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Environmental Consultant

April 1, 2005

Mr. John Da Massa, CCOS Program Manager
Chief, Modeling & Meteorological Branch
California Air Resources Board
P.O. Box 2815
Sacramento, California 95812

Dear Mr. Da Massa:

Enclosed please find a copy of the revised Technical Memorandum reporting the results of the flux chamber dairy emissions evaluation project conducted at a dairy located in Merced, California.

If you have any questions, lease feel free to call.

Sincerely,

CE Schmidt, Ph.D.

attachment- Technical Memorandum

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Environmental Consultant

TECHNICAL MEMORANDUM

Results of the Dairy Emissions Evaluation Using Flux Chambers
Merced Dairy- Summer Testing Event

Final

Prepared For:

Mr. John Da Massa, CCOS Program Manager
Chief, Modeling & Meteorological Branch
California Air Resources Board
P.O. Box 2815
Sacramento, California 95812

Prepared By:

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April 2005

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TABLE OF CONTENTS

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EXECUTIVE SUMMARY

The Central California Ozone Study (CCOS) group has sponsored a study designed to measure the air emissions of reactive organic gases (ROGs), also known as volatile organic compounds (VOCs), and ammonia/amines produced by dairies using the USEPA surface emissions isolation flux chamber (flux chamber). The goal of this research is to provide process-specific (i.e., portions of dairy) dairy emissions data for use in improving emission estimates required for State Implementation Plans (SIPs) and Senate Bill 700 (SB700). In addition, data from this research will be used to better evaluate dairy control strategies for ozone and particulate matter, and to support the CCOS emissions inventory and modeling efforts. This work was coordinated with other dairy research projects under the oversight of the Dairy Subgroup of the San Joaquin Valley Ag Tech Group. In addition, during field testing for this project, Fresno State University researchers conducted concurrent ambient upwind/down emissions sampling, and UC Davis researchers provided additional sample collection analysis.

The flux of ROG (VOC), ammonia/amines, and other study compounds was measured at multiple locations on a total of 11 types of emitting surface or in different unit processes over a two-day time period at a Northern California dairy. The unit treatment process testing included: solids from the water/solid separator, solids in storage piles, wastewater lagoon, barn turnout areas, freestall bedding pile materials, pre- and post-flushed diary lanes, milk parlor effluent, feed materials (silege) heifer (dry cow) pens, and bedding in freestall beds. Flux sample test locations were selected based on information regarding dairy information, scientific inspection in the field (visual inspection and screening using a real time instrument), and flux chamber testing using screening instrument readings to select which of multiple test locations would include sample collection and off site analysis.

A robust field program was conducted during the summer season and flux measurements were made using the USEPA flux chamber including quality control testing as described in the USEPA User's Guide. Flux chamber quality control testing included two flux chamber sample media blank tests (2), and replicate flux tests (2). Flux chamber measurements were performed following the USEPA flux chamber protocol including standard equipment decontamination protocols.

In order to provide the highest possible number of tests and to conserve project resources, dairy sources were sampled with a combination of screening-level, baseline analysis, and full compound analysis assessment. The screening-level testing provided information sufficient for overall emission estimates and help to evaluate process-to-process variability, spatial variability with a single process, and temperature variability of emissions. The baseline analysis included a minimum quantitation of ROGs or VOCs (USEPA Method TO-15) and ammonia (NIOSH 2010), and the full compound analysis provided for a more comprehensive chemical speciation

of the organic gases which is needed to evaluate the photochemical reactivity of the gases produced from livestock wastes.

In summary, an assessment of ROG species, total ROG (VOC), ammonia/amines, and other study compound air emissions was conducted over a two-day time period at a dairy in the San Joaquin Valley (Merced). Ten distinct potential emission sources were tested at multiple locations and at different times of the day for some sources. Analysis included quantitative ROG and ammonia/amine flux testing at all test locations with representative full characterization of other analytical species at a limited number of key locations. The testing was performed during the summer season.

Each unit process at the dairy tested showed unique air emissions characteristics, although there was some commonality in emissions for all unit processes. Observations for each unit process are described below. Significance in emission sources can only be determined after the flux data (ug/m2,min-1) are converted to unit treatment process emissions (ug/min or pounds per day) by knowing the surface area of these sources. Discussions given below reference flux data only and emission factors. Flux data above 1 ug/m2,min-1 are highlighted given that large surfaces areas at 1 ug/m2,min-1 can generate large emission factors.

