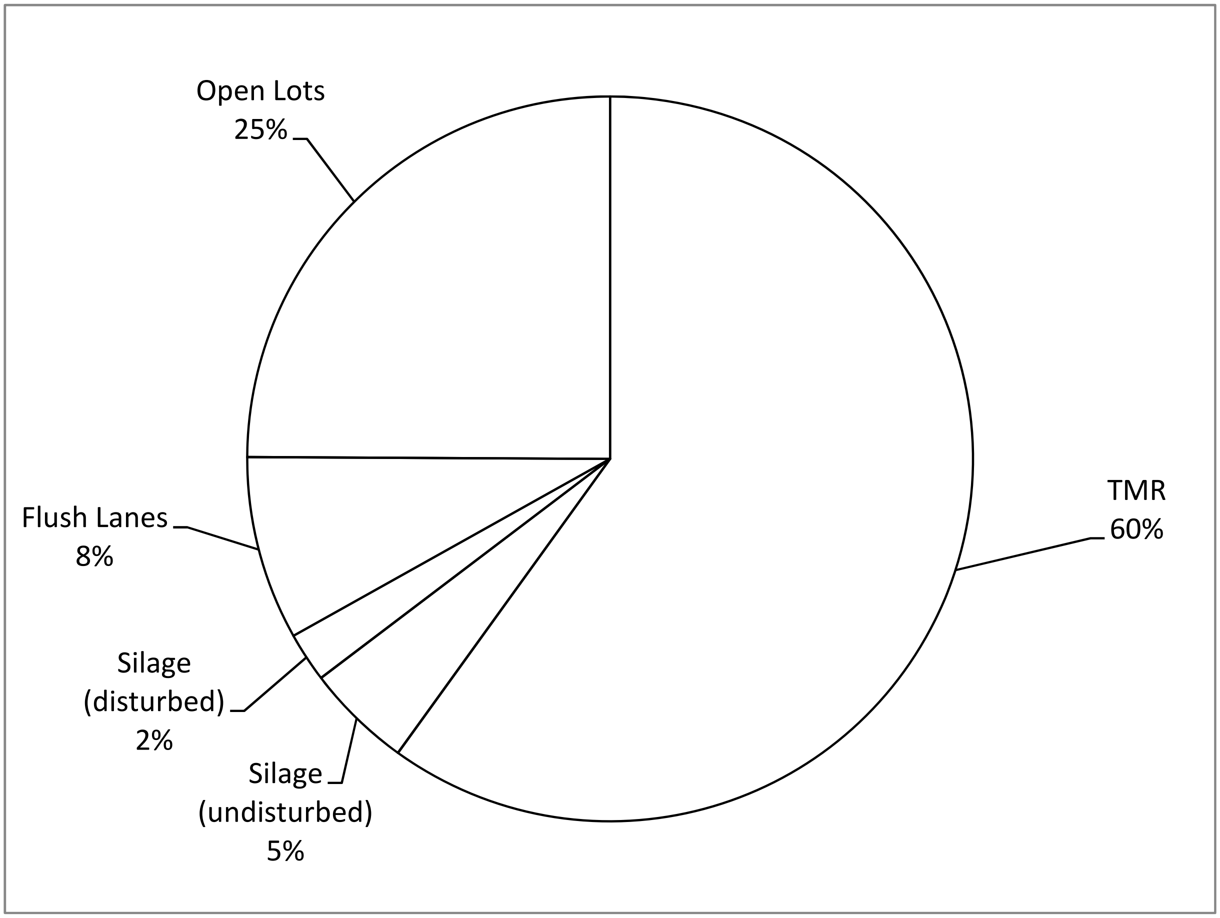


Figure 10. An example of the relative ROG source magnitudes at a fictitious dairy. These proportional values are calculated from the averaged flux rates for all six dairies for all sampling periods in Year-2, multiplied by the averaged areas of those sources for the six dairies. These are shown to illustrate the relative magnitude of the ROG sources Specific source rates and proportions will be different for different dairies and seasons.

This example calculation is not intended for use as an emission factor for dairies. The dimensions do not represent any specific facility and the fluxes are averages of a number of sampling events that have considerable variation. Another factor that must be considered is the nature of the flux chamber method. Flux chamber data can be used to calculate ROG emissions from a surface into the artificial, zero-air atmosphere of the chamber, immediately above the surface being sampled. Any atmospheric reactions that might occur with a flux into an ambient atmosphere or adhesive effects between ROG and surfaces at the dairy are not reflected in these results. Atmospheric and surface effects on the ROG components would probably reduce the concentrations so these reported flux values are most likely an overestimation of the emissions from these operations, especially those that take place in the barn areas. Downwind-upwind sampling or other similar monitoring methods would be required to determine the differences between the flux from these surfaces as measured by the flux chamber method and the actual emissions after the post-surface emission reactions have been included. That level of monitoring was beyond the scope of this project but is being conducted by other research groups in California and elsewhere.

Correlation of ROG flux rates with ambient conditions was one of the primary objectives of the original proposal. The winter, summer and fall sampling periods were selected to evaluate an expected seasonal effect on flux rates for the different dairy locations and operations. It was assumed that higher temperature surfaces would volatilize higher rates of emissions during warm weather. The only example where this is apparent with the data reported here is related to the open lots. Both the shallow and deep manure pack locations showed a strong, positive correlation with the temperature of the surface. Table A5 in Appendix A shows open lot surface temperatures ranging from 39.5 C down to 9.3 C. The higher flux rates were consistently found at the higher surface temperatures in both shallow and deep pack areas. Additional emissions and manure samples were collected for these areas by the related projects and will be statistically evaluated in the comprehensive report. Further data analysis may show other correlations with surface or air temperature but the open lots are the only areas where the correlation is obvious from the CARB data.

Recommendations

Recommendations for further research are, for the most part, related to the additional projects that were begun during the course of this study with the additional support from CSU ARI and the cooperating researchers described above. Completion of these related projects in the next year should significantly expand the data set and provide much more detailed conclusions with regard to fluxes of ROG and other gasses. The more intensive study of emissions from dairy operations recommended in the Summary and Conclusions section are necessary to determine the fate of ROG between emission from the source surface as measured by the flux in this study and the point at which the ROG is emitted from the dairy facility. Some studies of that nature are in progress and more should be encouraged to fully evaluate dairy ROG emissions.

The speciation of ROG emissions from dairies that was the first objective in this project is only the first step in characterizing these sources with regard to their potential contribution to ozone formation. These ROG species are different, not only by composition but also in their ability to participate in the ozone formation reaction. Some components may be present in significant amounts but have little effect on ozone formation because of a low reactivity. Other ROG's may be present in smaller amounts but be more significant precursors of ozone due to a higher reactivity. A complete evaluation of dairy emissions as they affect ozone formation will need to include the reactivity of these specific ROG's as well as their relative emission rates.

References

This study, as a data collection project, did not include a literature review in the proposal. An extensive review of current research was completed by members of the project advisory group as part of the contemporary DPAG activity. Though that review of literature was important to the planning and execution of this study, it was not done as part of this CARB funded activity and is not reported in this document.

The Dairy Permitting Advisory Group of the San Joaquin Valley Air Pollution Control District completed an extensive review of research related to dairy emissions in 2005, as this project was beginning. The public agency and industry members of the CARB/CDFA Dairy Sub-committee that became the advisory group for this project were also DPAG members. The research members of this project's advisory group participated in the DPAG process as well. The review of research and DPAG discussions were integral to the development of this project, especially the revisions to focus on ROG emissions, recommended by the advisory group as it progressed. A review of research and literature beyond that done for the DPAG report would have been superfluous. The DPAG report, with an extensive list of references may be found at:

<http://www.valleyair.org/busind/pto/dpag/DPA_%20EF_Report_Final.pdf>

List of Inventions and publications produced

No inventions or patentable processes were developed in the course of this project. No publications based on this data have yet been submitted by any of the investigators or cooperators. Several publications are expected to be submitted by collaborators and cooperators when the related projects are completed and the full data set is available.

APPENDIX A

The following tables list the individual samples collected by CSU Fresno and analyzed at UC Irvine that were averaged and summarized in the Results section. Only samples with corresponding field blanks are reported here. A small number of other samples were analyzed at UC Irvine for the special sampling and related projects but do not have UC Irvine field blanks and so cannot be evaluated until other QC data is available.

Table A1. Silage samples from material dislodged from the pile for use in the next TMR mix. Values are fluxes in μg/m^2/minute and are corrected by the subtraction of Field Blank values. The 6 major components of ROG are reported here. The UC Irvine analysis included ROG components from a list of 64 gasses identified in the analytical procedure.

Dairy	Date	Surface Description	Surface Temp.	Air Temp.	**Total ROG**	Ethanol	Methanol	**Total Alcohols**	**Total Alcohols**	Acetaldehyde	d-Limonene	DMDS	DMS
A	06/11/07	Silage Pile Disturbed Face	35.3	31.5	8,209	6,564	1,438	8,002	97%	76	49	1	0
A	09/25/07	Silage Pile Disturbed Face	25.3	26.2	17,068	13,471	1,694	15,212	89%	739	63	1	1,042
A	02/08/08	Silage Pile Disturbed Face	22.9	12.1	34,875	23,458	1,286	24,779	71%	509	199	1	9,246
A	06/02/08	Silage Pile Disturbed Face	19.3	20.1	15,919	8,510	1,114	9,634	61%	596	837	1	4,818
B	10/02/07	Silage Pile Disturbed Face	18.6	14	2,823	2,369	348	2,743	97%	64	9	1	10
B	02/19/08	Silage Pile Disturbed Face	28.8	12.6	3,546	3,041	442	3,482	98%	11	1	1	59
B	07/02/08	Silage Pile Disturbed Face	18.9	19.6	2,512	2,265	186	2,451	98%	23	0	1	32
C	06/25/07	Silage Pile Disturbed Face	30.8	27.3	56,107	55,797	46	55,843	100%	184	0	1	0
C	10/30/07	Silage Pile Disturbed Face	31.7	16.8	9,859	8,724	671	9,414	95%	440	5	0	1
C	04/09/08	Silage Pile Disturbed Face	15.2	12.1	6,105	4,145	569	4,757	78%	164	1	1	1,169
C	06/17/08	Silage Pile Disturbed Face	20.7	18.8	72,698	70,645	935	71,591	98%	425	31	1	633
D	10/23/07	Silage Pile Disturbed Face	23.7	16	83	82	5	86	104%	4	0	0	0
D	03/14/08	Silage Pile Disturbed Face	14.6	10.1	8,670	7,776	466	8,251	95%	44	20	1	351
D	06/26/08	Silage Pile Disturbed Face	32.5	24.4	60,816	13,189	1,456	14,707	24%	124	0	7	45,922
D	03/22/07	Silage Pile Disturbed Face	27.8	20	5,103	4,722	304	5,026	98%	0	0	1	55
D	07/24/07	Silage Pile Disturbed Face	39	32	18,425	18,283	62	18,346	100%	32	1	1	1
E	06/20/07	Silage Pile Face disturbed	38.8	24.9	28,187	27,829	48	27,877	99%	50	0	1	0
E	10/16/07	Silage Pile Disturbed Face	21.5	14.1	814	228	451	681	84%	134	0	0	1
E	03/10/08	Silage Pile Disturbed Face	15.4	9.2	16,023	5,857	784	6,656	42%	31	1	1	9,316
E	06/09/08	Silage Pile Disturbed Face	32.7	25.5	10,132	7,846	936	8,801	87%	89	1	1	1,227
F	04/17/07	Silage Pile Disturbed Face	18.8	18.4	1,477	1,274	197	1,471	100%	0	0	1	3
F	07/17/07	Silage Pile Disturbed Face	19.4	22	6,104	6,054	40	6,094	100%	4	0	0	0
F	11/06/07	Silage Pile Disturbed Face	18.2	14.8	4,845	3,321	260	3,581	74%	1,259	0	1	6
F	03/28/08	Silage Pile Disturbed Face	11.2	11.7	12,859	9,336	677	10,026	78%	111	1	1	2,719
F	07/09/08	Silage Pile Disturbed Face	29.5	30.8	75,977	15,572	1,393	17,015	22%	232	0	1	58,710

Dairy Averages

A	25.7	22.5	19,018	13,001	1,383	14,407	80%	480	287	1	3,776
B	22.1	15.4	2,961	2,558	325	2,892	98%	32	3	1	34
C	24.6	18.8	36,192	34,828	555	35,401	93%	303	9	1	451
D	27.5	20.5	18,620	8,810	459	9,283	84%	41	4	2	9,266
E	27.1	18.4	13,789	10,440	555	11,004	78%	76	1	1	2,636
F	19.4	19.5	20,252	7,111	513	7,637	75%	321	0	1	12,287

Table A2. Silage samples from undisturbed material. Values are fluxes in $\mu g/m^2$/minute and are corrected by the subtraction of Field Blank values. The 6 major components of ROG are reported here. The UC Irvine analysis included ROG components from a list of 64 gasses identified in the analytical procedure.

Dairy	Date	Surface Description	Surface Temp.	Air Temp.	**Total ROG**	Ethanol	Methanol	**Total Alcohols**	**Total Alcohols**	Acetaldehyde	d-Limonene	DMDS	DMS
A	09/25/07	Silage Pile Vertical Undisturbed Face	27.3	25	5,426	4,256	858	5,133	95%	265	3	1	22
A	02/08/08	Silage Pile Vertical Undisturbed Face	32.9	15	6,811	4,539	663	5,234	77%	304	13	0	1,248
A	06/02/08	Silage Pile Vertical Undisturbed Face	20.7	24.2	2,305	1,931	198	2,133	93%	8	15	0	143
B	02/19/08	Silage Pile Vertical Undisturbed Face	23.9	13.4	5,442	4,055	337	4,391	81%	9	2	1	1,046
B	07/02/08	Silage Pile Vertical Undisturbed Face	20.4	21.5	5,713	5,026	228	5,255	92%	23	0	1	431
C	10/30/07	Silage Pile Vertical Undisturbed Face	26.8	17.2	2,090	1,591	234	1,832	88%	247	8	0	3
C	04/09/08	Silage Pile Vertical Undisturbed Face	24.6	13.8	9,729	6,271	968	7,249	75%	88	3	1	2,361
C	06/17/08	Silage Pile Vertical Undisturbed Face	20.1	20.6	4,286	2,954	285	3,238	76%	121	5	1	921
D	10/23/07	Silage Pile Vertical Undisturbed Face	40.2	21.4	8,713	6,029	1,194	7,345	84%	1,322	35	0	4
D	03/14/08	Silage Pile Vertical Undisturbed Face	12.2	12	3,536	2,849	201	3,050	86%	9	2	1	474
E	10/16/07	Silage Pile Vertical Undisturbed Face	15.8	14	1,668	1,404	219	1,625	97%	33	0	0	9
E	03/10/08	Silage Pile Vertical Undisturbed Face	19.9	11.5	2,442	1,966	282	2,251	92%	15	3	1	168
E	06/09/08	Silage Pile Vertical Undisturbed Face	28.9	25	3,798	2,022	380	2,406	63%	24	2	0	1,362
F	11/06/07	Silage Pile Vertical Undisturbed Face	17.4	17.3	1,251	953	164	1,118	89%	132	0	1	2
F	03/28/08	Silage Pile Vertical Undisturbed Face	13	13.1	1,971	1,699	159	1,858	94%	2	1	1	108
F	07/09/08	Silage Pile Vertical Undisturbed Face	29.4	31.7	2,492	1,973	285	2,258	91%	25	0	1	207

Dairy Averages

Dairy	Surface Temp.	Air Temp.	Total ROG	Ethanol	Methanol	Total Alcohols	Total Alcohols	Acetaldehyde	d-Limonene	DMDS	DMS
A	27.0	21.4	4,848	3,575	573	4,167	88%	192	11	1	471
B	22.2	17.5	5,577	4,540	282	4,823	86%	16	1	1	738
C	23.8	17.2	5,368	3,605	496	4,107	79%	152	5	1	1,095
D	26.2	16.7	6,124	4,439	697	5,198	85%	665	18	0	239
E	21.5	16.8	2,636	1,798	294	2,094	84%	24	2	0	513
F	19.9	20.7	1,905	1,542	203	1,745	91%	53	0	1	106

Table A3. Individual samples of feed (TMR) fluxes. Values are in $\mu g/m^2$/minute and are corrected by the subtraction of Field Blank values.

Dairy	Surface Description	Surface Temp.	Air Temp.	**Total ROG**	Ethanol	Metanol	**Total Alcohols**	**Total Alcohols**	Acetaldehyde	d-Limonene	DMDS	DMS
A	Total Mixed Ration (0.5 h Post Placement)			10,561	4,634	3,028	7,662	73%	29	2,747	16	0
A	Total Mixed Ration (1.5 h Post Placement)			6,994	2,736	1,810	4,547	65%	33	2,288	18	0
A	Total Mixed Ration (0.5 h Post Placement)	25.9	18.8	12,148	6,699	2,527	9,257	76%	1,178	1,650	1	4
A	Total Mixed Ration (6 h Post Placement)	23.2	26.4	13,269	6,927	3,076	10,030	76%	1,313	1,825	0	4
A	Total Mixed Ration (6+h Post: consumed)	22.5	27	2,488	1,338	796	2,140	86%	77	266	0	1
A	Total Mixed Ration (0.5 h Post Placement)	19.2	10	10,250	4,293	2,485	6,812	66%	146	2,478	41	543
A	Total Mixed Ration (6 h Post Placement)	13.6	15	6,620	2,765	1,919	4,705	71%	69	1,649	12	80
A	Total Mixed Ration (6+h Post: consumed)	7.7	5.6	1,200	799	255	1,056	88%	83	45	1	11
A	Total Mixed Ration (0.5 h Post Placement)	24.2	19.6	32,477	22,553	5,073	27,637	85%	268	3,722	32	591
A	Total Mixed Ration (6 h Post Placement)	22	23.7	16,390	11,648	2,302	13,955	85%	251	2,053	7	55
A	Total Mixed Ration (6+h Post: consumed)	18.4	17.5	6,069	3,951	1,281	5,233	86%	190	615	3	18
B	Total Mixed Ration (1.5 h Post Placement)			3,114	2,384	646	3,029	97%	0	0	1	63
B	Wet Distillers Grain	13.9	12	830	804	17	821	99%	0	0	0	7
B	Total Mixed Ration (0.5 h Post Placement)	22	23	8,309	7,875	225	8,100	97%	46	1	101	0
B	Total Mixed Ration (1.5 h Post Placement)	23.5	24.4	2,692	2,530	76	2,607	97%	17	0	37	0
B	Total Mixed Ration (0.5 h Post Placement)	24.1	20.1	7,532	5,319	1,088	6,440	86%	1,017	0	0	34
B	Total Mixed Ration (6 h Post Placement)	26.8	26.3	7,054	3,543	1,347	4,906	70%	2,091	0	1	22
B	Total Mixed Ration (6+h Post: consumed)	21	24.2	681	471	142	613	90%	52	14	0	0
B	Total Mixed Ration (0.5 h Post Placement)	24.2	13.1	12,770	7,248	2,898	10,171	80%	56	0	44	2,329
B	Total Mixed Ration (6 h Post Placement)	10.8	9.8	1,380	856	480	1,338	97%	23	0	1	14
B	Total Mixed Ration (6+h Post: consumed)	9.7	8.8	207	137	63	201	97%	4	0	0	0
B	Total Mixed Ration (0.5 h Post Placement)	26.5	26.6	20,125	8,515	3,619	12,134	60%	317	3	152	7,336
B	Total Mixed Ration (6 h Post Placement)	24.5	29.2	34,254	27,030	6,025	33,067	97%	372	2	57	711
B	Total Mixed Ration (6+h Post: consumed)	24.2	29.8	507	399	77	477	94%	0	0	2	27
C	Total Mixed Ration (0.5 h Post Placement)	26.2	11.8	14,327	12,956	691	13,656	95%	503	108	1	2
C	Total Mixed Ration (6 h Post Placement)	20.1	19	8,512	6,970	862	7,838	92%	630	0	0	1
C	Total Mixed Ration (6+h Post: consumed)	17.6	18.4	2,060	1,575	226	1,800	87%	253	0	0	1
C	Total Mixed Ration (0.5 h Post Placement)	13.5	8.9	30,432	27,745	1,042	28,798	95%	630	55	29	790
C	Total Mixed Ration (6 h Post Placement)	16.3	16.7	5,040	4,210	502	4,714	94%	288	8	3	15
C	Total Mixed Ration (6+h Post: consumed)	14.6	16	3,704	3,408	221	3,631	98%	58	7	2	4
C	Total Mixed Ration (0.5 h Post Placement)	19.5	16.3	46,515	45,350	666	46,024	99%	199	5	3	259
C	Total Mixed Ration (6 h Post Placement)	20.6	23.4	26,376	24,542	967	25,517	97%	238	26	16	562
C	Total Mixed Ration (6+h Post: consumed)	21.4	22.5	2,974	2,629	240	2,871	97%	24	28	2	48
D	Total Mixed Ration (0.5 h Post Placement)	20.7	28.1	8,598	6,390	1,100	7,551	88%	965	53	0	2
D	Total Mixed Ration (6 h Post Placement)	17.9	24.5	16,483	9,964	2,313	12,324	75%	2,183	1,883	0	2
D	Total Mixed Ration (6+h Post: consumed)	20.1	25.5	2,893	1,568	517	2,091	72%	386	407	0	1
D	Total Mixed Ration (0.5 h Post Placement)	14.9	10.8	14,446	7,495	1,812	9,318	64%	217	3,883	10	423
D	Total Mixed Ration (6 h Post Placement)	14.6	14.6	9,022	4,433	1,668	6,107	68%	124	2,564	3	41
D	Total Mixed Ration (6+h Post: consumed)	15.1	15.3	1,821	1,061	301	1,363	75%	22	410	1	16
D	Total Mixed Ration (0.5 h Post Placement)	28.2	20.4	35,275	31,263	2,340	33,629	95%	140	0	33	1,424
D	Total Mixed Ration (6 h Post Placement)	26.7	24.8	20,460	17,922	1,795	19,732	96%	146	0	32	506
D	Total Mixed Ration (6+h Post: consumed)	25.3	25.2	22,859	20,289	1,972	22,276	97%	237	32	29	270
D	Total Mixed Ration (0.5 h Post Placement)	30.5	10.6	6,380	5,765	471	6,236	98%	0	21	1	40
D	Total Mixed Ration (1.5 h Post Placement)	21.4	14.2	3,720	3,333	322	3,655	98%	0	0	0	39
D	Total Mixed Ration (1.5 h Post Placement)	21.4	14.2	3,702	3,313	321	3,634	98%	0	0	1	41
D	Total Mixed Ration (1.5 h Post Placement)	21.4	14.2	4,415	3,840	520	4,360	99%	0	21	1	4
D	Total Mixed Ration (0.5 h Post Placement)	33.3	24.1	3,001	2,738	0	2,738	91%	24	12	1	0
D	Total Mixed Ration (1.5 h Post Placement)	28.4	30.9	3,742	3,589	90	3,679	98%	9	4	1	0
E	Total Mixed Ration (0.5 h Post Placement)	23.4	16.9	10,716	10,450	28	10,478	98%	38	0	89	0
E	Total Mixed Ration (1.5 h Post Placement)	21.6	21	7,282	7,105	50	7,155	98%	26	0	42	0
E	Total Mixed Ration (0.5 h Post Placement)	24.1	20.2	16,237	14,264	710	14,987	92%	1,208	0	1	26
E	Total Mixed Ration (6 h Post Placement)	17.6	18.5	2,672	2,507	112	2,622	98%	46	0	0	1
E	Total Mixed Ration (6+h Post: consumed)	16.8	17.2	1,730	1,286	40	1,326	77%	402	0	0	0
E	Total Mixed Ration (6+h Post: consumed)	16.8	17.2	1,416	1,047	122	1,170	83%	244	0	0	2
E	Total Mixed Ration (0.5 h Post Placement)	19.5	21	3,287	2,358	617	2,986	91%	52	0	8	111
E	Total Mixed Ration (6 h Post Placement)	15.4	15.3	1,683	1,025	494	1,520	90%	30	3	3	116
E	Total Mixed Ration (6+h Post: consumed)	15.2	15.3	1,476	967	466	1,436	97%	11	5	2	21
E	Total Mixed Ration (0.5 h Post Placement)	20.2	21.3	12,275	6,007	1,373	7,397	60%	50	13	17	4,784
E	Total Mixed Ration (6 h Post Placement)	22.2	28.6	7,179	4,829	1,753	6,599	92%	40	7	18	502
E	Total Mixed Ration (6+h Post: consumed)	23.5	27.9	851	500	207	708	83%	5	7	8	122
F	Total Mixed Ration (0.5 h Post Placement)	20.6	13.9	1,901	1,493	308	1,800	95%	0	0	1	84
F	Total Mixed Ration (1.5 h Post Placement)	19.1	16.9	1,533	1,166	347	1,513	99%	0	0	1	12
F	Wet Distillers Grain	42.4	22.5	1,191	1,155	22	1,177	99%	0	0	6	2
F	Total Mixed Ration (0.5 h Post Placement)	19.8	18.6	6,137	5,956	141	6,096	99%	19	1	3	0
F	Total Mixed Ration (1.5 h Post Placement)	21	20.8	1,385	1,145	53	1,198	86%	5	0	174	0
F	Total Mixed Ration (0.5 h Post Placement)	27.1	11.9	5,290	3,817	747	4,577	87%	698	0	2	6
F	Total Mixed Ration (6 h Post Placement)	17.5	20.4	2,474	1,569	488	2,064	83%	407	0	1	1
F	Total Mixed Ration (6+h Post: consumed)	18.7	21.1	309	236	61	298	96%	11	0	0	0

Table A4. Individual flush lane fluxes. The high value for Dairy A on 1/15/08 may be a sampling or analytical error (see text). The averages for each dairy are calculated both with and without that date. Values are in $\mu g/m^2/minute$ and are corrected by the subtraction of Field Blank values.

Dairy	Date	Surface Description	Surface Temp.	Air Temp.	**Total ROG**	Ethanol	Methanol	**Total Alcohols**	**Total Alcohols**	Acetaldehyde	d-Limonene	DMDS	DMS
A	6/14/2007	Flush Lane (Pre-Flush)	22.9	22.9	45	5	6	16	35%	24	0	0	1
A	2/15/2008	Flush Lane (Pre-Flush)?	8.2	4.5	3,722	238	14	1,025	28%	171	28	0	203
A	6/3/2008	Flush Lane (Pre-Flush)?	17.1	15.6	438	41	5	81	19%	7	2	0	8
B	4/10/2007	Flush Lane (Pre-Flush)	14.9	13.9	40	6	0	14	35%	1	0	0	0
B	7/12/2007	Flush Lane (Pre-Flush)	19.9	19.8	54	10	28	52	97%	0	0	0	0
B	10/4/2007	Flush Lane (Pre-Flush)?	14.9	19.3	26	8	3	11	43%	0	12	0	0
B	3/5/2008	Flush Lane (Pre-Flush)?	11.7	9.2	216	16	3	140	65%	6	4	0	5
B	7/3/2008	Flush Lane (Pre-Flush)?	21.6	27.6	893	24	9	110	12%	5	3	0	8
C	7/3/2007	Flush Lane (Pre-Flush)	23	20.9	164	0	0	12	7%	136	0	0	7
C	11/1/2007	Flush Lane (Pre-Flush)?	15	14.7	97	14	3	78	81%	4	13	0	0
C	4/4/2008	Flush Lane (Pre-Flush)	14	19	102	9	0	55	54%	2	1	0	1
C	6/16/2008	Flush Lane (Pre-Flush)?	18.7	20.5	735	16	0	86	12%	11	2	0	13
D	10/24/2007	Flush Lane (Pre-Flush)?	17.8	25	77	7	17	59	76%	4	13	0	0
D	3/11/2008	Flush Lane (Pre-Flush)?	13.4	14.2	234	23	66	167	71%	3	2	0	0
D	3/20/2007	Flush Lane (Pre-Flush)	17	17.6	36	6	5	25	68%	0	0	0	0
E	6/21/2007	Flush Lane (Post-Flush)			103	0	2	28	27%	69	1	0	4
E	10/18/2007	Flush Lane (Pre-Flush)	14.4	15.3	175	10	1	110	63%	0	64	0	0
E	3/7/2008	Flush Lane (Pre-Flush)?	11.8	9.9	168	12	11	75	45%	1	3	0	1
E	6/10/2008	Flush Lane (Pre-Flush)?	19.6	22.1	279	14	5	46	16%	3	2	0	7
F	7/19/2007	Flush Lane (Pre-Flush)	21.2	20.2	88	1	2	78	88%	2	0	0	0
F	11/8/2007	Flush Lane (Pre-Flush)	17.3	20	162	20	4	130	80%	9	17	0	0
F	3/24/2008	Flush Lane (Pre-Flush)?	16.5	15.8	175	14	4	66	38%	4	2	0	1
F	7/10/2008	Flush Lane (Pre-Flush)?	26.3	26.2	93	12	13	25	27%	1	0	0	6
D	10/24/2007	Flush Lane (Post-Flush)	14.4	21.1	8	3	3	6	82%	0	1	0	0
D	3/22/2007	Flush Lane (Post-Flush)	13	13.8	2	1	0	1	56%	0	0	0	0
F	4/24/2007	Flush Lane (Post-Scrape)	11.3	12.4	53	5	0	10	19%	0	0	0	1