The average flux data presented for all unit treatment process can be used to develop emission factors for northern California dairies. In addition, data from this dairy, along with process information can be used to provide estimates of compound emissions per cow. Note that speciated hydrocarbon data from Method TO-15 were used to calculate total ROG or VOC. Exempt compounds were not included in the summation. All non-exempt VOC were summed, along with ethyl amine, aldehydes, and ketones (except acetone) and reported as 'ROG' or 'VOC'. To avoid confusion in the data tables, the term 'ARB ROG' was used to represent the summation of all non-exempt compounds detected by the various analytical methods.

Separator Solids

Solids from the slurry effluent stream separator unit are stored for up to a day at the unit and moved to solids separator pile where they are stored unit application to fields off site or moved to the bedding storage pile. The age of the material tested was less than a day (fresh solid waste). The solid waste is sun exposed and was tested on two consecutive days at different time of the day. The average emissions from multiple test locations on the material included comparatively high methane flux (15,000 ug/m2,min-1) and ARB ROG flux (48 ug/m2,min-1), high ammonia flux (650 ug/m2,min-1) and high ethylamine flux (29 ug/m2,min-1), a wide range of low-level volatile organic compound species flux by TO-15 with high ethanol flux (13 ug/m2,min-1), acetone flux (2.5 ug/m2,min-1), carbon disulfide flux (2.9 ug/m2,min-1), toluene flux (1.3 ug/m2,min-1), and octane flux (1.2 ug/m2,min-1). Significant aldehyde flux was observed by the TO-11 including formaldehyde flux (0.076 ug/m2,min-1), acetaldehyde flux (0.2 ug/m2,min-1),

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acetone flux (1.1 ug/m2,min-1), and butyraldehyde flux (0.12 ug/m2,min-1). Volatile organic acids were not detected.

Solids in Storage Pile

Solids from the solids separator unit are stored for weeks or longer until the material is used for on site applications such as bedding material or application to crop fields off site. The age of the material tested was more than a week (aged solid waste). The solid waste is sun exposed and was tested on two consecutive days at different times of the day. The average emissions from multiple test locations on the material included comparatively high methane flux (220,000 ug/m2,min-1- note highest methane flux detected), low ARB ROG flux (3.4 ug/m2,min-1), high ammonia flux (630 ug/m2,min-1) but no ethylamine flux, a moderate range of low-level volatile organic compound species flux by TO-15 with higher acetone flux (2.4 ug/m2,min-1), and detectable but lower aldehyde flux was observed by TO-11 including formaldehyde flux (0.19 ug/m2,min-1), acetaldehyde flux (0.25 ug/m2,min-1), and acetone flux (0.92 ug/m2,min-1). Volatile organic acids were not detected.

Bedding Pile Solids

Solids (from the solids separator) are stored in the bedding pile for several months and then used for bedding material in the freestall beds. The age of the material tested was not know exactly but was from one-to-three months old. The solid waste pile is sun exposed and was tested on one day. The average emissions from multiple test locations included comparatively low methane flux (65 ug/m2,min-1), high ARB ROG flux (75 ug/m2,min-1), very high ammonia flux (22,000 ug/m2,min-1- note highest ammonia emissions detected), a large number of low-level volatile organic compound species flux by TO-15 with high oxygenated compound and chlorinated compound flux, including 2-butanone flux (330 ug/m2,min-1), acetone flux (35 ug/m2,min-1), and 15 other compounds over 1 ug/m2,min-1. Significant aldehyde flux was observed by TO-11 including formaldehyde flux (1.1 ug/m2,min-1), acetaldehyde flux (6.9 ug/m2,min-1), acetone flux (2.8 ug/m2,min-1), crotonaldehyde flux (0.92 ug/m2,min-1) and butyraldehyde flux (1.1 ug/m2,min-1). Volatile organic acids were not detected.

Freestall Bed

Solids (from the bedding pile solids pile) are taken into a corral where they are further aged and mechanically broken-down by cow traffic, and then used for bedding material in the freestall beds. The age of the material tested was not know exactly but is likely older that three months old. The freestall beds are located in the covered barns and two beds were tested with one measurement per bed on one day. The average emissions from the multiple bed test locations included low methane flux (24 ug/m2,min-1), moderate ARB ROG flux (16 ug/m2,min-1) and ammonia flux (830 ug/m2,min-1), a moderately low number of low-level volatile organic compound species flux by TO-15 with higher cyclohexane flux (9.4 ug/m2,min-1), acetone flux (6.7 ug/m2,min-1), and ethanol flux (3.7 ug/m2,min-1). Notable aldehyde flux was observed by

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the TO-11 including formaldehyde flux (0.21 ug/m2,min-1), acetaldehyde flux (0.69 ug/m2,min-1), acetone flux (39 ug/m2,min-1), crotonaldehyde flux (0.37 ug/m2,min-1) and butyraldehyde flux (0.25 ug/m2,min-1). Volatile organic acids were not detected.