Average of each dairy											
Flush Lane (Pre-Flush)	17.1	17.9	353	22	9	108	47%	20	7	0	12
Flush Lane (Post-Flush)	12.9	15.8	21	3	1	6	53%	0	0	0	0
A	16.1	14.3	1,402	95	8	374	27%	67	10	0	71
B	16.6	18.0	246	13	9	66	51%	2	4	0	3
C	17.7	18.8	275	9	1	58	38%	38	4	0	5
D	16.1	18.9	116	12	29	83	72%	2	5	0	0
E	15.3	15.8	181	9	5	65	38%	18	17	0	3
F	20.3	20.6	129	12	6	75	58%	4	5	0	2
Average of each dairy with Dairy A 2/15/08 deleted											
Flush Lane (Pre-Flush)	17.1	17.9	241	22	9	108	47%	20	7	0	12
Flush Lane (Post-Flush)	12.9	15.8	21	3	1	6	53%	0	0	0	0
A	16.1	14.3	207	12	9	69	27%	13	7	0	3
B	16.6	18.0	246	13	9	66	51%	2	4	0	3
C	17.7	18.8	275	9	1	58	38%	38	4	0	5
D	16.1	18.9	116	12	29	83	72%	2	5	0	0
E	15.3	15.8	181	9	5	65	38%	18	17	0	3
F	20.3	20.6	129	12	6	75	58%	4	5	0	2

Table A5. Open lot, exercise pen and corral fluxes. Values are in $\mu g/m^2$/minute and are corrected by the subtraction of Field Blank values.

Dairy	Date	Surface Description	Surface Temp.	Air Temp.	Total ROG	Ethanol	Methanol	Total Alcohols	Total Alcohols	Acetaldehyde	d-Limonene	DMDS	DMS
A	06/14/07	Open Lot/Corral (Shallow Manure Pack)	36.5	30.6	243	24	38	65	27%	134	0	0	38
A	09/27/07	Open Lot Shallow Manure Pack	17.2	17.2	38	16	17	34	89%	0	0	0	0
A	02/15/08	Open Lot Shallow Manure Pack	19.0	14.5	36	5	15	21	59%	1	0	0	5
A	06/03/08	Open Lot Shallow Manure Pack	30.9	22.8	119	17	9	99	84%	3	2	0	8
B	04/10/07	Open Lot/Corral (Shallow Manure Pack)	20.3	15.3	6	4	0	5	78%	0	0	0	0
B	07/12/07	Open Lot/Corral (Shallow Manure Pack)	31.5	25.5	131	11	14	27	20%	70	0	0	33
B	10/04/07	Open Lot Deep Manure Pack	13.4	13.4	41	25	10	35	84%	5	1	0	0
B	03/05/08	Open Lot Shallow Manure Pack	12.7	10.6	30	4	10	20	66%	1	0	0	7
B	07/03/08	Open Lot Shallow Manure Pack	39.5	40.2	105	33	26	60	57%	5	0	0	20
C	07/03/07	Open Lot/Corral (Shallow Manure Pack)	38.2	31.2	58	0	5	14	25%	40	0	0	4
C	04/04/08	Open Lot Shallow Manure Pack	23.9	24.4	60	16	31	47	78%	4	1	0	4
C	06/16/08	Open Lot Shallow Manure Pack	33.9	23.5	107	18	28	81	76%	8	2	0	6
D	10/24/07	Open Lot Deep Manure Pack	16.2	15.1	72	34	30	65	90%	3	3	0	0
D	03/11/08	Open Lot Shallow Manure Pack	16.1	15.2	25	6	14	20	83%	1	0	0	1
D	06/25/08	Open Lot Shallow Manure Pack	31.0	24.8	378	64	0	212	56%	13	4	0	33
D	07/26/07	Open Lot/Corral (Shallow Manure Pack)	32.4	30.0	125	1	0	1	1%	115	0	0	0
E	06/21/07	Open Lot/Corral (Shallow Manure Pack)	25.4	20.8	501	1	56	57	11%	363	0	0	80
E	10/18/07	Open Lot Shallow Manure Pack	18.3	14.0	57	10	45	55	96%	1	0	0	0
E	03/07/08	Open Lot Shallow Manure Pack	22.7	20.3	14	3	0	3	20%	1	0	0	3
E	06/10/08	Open Lot Shallow Manure Pack	36.2	27.2	95	19	19	53	55%	15	4	0	13
F	04/24/07	Open Lot/Corral (Shallow Manure Pack)	24.0	18.0	2	0	0	0	0%	0	0	0	0
F	11/08/07	Open Lot Deep Manure Pack	20.3	14.4	16	6	7	13	81%	0	2	0	0
F	03/24/08	Open Lot Shallow Manure Pack	19.3	15.0	91	18	15	48	52%	11	1	0	21
A	06/14/07	Open Lot/Corral (Deep Manure Pack)	28.9	22.7	180	22	28	52	29%	111	0	0	13
A	09/27/07	Open Lot Deep Manure Pack	16.5	14.4	20	4	14	18	91%	0	0	0	0
A	02/15/08	Open Lot Deep Manure Pack	17.5	14.2	73	11	31	46	62%	2	0	0	5
A	06/03/08	Open Lot Deep Manure Pack	24.0	21.4	93	31	27	58	63%	6	1	0	6
B	04/10/07	Open Lot/Corral (Deep Manure Pack)	24.5	22.4	22	14	0	14	62%	0	0	0	5
B	07/12/07	Open Lot/Corral (Deep Manure Pack)	24.2	21.8	29	10	15	26	89%	0	0	0	0
B	10/04/07	Open Lot Deep Manure Pack	21.0	22.9	41	19	14	33	81%	4	2	0	0
B	03/05/08	Open Lot Deep Manure Pack	9.3	9.2	22	2	6	12	53%	1	0	0	4
B	07/03/08	Open Lot Deep Manure Pack	30.3	28.5	942	62	90	176	19%	17	2	0	174
C	07/03/07	Open Lot/Corral (Deep Manure Pack)	35.2	26.8	141	0	15	26	18%	93	0	0	17
C	06/16/08	Open Lot Deep Manure Pack	37.0	22.8	113	30	23	76	68%	12	3	0	5
D	10/24/07	Open Lot Deep Manure Pack	16.2	15.1	86	40	36	76	88%	6	3	0	0
D	03/11/08	Open Lot Deep Manure Pack	14.6	12.2	62	8	10	58	93%	1	1	0	2
D	06/25/08	Open Lot Deep Manure Pack	35.1	24.2	327	54	0	69	21%	18	4	0	20
D	07/26/07	Open Lot/Corral (Deep Manure Pack)	26.3	26.6	220	21	42	85	39%	84	0	0	46
E	06/21/07	Open Lot/Corral (Deep Manure Pack)	33.8	30.2	1,132	2	74	76	7%	517	0	0	537
E	06/21/07	Open Lot/Corral (Deep Manure Pack)	36.0	30.2	1,657	2	87	89	5%	734	0	0	831
E	10/18/07	Open Lot Deep Manure Pack	11.9	10.6	61	9	50	59	97%	1	0	0	1
E	03/07/08	Open Lot Deep Manure Pack	21.6	19.9	99	13	11	67	68%	8	2	0	5
E	06/10/08	Open Lot Deep Manure Pack	29.7	27.2	129	27	25	82	63%	8	2	0	25
F	04/24/07	Open Lot/Corral (Deep Manure Pack)			17	6	0	6	35%	0	0	0	5
F	11/08/07	Open Lot Deep Manure Pack	20.0	20.0	57	23	27	51	90%	3	1	0	0
F	03/24/08	Open Lot Deep Manure Pack	16.3	12.2	112	48	16	68	61%	13	1	0	23
F	07/10/08	Open Lot Deep Manure Pack	31.4	29.5	197	32	31	109	56%	16	4	0	50

Table A6. Ambient samples taken prior to July, 2007. Values are concentrations (ppmV for Methane, ppbV for CO and pptV for all others). Samples were to be collected in canisters over a 5 minute period after 30 minutes of a consistent wind direction. Most samples reported did not meet these minimum modeling criteria. The number of samples collected for each category is shown in parentheses.

VOC	common name	mol.wt.	Conc.	Upwind (19)	Animals (22)	Lagoon (14)	Digester (4)
Methane (ppmv)	Methane	16.04	ppmV	6.7	4.3	6.0	186.6
CO (PPBV)	Carbon Monoxide	28.01	ppbV	881.8	180.7	453.0	199.0
Methanol (B)	Methanol	32.04	pptV	229,649.3	15,298.0	145,152.9	6,612.8
Ethanol (B)	Ethanol	46.07	pptV	2,730,499.5	57,571.5	544,337.1	8,333.3
Acetone (MS)	Acetone	58.08	pptV	26,759.8	7,497.5	5,260.6	3,162.0
D-Limonene (B)	D-Limonene	136.24	pptV	2,209.7	1,378.2	3,033.8	55.0
OCS (MS)	Carbonyl Sulfide	60.07	pptV	887.8	610.0	553.1	594.0
DMS (MS)	Dimethylsulfide	62.14	pptV	3,280.2	691.4	887.3	1,142.8
CFC-12 (C/D/MS)	Dichlorodifluoromethane	120.91	pptV	530.5	547.5	517.2	569.0
CS2 (MS)	Carbon Disulfide	76.14	pptV	18.6	42.8	57.7	71.0
CFC-11 (C/D/MS)	Trichlorofluoromethane	137.38	pptV	254.1	285.5	252.9	285.8
CFC-113 (MS)	Ethane, 1,1,2-trichloro-1,2,2-trifluoro-	187.37	pptV	76.3	84.1	75.9	83.3
CFC-114 (C/MS)	1,2-Dichloro-1,1,2,2-tetrafluoroethane	170.92	pptV	14.1	15.7	14.3	15.5
H-1211 (C/D/MS)	hexadecane	226.45	pptV	4.8	5.1	4.9	5.3
HCFC-141b (MS)	1,1-dichloro-1-fluoroethane	116.95	pptV	21.2	28.0	22.3	26.0
HCFC-142b (MS)	1-Chloro-1,1-difluoroethane	100.50	pptV	21.1	23.2	19.3	27.0
HCFC-22 (MS)	chlorodifluoromethane	86.47	pptV	308.7	406.6	266.0	489.0
HFC-134a (MS)	hafnium carbide	190.50	pptV	75.8	85.2	85.2	76.5
C2Cl4 (C/D/MS)	Tetrachloroethylene	165.83	pptV	61.6	62.5	89.6	22.0
C2HCl3 (D/MS)	Trichloroethylene	131.39	pptV	4.2	4.5	5.4	5.0
CCl4 (C/MS)	Carbon tetrachloride	153.82	pptV	91.3	101.4	93.7	102.8
CH2Br2 (D)	Methane, dibromo-	173.83	pptV	0.4	0.4	0.4	0.3
CH2Cl2 (MS)	Methylene chloride	84.93	pptV	50.4	77.0	53.6	68.5
CH3 Br (MS)	Methyl bromide	94.94	pptV	28.4	29.0	23.7	23.3
CH3CCl3 (C/MS)	Ethane, 1,1,1-trichloro-	133.40	pptV	16.9	19.2	16.9	18.5
CH3Cl (MS)	Methyl chloride	50.49	pptV	718.2	942.9	832.7	771.0
CH3I (C/MS)	Methyl iodide	141.94	pptV	2.1	1.3	2.5	1.0
CHBr3 (C/MS)	Methane, tribromo-	252.73	pptV	0.8	1.1	0.9	0.7
CHCl3 (MS)	Chloroform	119.38	pptV	20.9	17.4	15.4	16.0
MeONO2 (C/D)	Methyl nitrate	77.04	pptV	20.0	6.4	9.9	5.8
EtONO2 (C/D)		92.00	pptV	16.9	3.7	5.3	4.3
i-PrONO2 (C/D)		104.00	pptV	19.1	11.7	18.8	17.6
n-PrONO2 (D)		104.00	pptV	1.8	1.1	1.5	2.0
2-BuONO2 (C/D)		114.00	pptV	10.1	7.2	9.4	9.4
2-PeONO2 (C/D)		124.00	pptV	3.7	3.0	3.3	3.7
3-PeONO2 (C/D)		124.00	pptV	2.8	2.3	2.3	2.9
Propane (B/E)	Propane	44.10	pptV	1,658.7	1,292.1	1,798.4	12,603.8
Propene (B/E)	Propene	42.08	pptV	192.1	167.2	1,609.4	813.5
Ethane (E)	Ethane	30.07	pptV	2,174.7	1,523.5	2,066.9	3,373.0
Ethene (E)	Ethene	28.05	pptV	403.4	719.6	2,539.9	2,722.8
Ethyne (E)	Acetylene	26.04	pptV	382.9	401.5	383.7	630.5
n-Butane (B/E)	Butane	58.12	pptV	162.9	203.6	417.6	233.8
i-Butane (B/E)	Isobutane	58.12	pptV	199.2	171.5	509.6	262.8
1,3-Butadiene (B)	Butadiene	54.09	pptV	0.6	0.0	0.0	0.0
1-Butene (E)	1-Butene	56.11	pptV	2.1	6.6	5.6	0.0
trans-2-Butene (B)	2-Butene-trans	56.11	pptV	0.7	0.0	0.0	0.0
n-Pentane (E)	Pentane	72.15	pptV	120.2	166.3	129.7	152.8
i-Pentane (E)		72.00	pptV	206.7	390.0	292.1	299.5
n-Hexane (B/E/MS)	Hexane	86.18	pptV	100.9	290.5	391.5	81.0
Benzene (MS)	Benzene	78.11	pptV	86.3	109.7	110.6	97.0
Isoprene (MS)	Isoprene	68.12	pptV	150.5	77.2	73.1	58.0
Toluene (MS)			pptV	122.9	220.3	161.2	156.3
o-Ethyltoluene (MS)	2-Ethyltoluene	120.19	pptV	34.8	105.0	59.1	7.3
m-Ethyltoluene (MS)	3-Ethyltoluene	120.19	pptV	47.0	157.1	58.4	11.0
Ethylbenzene (MS)	Ethyl Benzene	106.17	pptV	118.4	441.9	131.1	54.0
2-Methylpentane (B)	2-Methylpentane	86.18	pptV	136.6	154.8	171.4	77.3
3-Methylpentane (B)	3-Methylpentane	86.18	pptV	119.4	99.1	103.6	12.5
alpha Pinene (MS)	alpha Pinene	136.24	pptV	21.7	103.5	25.4	6.5
beta Pinene (MS)	beta Pinene	136.24	pptV	4.1	95.3	13.8	6.3
m-Xylene (MS)	m-Xylene	106.17	pptV	46.1	152.7	63.1	25.5
p-Xylene (MS)	p-Xylene	106.17	pptV	46.0	152.5	63.4	25.0
o-Xylene (MS)	o-Xylene	106.17	pptV	16.6	62.4	22.9	6.3
1,2,4-Trimethylbenzene (I	1,2,4-Trimethylbenzene	120.19	pptV	88.2	314.7	124.4	22.8
1,3,5-Trimethylbenzene (I	1,3,5-Trimethylbenzene	120.19	pptV	4.2	22.1	9.9	0.0

APPENDIX B

This appendix is the report submitted October 1, 2007 to CARB for the Year-1 progress report. In order to comply with Task 4, a draft was prepared in April, 2007 and submitted to the project's advisory group to begin the process of finalizing the Year-2 sampling and analysis program for not only the CARB project but also the other, related monitoring programs for nitrogen compounds, alcohols and feed components. The report is included here in its original form as a reference for the development of the Year-2 monitoring program to collect the data used for this final project report.

Data in the figures and tables of appendix B were from the initial year of the project and were superseded by Year-2 data reported above. These data were used primarily to validate various sampling methods and did not include all the field and media blanks collected to correct Year-2 results. While much of the Year-1 results are sufficiently similar to the final results to add credibility to the conclusions, no data from Year-1, reported below, was referred to in the final report nor should it be used to draw conclusions regarding dairy emission rates.

Progress Report: January 1 to March 31, 2007
(Includes summary of results from Year 1)

Dairy Operations: An Evaluation and Comparison of Baseline and Potential Mitigation Practices for Emissions Reductions In the San Joaquin Valley

Principal Investigator:
Dr. Charles Krauter
California State University Fresno

Co-Principal Investigator:
Dr. Donald Blake
University of California Irvine

California Air Resources Board Contract No. 04-343
Project to be administered as CSU Fresno Foundation Project #37411

1. Narrative account of project tasks completed or partially completed during report period:

The activity covered by this contract period was primarily focused on completing the Year-1 tasks and developing the sampling and analytical program to be used for Year-2 sampling. The primary sampling procedure, as described in the proposal, was the collection of upwind and simultaneous downwind samples at each dairy for each sampling period. The wind conditions required for this canister sampling were not present for some of the fall and most of the winter attempts. The problems and proposed changes in the protocol for Year-2 will be discussed in detail below. The additional sampling with flux chambers was very successful and, combined with additional analytical methods supported by the supplemental funding from CSU-ARI, has filled the data gaps in the ambient sampling program very well. In fact, as discussed below, we are proposing to shift the emphasis to the flux chamber sampling and continue the ambient sample collection only when the wind conditions are suitable for sampling and modeling of the results.

Summaries of the data collected by both ambient and flux chamber sampling and analyzed by Dr. Blake's lab at UCI as well as the real-time monitoring and in-house analysis done at CSU Fresno are attached to this report. A revised Year-2 sampling program is also attached for review prior to discussion with the advisory group and adoption for the early summer sampling period (Task 4). The Year-2 monitoring program (Task 5) is scheduled to start late May, 2007.

2. Problems encountered during report period and their resolution:

The primary problem encountered during the initial year of field monitoring was the difficulty in collecting upwind and downwind ambient samples under conditions that would allow modeling of the results to calculate flux rates. Minimum wind conditions were initially determined to be a wind speed of at least 1 meter/second and a wind direction within 20 degrees of the mean for a period of at least 2 hours. That proved to be nearly impossible to achieve except for a few times in April and May. It was particularly difficult to find during the evening hours and for the dairies located south of Fresno. A revision of the "minimum wind conditions" was devised to reduce the time to 30 minutes at the end of which the canisters would be filled over a 5 minute period. It was determined that the upwind sample air would reach the downwind locations in 5 minutes or less at the minimum wind speed of 1 meter/second so those became the minimal sampling conditions. All the data reported for the ambient sampling in the attached summary was collected under these revised sampling limits. The expense and effort required to analyze a canister made it necessary to limit the sampling to those times when wind conditions would enable the results to be considered significant and for modeling to be possible. Less than half of the fall sampling and none of the planned winter ambient sampling was accomplished because minimal wind conditions were not present. It should be noted that the successful use of the flux chambers and the addition of the INNOVA gas analyzer were being developed at the same time the problems with ambient sampling was occurring. It became evident that the flux chamber method would provide more specific source sampling and was not subject to the wind requirements and so was a much better method for the systematic sampling of the different dairies for the three seasonal sampling periods.

3. Discussion of work planned before next report:

Task 4, the development of a revised Year-2 sampling/analysis program and its review by the advisory group will be the next work to be accomplished. A draft of the Year-2 program is attached to this report and a meeting or conference call with the advisory group should occur by early May. If the proposed program is approved, the first sampling period will begin later in May (Task 5). Sampling of the six dairies should be complete by the end of June and the next sampling period will start in September. Additional related sampling of land applications, feed supplements, and photosynthetic lagoons will be done at these and other dairies during the time between sampling periods (Task 7). This additional work will be supported by supplemental funding from CSU-ARI, USDA and the California Dairy Campaign.

4. Allocation of budget items during report period:

An up-to-date accounting of the expenditures is not currently available. The sub-contract with Dr. Blake at UC Irvine is in place. The Year-1 samples have been analyzed. UC Irvine will bill CSU Fresno for the work to date and it will be included in a billing to ARB in May.

5. Percentage of completion for each task:

Tasks 1, 2 and 3 are completed
Task 4 is approximately 50% completed
Task 5 is approximately 0% completed
Task 6 is approximately 0% completed
Task 7 is approximately 50% completed

The original proposal, written in early 2005, emphasized the use of samples collected in Summa Canisters taken simultaneously upwind and downwind of significant dairy operations such as the animal housing and lagoon areas. This method had been successfully employed in the previous study done at two of these six dairies and was expected to be an appropriate method if suitable analytical procedures were added. Net increases in ROG between the upwind and downwind samples were assumed to be emissions from that dairy operation. Modeling of the sampling results with a Gaussian Plume model would calculate the emissions from that operation for the sampling period. The original plan was to sample for a 2 hour period during the day for two consecutive days and also collect a night sample on one of the two days. This was to be done at each of the six dairies for each of the three sampling periods (May-June, September-October and January-February). This has proven to be impossible. Minimum wind conditions for ambient samples (1 meter/second and a deviation of no more than 20 degrees of direction) are rarely present except in the spring and for the dairies north of Fresno. The complete set of samples was collected twice out of the planned 18. Samples were collected for 5 minutes rather than 2 hours for most of the spring and summer sampling periods but no winter ambient samples were collected because wind conditions never approached the minimal levels required for modeling. Additionally, some of the spring samples were the initial canisters sent down to UCI for analysis. Dr. Blake is in the process of developing a standard gas that should increase the precision of the quantification of these samples considerably. Until that standard is used, the concentrations reported should be considered as relative values rather than absolute concentrations.

The complete data set of analysis by the UCI lab of all ambient samples taken in Year-1 is attached as an Excel file titled "Ambient Data UCI Year1". A summary of net increase for the 17 samples from animal housing, 12 samples from lagoons and 3 samples from the digester at Dairy E are shown on the next page. The list of species has been sorted to place the largest concentrations first. The methane (ppmV), CO (ppbV) and Acetone (pptV) are shown in the table but not included in the total ROG calculation. The values shown in the summary table are the average of the net difference (downwind – upwind) in concentration for each species.

Significant results from this data are:

1. The animal housing areas are a much greater source of ROG than the lagoons. The negative net differences seen for the lagoons will have to be evaluated and modeled on a case by case basis to determine the actual lagoon emission.
2. Alcohols are the primary ROG from animal housing. This is confirmed by flux chamber samples summarized below. The average total net ROG of 11.6 ppbV for animal housing is 70% Methanol plus Ethanol. The low and negative values for alcohols from lagoon samples may be from contributions to the upwind value from animal housing or feed storage, depending upon the specific dairy.

Table 1. Summary of Net concentrations of Year-1 ambient samples.

			Animal Housing		Lagoon		Digester (Dairy E	
			Total	Average	Total	Average	Total	Average
	units	common name						
Methane (ppmv)	ppmv	Methane	17	-3	12	-3	3	243
CO (PPBV)	ppbv	Carbon Monoxide	17	-415	12	-273	3	5
Ethanol (B)	pptv	Ethanol	17	2,966	12	-11,557	3	299
Methanol (B)	pptv	Methanol	17	5,199	12	-1,858	3	3,062
Acetone (MS)	pptv	Acetone	17	3,545	12	353	3	325
D-Limonene (B)	pptv	D-Limonene	17	495	12	-600	3	15
DMS (MS)	pptv	Dimethylsulfide	17	338	12	50	3	76
alpha Pinene (MS)	pptv	alpha Pinene	17	91	12	-1	3	1
n-Hexane (B/E/MS)	pptv	Hexane	17	46	12	-13	3	7
Ethane (E)	pptv	Ethane	17	-23	12	-136	3	259
OCS (MS)	pptv	Carbonyl Sulfide	17	141	12	63	3	142
2-Methylpentane (B)	pptv	2-Methylpentane	17	52	12	4	3	-54
3-Methylpentane (B)	pptv	3-Methylpentane	17	-12	12	-58	3	-8
Ethene (E)	pptv	Ethene	17	166	12	46	3	567
Propane (B/E)	pptv	Propane	17	-404	12	-634	3	1,549
Propene (B/E)	pptv	Propene	17	29	12	-6	3	205
CH3Cl (MS)	pptv	Methyl chloride	17	305	12	95	3	229
Isoprene (MS)	pptv	Isoprene	17	38	12	-31	3	51
beta Pinene (MS)	pptv	beta Pinene	17	117	12	14	3	-10
HCFC-22 (MS)	pptv	chlorodifluoromethane	17	119	12	10	3	-95
CFC-12 (C/D/MS) (PPTV)	pptv	Dichlorodifluoromethane	17	-2	12	-9	3	10
Ethylbenzene (MS)	pptv	Ethyl Benzene	17	422	12	16	3	15
CH2Cl2 (MS)	pptv	Methylene chloride	17	30	12	2	3	10
1,2,4-Trimethylbenzene (MS)	pptv	1,2,4-Trimethylbenzene	17	271	12	39	3	-20
Ethyne (E)	pptv	Acetylene	17	18	12	25	3	46
i-Pentane (E)	pptv	?	17	233	12	46	3	-80
CFC-11 (C/D/MS)	pptv	Trichlorofluoromethane	17	20	12	11	3	13
n-Butane (B/E)	pptv	Butane	17	38	12	-11	3	9
i-Butane (B/E)	pptv	Isobutane	17	-16	12	-24	3	-55
MeONO2 (C/D)	pptv	Methyl nitrate	17	0	12	-1	3	1
n-Pentane (E)	pptv	Pentane	17	116	12	3	3	16
EtONO2 (C/D)	pptv	?	17	-1	12	-1	3	0
m-Ethyltoluene (MS)	pptv	3-Ethyltoluene	17	140	12	11	3	-6
Toluene (B/MS)	pptv	Toluene	17	137	12	35	3	20
i-PrONO2 (C/D)	pptv	?	17	0	12	1	3	3
p-Xylene (MS)	pptv	p-Xylene	17	145	12	20	3	6
m-Xylene (MS)	pptv	m-Xylene	17	145	12	19	3	6
HFC-134a (MS)	pptv	hafnium carbide	17	14	12	6	3	-3
CHCl3 (MS)	pptv	Chloroform	17	2	12	0	3	1
CCl4 (C/MS)	pptv	Carbon tetrachloride	17	5	12	4	3	4
o-Ethyltoluene (MS)	pptv	2-Ethyltoluene	17	87	12	29	3	-13
CS2 (MS)	pptv	Carbon Disulfide	17	22	12	50	3	65
Benzene (MS)	pptv	Benzene	17	21	12	9	3	-6
2-BuONO2 (C/D)	pptv	?	17	0	12	0	3	0
CFC-113 (MS)	pptv	thane, 1,1,2-trichloro-1,2,2-trifluor	17	3	12	3	3	1
C2Cl4 (C/D/MS)	pptv	Tetrachloroethylene	17	15	12	13	3	9
o-Xylene (MS)	pptv	o-Xylene	17	60	12	5	3	-1
HCFC-141b (MS)	pptv	1,1-dichloro-1-fluoroethane	17	6	12	1	3	1
HCFC-142b (MS)	pptv	1-Chloro-1,1-difluoroethane	17	1	12	1	3	-10
1,3,5-Trimethylbenzene (MS)	pptv	1,3,5-Trimethylbenzene	17	23	12	6	3	0
CH3 Br (MS)	pptv	Methyl bromide	17	-1	12	2	3	2
C2HCl3 (D/MS)	pptv	Trichloroethylene	17	1	12	1	3	1
CH3CCl3 (C/MS)	pptv	Ethane, 1,1,1-trichloro-	17	2	12	0	3	0
CH3I (C/MS)	pptv	Methyl iodide	17	0	12	0	3	0
CFC-114 (C/MS)	pptv	2-Dichloro-1,1,2,2-tetrafluoroethar	17	1	12	1	3	0
n-PrONO2 (D)	pptv	?	17	0	12	0	3	0
1-Butene (E)	pptv	1-Butene	17	4	12	2	3	0
trans-2-Butene (B)	pptv	2-Butene-trans	17	1	12	-1	3	0
2-PeONO2 (C/D)	pptv	?	17	0	12	0	3	0
H-1211 (C/D/MS)	pptv	hexadecane	17	0	12	0	3	0
3-PeONO2 (C/D)	pptv	?	17	0	12	0	3	0
cis-2-Butene (B)	pptv	2-Butene-cis	17	0	12	0	3	0
1,3-Butadiene (B)	pptv	Butadiene	17	-1	12	0	3	-4
CH2Br2 (D)	pptv	Methane, dibromo-	17	0	12	0	3	0
CHBr3 (C/MS)	pptv	Methane, tribromo-	17	0	12	0	3	0
				11,630		**-14,298**		**6,333**
		Ethanol % of ROG		**26%**				**5%**
		Methanol % of ROG		**45%**				**48%**
		Total Alcohol % of ROG		**70%**				**53%**

Flux Chamber Data Summary

The use of the EPA Isolation Flux Chamber had not been adopted by our research group when this project was initially proposed. We had observed its use by Dr. Chuck Schmidt at two of the dairies in this study and we expected to develop the method as an additional monitoring technique with supplemental funding from CSU-ARI. The difficulties encountered with the ambient sampling provided a strong inducement to develop the flux chambers as an alternative that would both eliminate the problem of the minimum wind requirement and enable much more specific monitoring of different sources within the components of the dairy operation. The method has been very successful with respect to both of those goals. There is a US-EPA Protocol for the Isolation Flux Chamber that has been published and used by a number of researchers. We used the published protocol without modification for the sampling described below.