Primary Lagoon

Wastewater, primarily flush lane wastewater, is stored in a large lagoon where water volumes are reduced by evaporation and wastewater is used for silage crop irrigation. The lagoon in operated on an annual schedule and the lagoon was tested at the inlet and outlet ends of the lagoon on two consecutive days at different times of the day. The average emissions from multiple test locations (inlet and outlet) on the lagoon included comparatively lower methane flux (2,300 ug/m2,min-1), moderate ARB ROG flux (16 ug/m2,min-1), moderate ammonia flux (250 ug/m2,min-1), an extensive range of low-level volatile organic compound species flux by TO-15 with higher trans-1,4-dichloro-2-butene flux (0.55 ug/m2,min-1), 1,2-dichlorobenzene flux (0.52 ug/m2,min-1), tetraethyl lead flux (0.42 ug/m2,min-1), 1,2,4-trichlorobenzene flux (3.3 ug/m2,min-1), and naphthalene flux (1.5 ug/m2,min-1). Lower levels of aldehyde flux was observed by TO-11 including formaldehyde flux (0.13 ug/m2,min-1), acetaldehyde flux (0.25 ug/m2,min-1), and acetone flux (0.52 ug/m2,min-1). Volatile organic acids were not detected.

Flushed Lane; Pre-flushed

Solid waste from the barn lanes are flushed several times per day and directed to the solid/liquid waste stream separator. The barn lanes accumulate fresh manure and manure layers range up to several inches over a six to eight hour time period. The pre-flushed barn lanes were tested with multiple locations on both test days. The average emissions from the multiple test locations included moderate methane flux (430 ug/m2,min-1), moderate ARB ROG flux (34 ug/m2,min-1), moderately high ammonia flux (2,400 ug/m2,min-1) and ethylamine flux (19 ug/m2,min-1), a moderately low number of low-level volatile organic compound species flux by TO-15 with higher ethanol flux (10 ug/m2,min-1), and some aldehyde flux by TO-11 including formaldehyde flux (0.15 ug/m2,min-1), acetaldehyde flux (6.1 ug/m2,min-1), and acetone flux (1.2 ug/m2,min-1). Volatile organic acids were not detected.

Flushed Lane; Post-flushed

Testing was also conducted after the barn lanes were flushed. There was very little manure in the lanes post flushing, and the source appeared to more like a dilute wastewater stream as compared to the pre-flushed lane surface. The post-flushed barn lanes were tested with multiple locations on both test days. The average emissions from the multiple test locations included non-detect methane flux (<1.2 ug/m2,min-1), moderate ARB ROG flux (30 ug/m2,min-1), moderately low ammonia flux (480 ug/m2,min-1) and ethylamine flux (23 ug/m2,min-1), a moderately low number of low-level volatile organic compound species flux by TO-15 with moderate ethanol flux (4.7 ug/m2,min-1), vinyl acetate flux (0.40 ug/m2,min-1) and no aldehyde flux was observed by TO-11. Volatile organic acids were not detected.

Feed Lane (pile)

The original unit process of interest regarding feed was feed storage, however, feed storage was housed off site and feed storage consisted of many large piles of feed stock materials that are blended into the feed material presented to the cows in the barns. The feed lane was refilled several times per day, and there was always a piled feed in the barn feed lanes. The feed was tested at one location per day. The average emissions from the testing on multiple days included low methane flux (29 ug/m2,min-1), high ARB ROG flux (890 ug/m2,min-1), low ammonia flux (31 ug/m2,min-1), and many higher-level volatile organic compound species flux by TO-15 including high-level ethanol flux (870 ug/m2,min-1), vinyl acetate flux (13 ug/m2,min-1), acetone flux (13 ug/m2,min-1), hexane flux (10 ug/m2,min-1- highest hexane flux detected), and 2-propanal flux (5.8 ug/m2,min-1- highest 2-propanal flux detected) and no aldehyde flux was observed by TO-11. Volatile organic acids were not detected.

Turnouts

Turnouts are the areas in the corral where cows travel from the covered barns to the corrals. Cows spend most of the day light hours in the barns but migrate to the corrals depending on cloud cover, temperature, and other factors. Areas of a corral were selected with three types of ground cover: fresh manure, thin layer of dry manure, and the thicker layers of dry manure. Three locations were tested in the same corral on two days and samples were collected at the highest emitting surfaces of two of the locations. The average emissions from multiple test locations in the corral for milk cows on two days included comparatively moderate methane flux (1,700 ug/m2,min-1), lower ARB ROG flux (7.0 ug/m2,min-1), moderately high ammonia flux (3,600 ug/m2,min-1), an extensive range of low-level volatile organic compound species flux by TO-15 with higher ethanol flux (3.8 ug/m2,min-1), and acetone flux (2.2 ug/m2,min-1). Lower levels of aldehyde flux was observed by TO-11 including formaldehyde flux (0.092 ug/m2,min-1), acetaldehyde flux (0.25 ug/m2,min-1), and acetone flux (0.85 ug/m2,min-1). Volatile organic acids were not detected.