Unlike the ambient, upwind/downwind sampling where the dairy could only be differentiated into major components such as the animal housing and lagoon systems; sampling with the flux chambers enables very specific areas to be isolated and sampled without interference or contamination from other, nearby sources. We have developed a monitoring program with the flux chambers that has proven to be effective in the last two sampling periods and will be proposed as the primary method for the Year-2 protocol. The flux chambers have nearly the opposite problem compared to the ambient canister samples. The flux chamber is limited to the $0.5M^2$ area that it covers and the sampling period is limited to about 30 minutes following the 30 minute flush/preparation time. Replication of the flux chamber data is therefore necessary. At least 2 chambers are used for each measurement and 4 will sometimes be required when variability is expected to be high. We currently have 4 chambers with an additional 4 on order. That should be sufficient for the proposed Year-2 monitoring program.

The ability to sample more discrete locations within the dairy has already shown the flux chambers to be an ideal method for work such as this. The initial discovery that alcohols, particularly ethanol, are the dominant ROG in many samples led us to suspect the silage and feed as possible significant sources. Flux chambers were used to monitor those components as well as fresh manure on the flush lanes, the manure pack on the exercise corrals and some monitoring of solids and effluent applications to crop land. The emerging importance of ethanol and methanol created the need to monitor those ROG's more frequently and at less cost than the canister samples that required GC-MS analysis either at UCI or in-house. A photo-acoustic, multi-gas analyzer was purchased to monitor N_2O and NH_3 from the flux chambers at the six dairies for the Denitrification/Decomposition project in collaboration with Bill Salas at New Hampshire. This INNOVA has the capability to monitor six gasses in real time at sub-ppb concentrations. We had the INNOVA configured for ethanol and methanol along with the CO_2, water vapor, N_2O and NH_3 needed for the UNH project. The INNOVA data for the alcohols was very consistent when compared to the analysis of a canister taken at the same time and analyzed at UCI or in-house. The real-time INNOVA values for silage were consistently 3-4 times greater than the UCI analysis of a canister from the same flux chamber (see Table 2). Dr. Blake as well as others collaborating on the project have questioned the ability of the GC-MS system to extract all of the water soluble gasses such as these alcohols from the canisters when they are analyzed. There is the possibility that ethanol and methanol values from canister analysis are reduced by this sampling problem and so the higher INNOVA measurements may, in fact be more accurate.

In addition to canisters sampled from the flux chamber for GC-MS analysis and the INNOVA monitoring that is done at the same time, NH_3 is also monitored with a denuder and we have recently been sampling with sorbent tubes for VFA analysis. The VFA data is not yet available but the method will be used in the Year-2 program if it proves to be effective.

The components of the dairy operations for which flux chambers were used are silage, feed (Total Mixed Ration or TMR), exercise corrals, and flush lanes on a regular basis beginning with the fall-’06 sampling period. Some data is available from summer-’06 for these sources as well as others such as feed supplements, solids storage, and land applications. The flux chambers are being adapted to float on lagoons but no work other than method development has been done to date. A summary of the data from canister sampling in the flux chambers and a comparison with INNOVA data taken at the same time is shown below for silage, TMR, exercise corrals and flush lanes. This is only a small amount of the INNOVA data since only those measurements that coincided with canister samples are reported here. Additional INNOVA data is shown where it is needed to support the results for this project.

Silage

The most likely source of ethanol at a dairy was expected to be the silage pile where it would be produced by yeast fermentation of the plant material as part of the ensiling process. Flux chambers were placed at the face of the pile where it is exposed for the feed mixing operation. No monitoring of the larger, covered portion of the silage pile has been done to date. Both the undisturbed face of the pile and the loose silage disturbed by the feed mixing equipment were sampled with the flux chambers. Canisters were used to sample from the flux chamber and analyzed at both UCI and CSUF. The INNOVA gas analyzer sampled and reported the alcohols in real-time from the chambers. Three INNOVA samples of one minute each were analyzed and recorded either just before or just after the canister sample was taken. Both samples were completed within the same 10 minute period. The averages of the 8 canisters analyzed at UCI are shown in Table 2. The INNOVA unit became available in late June and was matched with five of the canister samples, also shown in Table 2. The complete data set can be found in the Excel file titled “Year 1 Flux Chamber data”.

Table 2. Summary of total ROG and alcohol fluxes in silage samples.

Silage
Emission Rate (μg/m²/min)
5 INNOVA samples with 8 UCI canisters
Summary and Comparison of UCI Canisters with INNOVA data

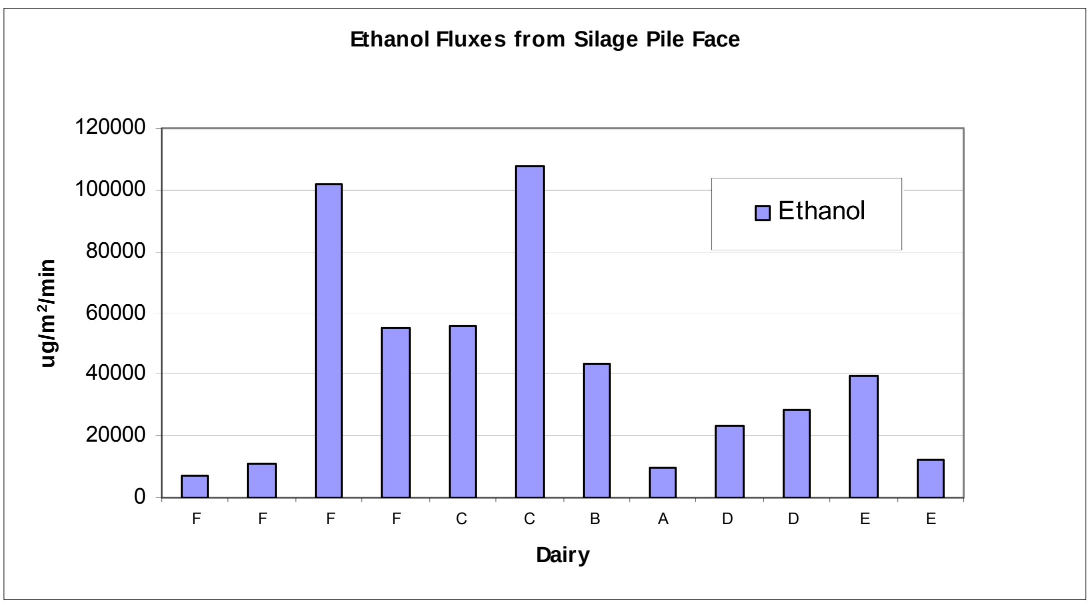
UCI Canister Ethanol μg/m²/min.	14,897
UCI Canister Methanol μg/m²/min.	695
INNOVA Ethanol μg/m²/min.	60,598
INNOVA Methanol μg/m²/min.	12,892
INNOVA/UCI Ethanol ratio	5.14
INNOVA/UCI Methanol ratio	11.53
Total VOC's (UCI) μg/m²/min.	16,303
Total ROG (UCI) μg/m²/min.*	15,783
Ethanol %	87.8%
Methanol %	9.2%
Total Alcohol %	97.0%

*Total ROG's = UCI total VOC - (methane+CO+Acetone)

The alcohols, ethanol and methanol, were nearly all of the ROG measured from the silage. They were 97% of the total measured by the canister analysis. Ethanol concentrations were the dominant ROG at about 10 times the methanol levels. The INNOVA measured the alcohols at higher concentrations than the UCI canister analysis. There was one anomalous ethanol value and one methanol flier from the INNOVA. If those are removed from the average ratios, the INNOVA/Canister ratio is consistently between 3 and 4 for both alcohols. The INNOVA was returned for recalibration of the alcohol channels late in the summer and the data from the unit following that was much more consistent. Further comparisons between canister analysis and INNOVA data will be available in Year-2. The development of a standard at UCI to improve the quantification of those analyses will increase the validity of the comparison.

The contribution of silage to Ethanol emissions from dairies was rather variable as shown in the data files and summarized in Figure 1 below. The data in Fig. 1 is from the INNOVA and includes those values from Table 2 along with others taken when no canister sample was collected.

Figure 1. Ethanol flux rates from silage piles monitored at the six dairies from April to November, 2006. Each value is the average of 3 measurements taken within a 4 minute period.



The considerable variability could be due to a number of factors. Some silage is made from corn, including the grain, while other silage is made from grass and winter grown cereals with a lower carbohydrate content that should produce less ethanol. A more interesting variable from the point of view of potential mitigation is the density of the silage pile as a result of the amount of compaction during its construction. Ethanol production from yeast fermentation is a symptom of low quality silage. Good silage is made when the plant material is compacted to the point where no oxygen is present and lactic acid bacteria are the predominant microbe. Lactic acid formation reduces the pH of the silage and preserves it. Incomplete compaction allows sufficient oxygen into the silage for yeast to exist and ferment carbohydrates to ethanol. The density of the silage piles monitored by the flux chambers was measured by taking a core according to a published method and weighing it. The resulting densities are shown in Table 3.

Table 3. Silage density of piles monitored at the six diaries during 2006.

Dairy	Date	Avg. DM Denstiy
CSUF	3/24/2006	18.7
CSUF	4/7/2006	11.2
A	4/10/2006	17.9
A	4/13/2006	15.1
A	4/24/2006	16.9
A	9/26/2006	11.1
B	7/10/2006	14.1
B	9/6/2006	9.3
C	1/11/2007	11.3
C	8/8/2006	6.2
D	6/1/2006	14.1
D	11/14/2006	12.2
E	6/23/2006	9.9
F	7/24/2006	8.6

The high ethanol fluxes in Fig. 1 for the silage at dairy C was measured on August 8 and corresponds to the lowest density (6.2) of all the measured silage. The high ethanol found at dairy F was measured on July 24, matching the next lowest silage density (8.6). It appears that high ethanol fluxes from silage are linked to low density silage. The density of silage recommended by UC is 12 to 15. The ethanol fluxes from silage in that range were much lower, presumably because the yeast fermentation was reduced by the more anaerobic conditions. The monitoring of ethanol and comparison with silage density will be continued at each dairy in Year-2.

Total Mixed Ration (Feed)

The feed is a mixture of various components formulated to provide the proper amount of energy and nutrition to the various groups of animals at the dairy. The solid and liquid components are loaded into a large bin on a truck or trailer where they are mechanically mixed and delivered to the animals through a chute while the feed wagon is driven along the feed lane. This operation typically takes place two or three times each day and the Total Mixed Ration (TMR) is consumed by the cows in about a 6 hour period. Silage is usually the largest component of the TMR so significant ethanol fluxes might also be expected from the feeding operation. Since the feed is spread over a much larger area than that of the silage pile face, the potential for emissions is greater.

The fluxes from the TMR were monitored by placing chambers on the feed as soon as it was delivered to the animals. The emission of ethanol was expected to change as the feed was consumed and as the initial volatile ROG rapidly vaporized. A second set of flux chambers was placed on the feed after an hour to monitor any change in emissions with time. The flux chambers must be flushed with zero air for 30 minutes before sampling or measurements are taken according to the US-EPA published protocol so the values reported are for 30 minutes and

90 minutes after feeding. The average of 18 canisters collected between May and November, 2006 are shown along with 12 corresponding INNOVA samples in Table 4.

Table 4. Summary of total ROG and alcohol fluxes in feed (TMR) samples.

FEED

Emission Rate (μg/m²/min)

12 INNOVA samples with 18 UCI canisters

Summary and Comparison of UCI Canisters with INNOVA data

UCI Canister Ethanol μg/m²/min.	5,194
UCI Canister Methanol μg/m²/min.	764
INNOVA Ethanol μg/m²/min.	23,697
INNOVA Methanol μg/m²/min.	2,922
INNOVA/UCI Ethanol ratio	3.98
INNOVA/UCI Methanol ratio	3.73
Total VOC's (UCI) μg/m²/min.	6,671
Total ROG (UCI) μg/m²/min.*	6,211
Ethanol %	82.8%
Methanol %	16.2%
Total Alcohol %	99.0%

*Total ROG's = UCI total VOC - (methane+CO+Acetone)

Alcohols are the dominant ROG in the TMR as they were in silage. The flux rates are lower since not all the components are subject to fermentation. The higher moisture content of the TMR compared to silage may also be a factor if the soluble alcohols are being trapped in water. The ethanol:methanol ratio is somewhat lower than in silage as well. The ratio of the INNOVA data to the canister samples is even more consistent than it was for silage.

A comparison of the initial TMR emissions measured at 30 minutes to those measured at 90 minutes (Fig. 2) shows a considerable decrease in volatile ethanol over time. The flux of ethanol appears to decrease by nearly half from the initial hour to the second hour. A few samples have been taken over a longer period of time. Those indicate this decrease in alcohol flux continues through the several hours that the TMR is in place.

The third significant ROG found in the TMR samples after ethanol and methanol was limonene. It was found at concentrations of about 10% of the methanol flux at dairies A, C and E, at times. Dairy A frequently uses citrus pulp as a component of their TMR and the other dairies occasionally do the same. The presence of limonene in the TMR was always correlated with the use of citrus pulp as a supplement.

Flush Lanes and Fresh Manure

Flux chambers were used on the surface of the flush lanes to monitor emissions from both the fresh manure as it is deposited when the animals are feeding and the flushed lanes when the manure had been removed to the lagoon system. The highest fluxes were expected to be just prior to flushing and that appears to be the case. Flux chambers were used 8 times on 5 of the dairies to monitor the pre-flush fluxes in the summer and fall of 2006. The dominant ROG is ethanol, followed by methanol as it was for the feed and silage. The presence of limonene that was correlated with citrus pulp in the TMR also occurred as a flux from the fresh manure at some of those same times. The magnitude of the ROG flux from the fresh manure is less than 10% of that measured for the feed but the area of the flush lane is considerably larger so they may be similar with respect to actual emissions. The sampling program in Year-2 will include flux chamber monitoring at several intervals to characterize the changes in flux from the clean lanes to the heaviest manure load just prior to flushing.

Table 5. Summary of total ROG and alcohol fluxes in fresh manure samples.

Flush Lane (Pre Flush)		
Emission Rate (μg/m²/min)		
	8 UCI canisters	
Summary Comparison of UCI Canisters		
UCI Canister Ethanol μg/m²/min.		265
UCI Canister Methanol μg/m²/min.		43
Total VOC's (UCI) μg/m²/mir Total Alcohol %		541
Total ROG's*		317
	Ethanol %	76.5%
	Methanol %	15.5%
	Total Alcohol %	92.1%
	Methane % of VOC's	41.4%

*Total ROG's = UCI total VOC - (methane+CO+Acetone)

The range of flux values for these samples runs from a low of 12 mg/M^2/min. to nearly 800. The wide variation may be due to amount or age of the manure or some other factor at the dairy. The full data set can be found in the Excel file titled "Year 1 Flux Chamber data".

Exercise Corrals

The open areas next to the free stalls are used by the cows in good weather for exercise and bovine socializing. After the flush lanes, these exercise pens collect the most manure and are a potential emission source. Flux chambers were set up on several of these corrals to monitor emissions from the manure pack during the summer and fall of 2006. Data from 3 canisters collected from those chambers and analyzed at UCI are summarized below. The full data set may be found in the Excel file titled "Year 1 Flux Chamber data".

Table 6. Summary of Total ROG and alcohols in exercise corral samples.

Corrals		
Emission Rate (μg/m²/min)		
3 INNOVA samples with 3 UCI canisters		
Summary and Comparison of UCI Canisters with INNOVA data		
UCI Canister Ethanol μg/m²/min.		12.4
UCI Canister Methanol μg/m²/min.		13.6
Total VOC's (UCI) μg/m²/min.		305
Total ROG (UCI) μg/m²/min.*		29
	Ethanol %	42.6%
	Methanol %	47.0%
	Total Alcohol %	89.6%
	Methane % of VOC	38.8%

*Total ROG's = UCI total VOC - (methane+CO+Acetone)

Fluxes of ROG from the surface of the exercise corrals are considerably lower than those from TMR, silage or fresh manure but it is still potentially significant because of the large area involved. The limited number of samples analyzed to date does not allow conclusions to be drawn but it can be pointed out that the alcohols are still the dominant ROG. The ROG is a much smaller fraction of the total VOC primarily because the methane and CO were proportionally higher in 2 of these 3 samples. The regular sampling of the corrals at each dairy in each sampling season proposed for the Year-2 program should provide sufficient data to estimate emission fluxes from the corrals.

Additional sampling and analysis

These same six diaries are used for related projects to investigate a number of additional air and water quality parameters. The sampling periods are generally similar except for the land application monitoring and other practices that do not occur on a regular basis. The sampling and analysis for those related projects are included in the Year-2 sampling program.

Year-2 Sampling Program

Task 4 of the project calls for the development of a sampling and analysis program to monitor the six dairies in the second year of the study. This Year-2 program is to be developed from the initial monitoring program used in Year-1. The field sampling methods, analytical procedures and schedule to be followed in Year-2 will be adopted after a review of the Year-1 results and consultation with the designated advisory group and ARB staff. This proposed Year-2 program is, therefore subject to revision until it is adopted for the summer-07 sampling period.

Sampling schedule:

In order to characterize volatile organic compound emissions from San Joaquin Valley dairies a total of six dairies were selected for their differing manure management styles as well as to provide a sense of facility variability of emissions. The six dairies are to be sampled three times per year to evaluate season emission characteristics. These periods chosen were:

1. Winter (December to March)
2. Summer (May to July)
3. Late Summer/Fall (September to November)

Field sampling methods:

Two methods of emissions monitoring are used in the project:

1. Upwind/Downwind ambient sampling utilized a dispersion model (ISC st3) to derive emission fluxes.
2. USEPA Emission Isolation Flux Chamber used according to the published protocol for monitoring fluxes from surfaces.

1. The upwind/downwind method is not a discrete sampling method and can only break down emission sources into two categories on the dairy facility. The method also requires a consistent wind speed and direction for proper modeling conditions. The following samples will be taken when wind conditions are present to enable modeling of the results: When minimum wind conditions are not present, these samples will not be collected. Additional flux chamber samples may be taken in place of the ambient samples.

1. Animal Housing
    a. Free Stalls
    b. Open Lot/Corrals

2. Lagoon Systems
    a. Treatment Lagoons
    b. Storage Ponds

When minimum wind conditions are not present, these samples will not be collected. Additional flux chamber samples may be taken in place of the ambient samples.

2. Use of the flux chamber method provides the capability to discretely sample individual sources within the animal housing area. Four sources were chosen to sample from the animal housing:

1. Total Mixed Ration
    a. 0.5 to 1 hour post feeding
    b. 1.5 to 2 hours post feeding
2. Flush Lane
    a. Pre-Flush (Pre-Scrape, Pre-Vacuum)
    b. Post-Flush (Post-Scrape, Post-Vacuum)
3. Bedding
4. Open Lot/Corral
    a. Deep Manure Pack
    b. Shallow Manure Pack
    c. Harrowed Manure Pack (when available)
5. Silage Pile Face
    a. Disturbed
6. Wet Distillers Grain (currently fed at 2 of 6 dairies) or other significant feed components

Analytical Methods

1. UC Irvine - Gas Chromatography/MS, ECD, FID Detectors
    a. Sample Media = 2L canisters
    b. Number of Compounds Quantified = 64
2. CSUF – Gas Chromatography/MS (TO-15 and PAMS)
    a. Sample Media = 6L summa-type
    b. Number of Compounds Quantified
        i. TO-15 =62
        ii. PAMS (Photochemical Assessment Monitoring Stations) = 57
3. INNOVA 1412 Photoacoustic Field Gas Analyzer (1st unit in use since August, ’06)
    a. Ammonia
    b. Ethanol
    c. Methanol
    d. Carbon Dioxide
    e. Nitrous Oxide
4. INNOVA 1412 Photoacoustic Field Gas Analyzer (2nd unit ordered April, ’07)
    a. Methane
    b. Trimethylamine
    c. Total Hydrocarbons as Propane
    d. Acetic Acid
    e. Propanol
5. EAS Lab Inc. TO-17 Volatile Organic Acids from Sorbent Tube
    a. Sample Media - Sorbent Tube
    b. Number of Compounds Quantified = 5

Emission Source Analysis

Silage and total mixed ration samples are collected from chamber locations immediately following emissions monitoring, placed into a plastic bag, and stored in a sample cooler. Samples are given specific sample numbers, logged into a log sheet, and prepared for shipment to the analytical laboratory. Analysis of feed samples are provided by Dairyland Laboratories Inc. (Arcadia, WI) who performs a commercially available analysis called a Fermentation Quality Analysis or VFA Profile. This analysis measures the following parameters on a dry matter basis.

1. Moisture (%)
2. Dry Matter (%)
3. pH
4. Lactic Acid (%)
5. Acetic Acid (%)
6. Propionic Acid (%)
7. Butyric Acid (%)
8. Iso-Butyric Acid (%)
9. Ethanol (%)
10. Methanol (%)
11. Crude Protein (%)
12. Ammonia-N (% of crude protein)
13. Total Acids (%)

Manure samples are collected from chambers locations immediately following emissions monitoring, placed into a plastic bag, and stored in a sample cooler. Samples transported to CSUF lab facilities and stored until delivery to an analytical laboratory. Manure samples are analyzed for the following:

1. Total Nitrogen
2. Ammonium (NH_4-N)
3. Nitrate (NO_3-N)
4. Organic Matter (%)

Sampling Program: Year-1

The sampling program in Year-1 was developed from spring-06 through the winter-07 sampling periods. The initial, ambient sampling was supplemented by the flux chambers, CSUF canister sampling and INNOVA monitoring as additional funding became available. The sampling shown in Table 7 is the final program as it was developed for the winter ’06 period.

Table 7.

Sampling Program - Year 1

	Analytical Method			
Source	**UC Irvine**	**CSUF**	**Innova 1412**	**Total**
Ambient Upwind - 2 day & 1 night	3	3		6
Ambient Downwind Housing - 2 day & 1 night	3	3		6
Ambient Downwind Lagoon - 2 day & 1 night	3	3		6
Total Mixed Ration (0.5 - 1 h post)	1	1	2	4
Total Mixed Ration (1.5 - 2 h post)	1	1	2	4
Silage Pile Face (Disturbed)	1	1	2	4
Flush Lane (Pre-Flush)	1	1	2	4
Flush Lane (Post-Flush)		1	2	3
Bedding		1	2	3
Open Lot/Corral (Deep Manure Pack)	1	1	2	4
Open Lot/Corral (Shallow Manure Pack or Harrowed)	1	1	2	4
Field Blank	1	1	1	3
Field Replicate	2	2	6	10
Totals	18	20	23	61

Samples are from flux chambers except for those designated as “Ambient”

In addition to the dairy sampling program shown in Table 7, land application of liquid effluent and solids were also monitored for ROG and various N emissions. Lagoon sampling with the flux chambers is under development and will be included for selected sites in the Year-2 program.

Sampling Program: Year-2
The sampling and analysis program proposed for Year-2 will begin with the summer-07 sampling period and will be maintained in this form throughout the year. Additional sampling and analysis may be added and a Year-3 program will be developed for the ARI and USDA funded portions of the project through 2009.

Table 8.

Proposed Sampling Program - Year 2

	Analytical Method				
Source	**UC Irvine**	**CSUF**	**TO-17**	**Innova 1412**	**Total**
Ambient Upwind - 1 & 1 (when possible)	2	2			4
Ambient Downwind Housing - 1 day & 1 night	2	2			4
Ambient Downwind Lagoon - 1 day & 1 night	2	2			4
Total Mixed Ration (0.5 - 1 h post)	1	1	1	2	5
Total Mixed Ration (1.5 - 2 h post)	1	1	1	2	5
Silage Pile Face (Disturbed)	1	1	1	2	5
Flush Lane (Pre-Flush)	1	1	1	2	5
Flush Lane (Post-Flush)		1		2	3
Bedding		1		2	3
Open Lot/Corral (Deep Manure Pack)	1	1	1	2	5
Open Lot/Corral (Shallow Manure Pack or Harrowed)	1	1	1	2	5
Field Blank	1	1	1	1	4
Field Replicate	2	2	1	6	11
Totals	15	17	8	23	63

Samples are from flux chambers except for those designated as “Ambient”

In addition to the proposed dairy sampling program shown in Table 8, land application of liquid effluent and solids will also monitored for ROG and various N emissions when the opportunity arises. Solids applications in the winter and spring as well as effluent irrigations in the spring and summer will be monitored on at least half of the dairies, if possible. Canisters designated for ambient sampling that cannot be used due to insufficient wind will be employed for additional flux chamber samples of silage, TMR, flush lanes, lagoons and land applications. Lagoon sampling with the flux chambers at selected sites will be added for the CDC project and included in the Year-2 program.

APPENDIX C

Appendix C is a description of the analytical systems and procedures provided by Dr. Donald Blake in the Department of Chemistry at UC Irvine. This contract from CARB specified the use of Dr. Blake and this laboratory for the analysis of samples collected by CSU Fresno field staff for the study. This document was originally part of the proposal and is included here for the details of the analytical processes.

Organics Analysis – Detailed Description

Responsibilities

Dr. Donald Blake and his UC Irvine team will analyze project test canisters collected at dairies for analysis of methane, carbon monoxide, selected C_2-C_{10} nonmethane hydrocarbons, selected C_1-C_2 halocarbons, C_1-C_5 alkyl nitrates, and selected sulfur gases. Canisters will be assayed within 2 weeks of their being received and preliminary data will be transmitted to the PI within$_2$ 2 weeks after the sample analysis is complete. A detailed description of the analytical methods to be used for the project is described below.

Reports, Data and Other Deliverables

Prepare monthly progress reports to CSU Fresno that will include QA/QC checked and flagged data in spreadsheet format.

Experimental Setup

A 1215 cm^3 sample aliquot (standard temperature and pressure) from an individual canister is introduced into the system manifold and passed over glass beads maintained at liquid nitrogen temperature. The flow is regulated by a Brooks Instrument mass flow controller model 5850E, and is kept below 500 cm^3/min to ensure complete trapping of the relevant components. This procedure has the effect of pre-concentrating the relatively less-volatile components of the sample (such as halocarbons and hydrocarbons) while allowing volatile components (such as N_2, O_2, and Ar) to be pumped away. The less volatile compounds are then re-volatilized, by immersing the loop containing the beads in hot water (80°C), and subsequently flushed into an helium carrier flow (head pressure 48 psi). This sample flow is then split into six streams. Each stream is chromatographically separated on an individual column and detected by a single detector. Three HP 6890s form the core of the analytical system. Electron-capture detectors (ECD, sensitive to halocarbons and alkyl nitrates), flame-ionization detectors (FID, sensitive to hydrocarbons), and a quadrupole mass spectrometer (MS, for unambiguous compound identification and selected ion monitoring) will be employed.

The first HP-6890 (GC-1) contains two columns. The first column is a J&W DB-5 (30 m, I.D. 0.25 mm, film 1 mm) connected to a Restek 1701 (5 m, I.D. 0.25 mm, film 0.5 mm), which is outputted to an ECD detector. The second column is a DB-5ms (60 m, I.D. 0.25 mm, film 0.5 mm), which is outputted to an MS detector (HP-5973). The DB-5/Restek 1701 receives 7.2% of the total carrier flow, and the DB-5ms receives 10.1%. The second HP-6890 (GC-2) contains two columns. The first is a J&W DB-1 column (60 m, I.D. 0.32 mm, film 1 mm) output to an FID detector. This column receives 14.7% of the flow. The second is a J&W Cyclodex (60 m, I.D. 0.32 mm, film 0.5 mm) receives 10.8% of the flow and is plumbed to an FID. The third HP-6890 (GC-3) contains a J&W GS-Alumina PLOT column (30 m, I.D. 0.53 mm) connected to a DB-1 (5 m, I.D. 0.53 mm, film 1 mm), which is output to an FID detector, and a Restek 1701 (60 m, I.D. 0.25

mm, film 0.50 mm), which is output to an ECD detector. The GS-Alumina PLOT column receives 49.9% of the flow, and the Restek 1701 receives the remaining 7.3%. Output from each detector is recorded digitally using Chromeleon software (Spectra Physics, San Jose, CA). Each resulting chromatogram will be manually modified, and each peak shape individually checked. This type of quality control is very important for datasets of this size because a slight change in retention time or peak shape can cause We at UC Irvine generate our own zero-air and nitrogen for use in our FID and ECD detectors. House air is passed through a CUNO Inc. model AP101T aqua pure water filter filled with glass wool, then through a Whatman 64-02 Air Dryer equipped with a 100-12 BX prefilter. This removes oil, water, and particulates from the air stream, which is then split and directed into a Domnick Hunter nitrox-nitrogen generator (NG7-0) and a Praxair zero-air generator (model Airlab WHA 76803). The output from these devices are split further and directed into gas regulators for head pressure regulation. Before entering our system all gases employed are passed through homemade graphite/molecular sieve traps to remove any remaining contaminants. These traps are preconditioned (and regenerated) by flowing gas through them at a temperature of 350˚C for at least 5 hours. The three FIDs operate at a detector temperature of 250˚C with a zero-air flow of 450 mL/min, an $H_{2(g)}$ flow of 40 mL/min, and a detector makeup gas flow of 20 mL/min $N_{2(g)}$. The ECDs detector temperatures are 250˚C with a detector makeup flow of 50 mL/min $N_{2(g)}$.

The relative flow passing through an individual column depends primarily on its inner diameter. At UC Irvine we split the flow among the channels in such a way as to facilitate detection of a variety of halo- and hydrocarbon species. The majority of the flow is directed to the PLOT column due in part to the lower per-molecule sensitivity of the FID detector, and the low ambient concentrations of many non-methane hydrocarbons in remote regions. The split ratios are found to be highly reproducible as long as the specific humidity of the injected air is above 2 g-H_2O/kg-air. For this reason (as well as to increase the stability of certain compounds in the canisters) 20 torr of water is added to each (preconditioned, evacuated) canister before being sent into the field.

Multiple standards will be employed during the 8 week period of sample analysis. Working standards will be run roughly every two hours, and absolute standards will be run at least twice daily. Our lab regularly collects and calibrates pressurized cylinders of air from different environments for use as working standards. A primary reference standard for halocarbons was previously calibrated from static dilutions of standards prepared in this lab. Its absolute accuracy is tied to a manometer measurement and how accurately the appropriate volume ratios for the dilution line used are known. At UC Irvine we also have primary halocarbon standards provided by other research groups involved in halocarbon analysis.

For hydrocarbons, we use a propane standard purchased from the National Bureau of Standards (SRM 1660A) to calculate a Per-Carbon-Response-Factor (PCRF) for the FIDs. This is compared to PCRFs calculated from more readily available commercial standards to check the absolute accuracy of the commercial standard, as well as the appropriateness of using the same PCRF for different compounds. From analysis of the commercial standard we assign a different PCRF for each alkane, from ethane to octane. This PCRF is then used for any compound with an equivalent number of carbons. For example, the PCRF determined for butane is employed during quantification of the butenes. We have cross-checked our calibration scheme against absolute standards from other groups for both hydrocarbons and halocarbons. Additionally, we participate in the Non-Methane Hydrocarbon Intercomparison Experiment (NOMHICE). The results of this experiment demonstrate that our analytical procedures consistently yield accurate identification of a wide range of unknown hydrocarbons and produce excellent quantitative results. We estimate our typical absolute accuracy as 2-10%, increasing as we approach our detection limits.

At UC Irvine, our analytical accuracy ranges from 2 to 20%. The precision of the measurements varies by compound and by mixing ratio. For example, the measurement precision is 1% or 1.5 pptv (whichever is larger) for the alkanes and alkynes, and 3% or 3 pptv (whichever is larger) for the alkenes. The precision for C_2Cl_4 at 5 pptv is ±0.05 pptv. The limit of detection (LOD) is 3 pptv for all NMHCs.

Typical alkyl nitrate detection limits are 0.03 pptv (0.03 pptv for methyl nitrate) and precision ±5% at mixing ratios above 5 pptv and ±10% below 5 pptv. The detection limits for methyl iodide (CH_3I), bromoform ($CHBr_3$) and DMS are 0.02, 0.02, and 1 pptv, respectively. Precision values of 1 and 2%, respectively for CH_3I and $CHBr_3$ are typical. For DMS, the precision is approximately 3% at mixing ratios >25 pptv, and 1 pptv or 15%, whichever is higher, at mixing ratios <10 pptv.

We have been involved in numerous NASA and NSF airborne projects during which more than twenty-five thousand samples have been collected and assayed for a wide range of hydrocarbons and halocarbons. Once samples are assayed, the stored chromatograms are individually inspected the reports from those chromatograms are then summarized in spreadsheet format and checked for inconsistencies. Once the quality control is complete the data are ready for archive.

At UC Irvine we will quantify the gases using our 6 column/6 detector analytical system. The table on the next page lists the gases that are usually quantified and the associated limits of detections (LODs). Additional gases can be added if necessary.

Gases Usually Quantified at UC Irvine by Dr. Donald Blake

Gas	LOD (ppt)	Gas	LOD (ppt)
Ethane	3	DMS	1
Ethene	3	OCS	50
Ehtylene	3	Methyl Nitrate	0.03
Propane	3	Ethyl Nitrate	0.03
Propene	3	n-Propyl Nitrate	0.03
n-Butane	3	i-Propyl Nitrate	0.03
i-Butane	3	2-Butyl Nitrate	0.03
1-Butene	3	2-Pentyl Nitrate	0.03
cis-2-Butene	3	3-Pentyl Nitrate	0.03
trans-2-Butene	3	CH2FCF3 (HFC-134a)	1
1,3-Butadiene	3	CH3CCl2F (HCFC-141b)	1
n-Pentene	3	CH3CClF2 (HCFC-142b)	1
i-Pentene	3	CHClF2 (HCFC-22)	1
Isoprene	3	CBrClF2 (H-1211)	0.05
n-Hexane	3	Acetone	50
2-Methylpentane	3	CCl3F (CFC-11)	1
3-Methylpentane	3	CCl2F2 (CFC-12)	10
Benzene	3	CCl2FCClF2 (CFC-113)	1
Toluene	3	CClF2CClF2 (CFC-114)	1
o-Ethyltoluene	3	CH3Cl	10
m-Ethyltoluene	3	CCl4	0.1
1,2,4-Trimethylbenzene	3	CH3CCl3	1
1,3,5-Trimethylbenzene	3	CHClCCl2	0.05
o-Xylene	3	CH3Br	1
m-Xylene	3	CH2Br2	0.02
p-Xylene	3	CHBr3	0.02
Ethylbenzene	3	CH3I	0.02
a-Pinene	3	CH2Cl2	0.2
b-Pinene	3	CCl2CCl2	0.1

APPENDIX D

Appendix D is primarily a description of the field procedures used for the US-EPA Isolation Flux Chambers. The methodology listed on the EPA website was used as closely as possible with some variations to accommodate sampling conditions at the specific dairy locations described above. The flux chambers were purchased from Odotech of Toronto, Ontario. The specific methodology is detailed below. Some data in this report (Fig. 6 & 7) is from a multi-gas analyzer acquired for a project related to this one and used along with the sampling canisters for UCI analysis. The calibration documents for that analyzer along with the field sheets to show all of the samples and field data collected at the same time as the UCI canisters are also included in this appendix.

TESTING METHODOLOGY FOR CSUF SURFACE EMISSION FLUX CHAMBER MEASUREMENTS

Testing will be conducted using Surface Isolation Flux Chamber (flux chamber) to collect emission data. The main technical reference for flux chamber measurement is a study performed under contract with USEPA that provides a recommended protocol (Measurement of Gaseous Flux rates from Land Surfaces Using an Emission Isolation Flux Chamber, Users Guide, EPA /600/8-86/008, Radian Corporation, February 1986).

The flux chamber used in this experiment is a clear cylindrical enclosure with a clear spherical top and the following technical data:

- Material of flux chamber: Acrylic resin
- Material of tubing: Teflon
- Height of cylinder: 0.24 m
- Height of half sphere: 0.17 m
- Total Height: 0.41 m
- Diameter: 0.495 m
- Ground surface area: 0.19 m^2
- Total volume: 64.5 liters

The testing methodology is given below:

1- Measurements of feed and manure sources will be made in two (2) separate days. All measurements will be made in the same sequence in all six dairies to provide consistency in environmental conditions between dairies, if possible (e.g., total mixed ration+0.5 h post placement will be measured first, then silage pile, then total mixed ration +6 post placement; or flush lane-pre flush will be measured first, then open lot, then flush lane-post flush). At each dairy, field and media blanks will be measured twice at the end of each daily measurement.

2- The sampling plan contains a site map (aerial photo) with location numbers marked. Each location will represent an average condition for the designated areas at the time of measurements.

3- Date, time, test site information, and field and equipment data will be documented on the CSUF SURFACE FLUX MEASUREMENT DATA FORM. Separate data forms will be used for total mixed ration, silage pile, main feed commodities, and manure sources for regular sampling in the six dairies. Additional data will be collected in special sampling for feed sources in two selected dairies. Data forms are shown on pages 8 to13. All the pertinent information of the test sites will be collected at the time of measurements (e.g., number and time of feeding, number and time of daily disturbance of silage pile). Information about silage practices and management will be collected separately via survey (see page 14).

4- All measurements will be performed in normal test site conditions without any physical or environmental modifications (e.g., surface of test sites will not be disturbed; total mixed ration and flush lanes will be measured in shade, and normally open lots and silage piles will be measured in sunlight). If possible, the rim of the chamber will be inserted into the measurement surface 2–3 cm to achieve sealing and minimize ambient air intrusion. Additional sealing will be provided around outside perimeter of the flux chamber if possible.

5- All interior surfaces of flux chambers will be fully washed, rinsed with water, and wiped before the start of measurements. Flux chambers will be fully dry wiped with a clean paper towel between measurements and rinsed with water if necessary.

6- Multiple flux chambers will be used at each test site. INNOVA will collect samples from both flux chambers but only one of the chambers will be used for other sampling (one UCI canister, one CSUF canister, and one TO-17 sample will be collected at each test site). Based on INNOVA real-time data, the flux chamber with higher ethanol or methanol emissions will be selected for other sampling in feed sources, and for manure sources, the flux chamber with higher ammonia emissions will be chosen for other sampling.

7- Sweep air flow (ultra zero compressed air) will be initiated immediately after the placement of flux chambers using 1/4-inch Teflon tubing with stainless still quick-disconnect fitting. The sweep air will be adjusted and constantly maintained to the desired flow rate throughout the measurements using rotameters, metering valves, and pressure regulators. The sweep air flow rate will be set at 10 liters per minute. Sample collection will be performed at steady-state, assumed to be after four residence intervals, or 30 minutes. All 1/4-inch Teflon sample lines will be purged with ultra zero air before sampling.

8- High air temperature inside the flux chamber may cause backpressure and hence could limit diffusional emissions. Ambient and flux chamber air and surface temperatures inside and outside the chambers will be measured immediately when flux chamber is placed and right before sampling using a hand-held digital thermocouple. Further, air temperature of ambient and flux chamber air will be recorded at all time when flux chamber is placed at the test site using HOBO data logger.

9- Condensation may occur inside the flux chambers in some occasions, which may reduce the concentration of water-soluble volatile organic compounds. The occurrence and degree of condensation will be noted in the data forms. Further, humidity of ambient and flux chamber air will be monitored during the course of measurement using HOBO data logger.

10- Rainfall events could alter surface flux rates. Flux chamber measurements will not be taken during and immediately after rainfall in open lots and silage piles.

11- After flux chamber measurements, surface samples will be taken from all chamber locations, labeled, and stored in ice chests for laboratory analysis. All feed and manure samples should reach the laboratory within 24 hours.

ANALYSIS SUMMARY

The flux chambers will be used for the following procedures at each sampling location:

1. INNOVA unit A
   a. Ethanol
   b. Methanol
   c. Trimethylamine
   d. Isopropanol
   e. THC as n-Hexane
2. INNOVA unit B
   a. Ammonia
   b. Nitrous Oxide
   c. Carbon Dioxide
   d. Methane
   e. Acetic Acid

   INNOVA units will be calibrated at the beginning and at the end of annual measurements or more frequently if needed. Recent (8-9-07) calibration results are shown at the end of this document.
3. UC Irvine - Gas Chromatography/MS, ECD, FID Detectors
   a. Sample Media= 2L canisters
   b. Number of Compounds Quantified = 64
4. CSU Fresno – Gas Chromatography/MS (TO-15 and PAMS)
   a. Sample Media= 6L summa-type
   b. Number of Compounds Quantified:
      i. TO-15 =62
      ii. PAMS (Photochemical Assessment Monitoring Stations) = 57
5. EAS Lab Inc. (commercial lab) TO-17 Volatile Organic Acids from Sorbent Tube
   a. Sample Media- Sorbent Tube
   b. Number of Compounds Quantified = 5

Documentation of ambient conditions along with material sample documentation and information for sample custody was accomplished through the use of field forms to be filled out for each sampling event. The following forms used for each type of sample. The originals are kept at CSU Fresno as a sample log and the data from the forms will be posted to the data website in the near future.

CSUF SURFACE FLUX MEASUREMENT DATA FORM- TOTAL MIXED RATION

Date: - - 2007 Dairy: Samplers:

Location # North □ South □ West □ East □

Current Activity:

Ambient Conditions: Sun □ P. Sun □ Cloudy □ Rain: Yes □ No □

Notes:

Flux Chamber ID: Prior Chamber Cleaning: Full Wash □ Dry Wipe □ Wet Wipe □ None □

Flux Chamber Measurements			Temperature (°C)				Notes
Time	Sweep Air (L/Min)	Residence Number	Chamber		Ambient		
			Surface	Air	Surface	Air	
	10	0					Condensation: Yes □ No □
	10	1					
	10	2					Degree of Condensation:
	10	3					Chamber Base: %
	10	4					
	10	5					Chamber Dome: %

TMR Information		Site Diagram
Main Feed Sources:		
1-	4-	
2-	5-	
3-	6-	
Number of Feeding per Day:		
Hours of Feeding:		
Number of TMR Push Ups per Day:		
Hours of TMR Push Ups:		
Length of Feed Lane (m):		
Average Width of Feed Lane (cm):		
At TMR+0.5 h:		Notes:
At TMR+3 h:		
At TMR+6 h:		
Area of Feed Lane (m^2):		
At TMR+0.5 h:		
At TMR+3 h:		
At TMR+6 h:		

Measurement	Number	Time	Notes
INNOVA □	Event #	—	Sample Line Flushed □
UCI □	Canister #	—	Sample Line Flushed □
CSUF □	Canister #	—	
TO-17 □	Tube #	—	

Photo Taken □

Surface Sample Taken □ Lab Number: Lab: Dairyland Laboratories Inc.

CSUF SURFACE FLUX MEASUREMENT DATA FORM- SILAGE PILE

Date: - - 2007 Dairy: Samplers:

Location # North □ South □ West □ East □

Type of Measurement: Pile Disturbed Face □ Vertical Undisturbed Face □ Measurement Height: m

Current Activity:

Ambient Conditions: Sun □ P. Sun □ Cloudy □ Rain: Yes □ No □

Notes:

Flux Chamber ID: Prior Chamber Cleaning: Full Wash □ Dry Wipe □ Wet Wipe □ None □

Flux Chamber Measurements			Temperature (°C)				Notes
Time	Sweep Air (L/Min)	Residence Number	Chamber		Ambient		
			Surface	Air	Surface	Air	
	10	0					Condensation: Yes □ No □
	10	1					
	10	2					Degree of Condensation:
	10	3					Chamber Base: %
	10	4					
	10	5					Chamber Dome: %

Silage Information	Site Diagram
Type of Silage:	
Dates:	
Established:	
First Disturbed:	
Finished (est.):	
Disturbance:	
Number of Daily Disturbance:	
Time of Daily Disturbance:	
Date and Time of Last Disturbance:	
Area of Exposed Surface (m^2)	
Vertical Undisturbed Exposed Face:	
Pile Disturbed Exposed Face:	

Notes:

Silage Density Measurements:

	Height=0.9 m	Height=1.8 m	
Probe Depth:			cm
Probe Diameter:	4.826	4.826	cm

Measurement	Number	Time	Notes
INNOVA □	Event #	—	Sample Line Flushed □
UCI □	Canister #	—	Sample Line Flushed □
CSUF □	Canister #	—	
TO-17 □	Tube #	—	

Photo Taken □

Surface Sample Taken □ Lab Number: Lab: Dairyland Laboratories Inc.

CSUF SURFACE FLUX MEASUREMENT DATA FORM- MANURE SOURCES								
Date: - - 2007			Dairy:			Samplers:		
Location	#		North □		South □	West □	East □	
Open Lot Deep Manure Pack		□	Depth=	cm				
Open Lot Shallow Manure Pack		□	Depth=	cm				
Bedding		□	Depth=	cm				
Flush Lane (Pre-Flush)		□	Depth=	cm				
Flush Lane (Post-Flush)		□						
Current Activity:								
Ambient Conditions:		Sun □	P. Sun □		Cloudy □	Rain:	Yes □	No □
Notes:								
Flux Chamber ID:		Prior Chamber Cleaning:		Full Wash □		Dry Wipe □	Wet Wipe □	None □

Flux Chamber Measurements			Temperature (°C)				Notes
Time	Sweep Air (L/Min)	Residence Number	Chamber		Ambient		
			Surface	Air	Surface	Air	
	10	0					Condensation: Yes □ No □
	10	1					
	10	2					Degree of Condensation:
	10	3					Chamber Base: %
	10	4					
	10	5					Chamber Dome: %

Notes	Site Diagram

Measurement	Number	Time	Notes
INNOVA □	Event #	—	Sample Line Flushed □
UCI □	Canister #	—	Sample Line Flushed □
CSUF □	Canister #	—	
TO-17 □	Tube #	—	
Photo Taken □			
Surface Sample Taken □	Lab Number:		Lab: Dellavalle Laboratory

CSUF SURFACE FLUX MEASUREMENT DATA FORM- TOTAL MIXED RATION, SPECIAL SAMPLING (2 DAIRIES)

Date: - - 2007 Dairy: Samplers:

Location # North □ South □ West □ East □

Current Activity:

Ambient Conditions: Sun □ P. Sun □ Cloudy □ Rain: Yes □ No □

Notes:

Flux Chamber ID: Prior Chamber Cleaning: Full Wash □ Dry Wipe □ Wet Wipe □ None □

Flux Chamber Measurements			Temperature (°C)				Notes
Time	Sweep Air (L/Min)	Residence Number	Chamber		Ambient		
			Surface	Air	Surface	Air	
	10	0					Condensation: Yes □ No □
	10	1					
	10	2					Degree of Condensation:
	10	3					Chamber Base: %
	10	4					
	10	5					Chamber Dome: %

TMR Information		Site Diagram
Main Feed Sources:		
1-	4-	
2-	5-	
3-	6-	
Number of Feeding per Day:		
Hours of Feeding:		
Number of TMR Push Ups per Day:		
Hours of TMR Push Ups:		
Length of Feed Lane (m):		
Average Width of Feed Lane (cm):		
At TMR+0.5 h:	At TMR+1 h:	Notes:
At TMR+2 h:	At TMR+3 h:	
At TMR+4 h:	At TMR+5 h:	
At TMR+6 h:		
Area of Feed Lane (m^2):		
At TMR+0.5 h:	At TMR+1 h:	
At TMR+2 h:	At TMR+3 h:	
At TMR+4 h:	At TMR+5 h:	
At TMR+6 h:		

Measurement	Number	Time	Notes
INNOVA □	Event #	—	Sample Line Flushed □
UCI □	Canister #	—	Sample Line Flushed □
CSUF □	Canister #	—	
TO-17 □	Tube #	—	

Photo Taken □

Surface Sample Taken □ Lab Number: Lab: Dairyland Laboratories Inc.

CSUF SURFACE FLUX MEASUREMENT DATA FORM- SILAGE PILE, SPECIAL SAMPLING (2 DAIRIES)

Date: - - 2007 Dairy: Samplers:

Location # North □ South □ West □ East □

Type of Measurement: Pile Disturbed Face □ Vertical Undisturbed Face □ Measurement Height: m

Current Activity:

Ambient Conditions: Sun □ P. Sun □ Cloudy □ Rain: Yes □ No □

Notes:

Flux Chamber ID: Prior Chamber Cleaning: Full Wash □ Dry Wipe □ Wet Wipe □ None □

Flux Chamber Measurements			Temperature (°C)				Notes
Time	Sweep Air (L/Min)	Residence Number	Chamber		Ambient		
			Surface	Air	Surface	Air	
	10	0					Condensation: Yes □ No □
	10	1					
	10	2					Degree of Condensation:
	10	3					Chamber Base: %
	10	4					
	10	5					Chamber Dome: %

Silage Information	Site Diagram
Type of Silage:	
Dates:	
Established:	
First Disturbed:	
Finished (est.):	
Disturbance:	
Number of Daily Disturbance:	
Time of Daily Disturbance:	
Date and Time of Last Disturbance:	
Area of Exposed Surface (m^2)	
Vertical Undisturbed Exposed Face:	
Pile Disturbed Exposed Face:	

Notes:

Silage Density Measurements:

	Height=0.9 m	Height=1.8 m	
Probe Depth:			cm
Probe Diameter:	4.826	4.826	cm

Measurement	Number	Time	Notes
INNOVA □	Event #	—	Sample Line Flushed □
UCI □	Canister #	—	Sample Line Flushed □
CSUF □	Canister #	—	
TO-17 □	Tube #	—	

Photo Taken □

Surface Sample Taken □ Lab Number: Lab: Dairyland Laboratories Inc.

CSUF SURFACE FLUX MEASUREMENT DATA FORM- MAIN COMMODITIES, SPECIAL SAMPLING (2 DAIRIES)

Date:	-	- 2007	Dairy:		Samplers:	
Location	#	North □	South □	West □	East □	
Feed Source:						
Current Activity:						
Ambient Conditions:	Sun □	P. Sun □	Cloudy □	Rain:	Yes □	No □
Notes:						
Flux Chamber ID:	Prior Chamber Cleaning:	Full Wash □	Dry Wipe □	Wet Wipe □	None □	

Flux Chamber Measurements			Temperature (°C)				Notes
			Chamber		Ambient		
Time	Sweep Air (L/Min)	Residence Number	Surface	Air	Surface	Air	
	10	0					Condensation: Yes □ No □
	10	1					
	10	2					Degree of Condensation:
	10	3					Chamber Base: %
	10	4					
	10	5					Chamber Dome: %

Commodity Information	Site Diagram
Type of Commodity:	
Dates:	
Hauled:	
First Disturbed:	
Finished (est.):	
Disturbance:	
Number of Daily Disturbance:	
Time of Daily Disturbance:	
Date and Time of Last Disturbance:	
Area of Exposed Surface (m^2)	
Vertical Undisturbed Exposed Face:	
Pile Disturbed Exposed Face:	

Notes:

Measurement	Number	Time	Notes
INNOVA □	Event #	—	Sample Line Flushed □
UCI □	Canister #	—	Sample Line Flushed □
CSUF □	Canister #	—	
TO-17 □	Tube #	—	

Photo Taken □		
Surface Sample Taken □	Lab Number:	Lab: Dairyland Laboratories Inc.

INNOVA Calibration Data (8-9-07)

California Analytical

1412/1314/1312 /1302 FILTER AND CALIBRATION DATA
N.I.S.T. TRACEABLE

Customer: CalState Fresno
Phone: 559-298-6072

Serial # 710-231
Model # 1412

FILTERS

Position	UA #	Filter Bank #	Component	Zero Level µ Volts	Span Concentration PPM
A	974	1	Ethanol	4.99	12.28
B	936	1	Methanol	4.58	17.29
C	979	1	Trimethylamine	5.06	4.9
D	975	1	Isopropanol	4.44	4.9
E	987	1	THC as n-Hexane	20.5	0.23
W	SB0527		H2O	6.59	13.9 C

Zero Calibration:
Date: 08-08-2007

Humidity Interference Calibration
Date: 08-08-2007

Span Calibration
Date: 08-08-2007

Calibration Gas: UHP Nitrogen
Ambient Temp. 22° C:

Source : Humidified UHP Nitrogen
Ambient Pressure (mmHg) : 759

Measurement Results:

INPUT CONCENTRATION (ppm)		MEASURED CONCENTRATION (ppm)
12.28, 7.84, 4.7	Ethanol	12.15, 7.58, 4.53
17.29, 11.04, 6.63	Methanol	17.25, 10.59, 6.46
4.9, 2.57, 1.14	Trimethylamine	4.88, 2.59, 0.994
4.9, 3.12, 1.88	Isopropanol	4.99, 3.09, 1.96
0.23, 0.115, 0.07	THC as n-Hexane	0.251, 0.107, 0.099

SO# 16298

Date: 08-09-2007

R.M.Neti
CAI/R.M.Neti

INNOVA Calibration Data (8-9-07)

California Analytical

1412/1314/1312 /1302 FILTER AND CALIBRATION DATA
N.I.S.T. TRACEABLE

Customer: Cal State Fresno-
Phone: 559-284-3692

Serial # 710-137
Model # 1412

FILTERS

Position	UA #	Filter Bank #	Component	Zero Level µ Volts	Span Concentration PPM
A	976	1	Ammonia	3.65	48.05
B	985	1	Nitrousoxide	3.29	20.2
C	983	1	Carbondioxide	1.29	1245
D	969	1	Methane	8.72	24.55
E	971	1	Acetic acid	8.81	18.4
W	SB0527		H2O	6.68	13.5 C

Zero Calibration:
Date: 08-08-2007

Humidity Interference Calibration
Date: 08-08-2007

Span Calibration
Date: 08-08-2007

Calibration Gas: UHP Nitrogen
Ambient Temp. 22° C:

Source : Humidified UHP Nitrogen
Ambient Pressure (mmHg) : 759

Measurement Results:

INPUT CONCENTRATION (ppm)		MEASURED CONCENTRATION (ppm)
96.1, 48.05, 19.22	Ammonia	93.77, 47.98, 19.3
30.3, 20.2, 10.1	Nitrousoxide	30.2, 20.2, 10.15
2490, 1245, 498	Carbondioxide	2474, 1250, 505.8
49.1, 24.55, 9.82	Methane	47.33, 24.13, 9.45
18.4, 11.5, 6.91	Acetic acid	18.4, 11.4, 6.9

SO# 7586900

Date: 08-09-2007

R.M.Neti

CAI/R.M.Neti