Heifer Pens

Heifer pens were tested because dry cow pens were not available for testing. The heifer cows are fed a lower energy diet and the unit process is similar to the milk cow corral source (turnouts). Thicker layers of dry manure were selected for testing. Two locations were tested in the same corral on two days at different times of the day. The average emissions from multiple test locations in the corral for milk cows on two days included non-detect methane flux, moderate ARB ROG flux (19 ug/m2,min-1), moderate ammonia flux (530 ug/m2,min-1), moderate-to-low ethyl amine flux (15 ug/m2,min-1), a range of low-level volatile organic compound species flux by TO-15 with higher acetone flux (1.1 ug/m2,min-1) and m/p-xylene flux (0.91 ug/m2,min-1). Aldehyde flux was not observed by TO-11. Volatile organic acids were not detected.

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Milk Parlor

Wastewater from the milk parlor and cow washing area was tested at the process effluent channel at one location on two days. The level and type of emissions was similar to the post-flush lane source. The average emissions from multiple test days at one location in the milk parlor effluent channel included non-detect methane flux (<1.2 ug/m2,min-1), moderately high ARB ROG flux (47 ug/m2,min-1), moderately high ammonia flux (340 ug/m2,min-1) and ethylamine flux (29 ug/m2,min-1), an range of low-level volatile organic compound species flux by TO-15 with higher chloroethane flux (3.0 ug/m2,min-1), chloromethane flux (3.7 ug/m2,min-1), toluene flux (4.6 ug/m2,min-1), chloroform flux (2.5 ug/m2,min-1), carbon disulfide flux (2.3 ug/m2,min-1), acetone flux (1.4 ug/m2,min-1), ethanol flux (1.3 ug/m2,min-1), and 1,2-dibromo-3-chloropropane flux (0.32 ug/m2,min-1). Aldehyde flux was not observed by TO-11. Volatile organic acids were not detected.

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I. INTRODUCTION

This technical memorandum describes the field testing that was conducted in order to assess the ROG and ammonia/amine air emissions from a selected dairy located in Merced, California during the summer season. Area source flux data were collected with the intention of using the flux data to generate air emission factors from unit process at dairies and to calculate study compound emission factors per cow at a Northern California, flushed lane dairy. Field testing was conducted by Dr. C.E. Schmidt, Mr. Tom Card, and Mr. Hoby Rash on September 15 and 16, 2004. Two representatives of a research group from Fresno Sate were present for the testing, and representatives from ARB conducted a site visit of the field testing activities. Test locations are described in Table 1 and are identified in ATTACHMENT A on the flux sampling data sheets.

The Central California Ozone Study (CCOS) group has sponsored this study to evaluate the air emissions of reactive organic gases (ROGs) or volatile organic compounds (VOCs), ammonia/amines, and other study compounds produced by dairies. This research provided process specific dairy emissions data for use in improving emission estimates required for State Implementation Plans (SIPs) and Senate Bill 700 (SB700). In addition, data from this research will be used to better evaluate dairy control strategies for ozone and particulate matter, and to support the CCOS emissions inventory and modeling efforts.

This dairy air emissions assessment project includes conducting the research as a three phase program: Phase I- planning and work plan development; Phase II- field testing and reporting for testing conducted during one season at one dairy on two consecutive days; and
Phase III- optional, follow-on testing which is dependent on the results obtained in Phase ll testing.

This work is also being coordinated with other dairy research projects under the oversight of the Dairy Subgroup of the San Joaquin Valley Ag Tech Group. In addition, during field testing for this project, Fresno State University researchers conducted concurrent ambient upwind/down emissions sampling, and UC Davis researchers performed additional sample collection. The results from these related efforts are reported elsewhere.

This memorandum includes a discussion of the testing methodology, quality control procedures, results, discussion of the results, and summary statements.

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II. TEST METHODOLOGY

Testing for surface flux was conducted using the US EPA recommended Surface Isolation Flux Chamber (US EPA. Radian Corporation, February 1986). Flux chamber sampling locations were selected using direction from other research scientists and literature, and site screening information.

The technical approach has been designed around the efficiency of conducting emission flux chamber testing, the need to conduct multiple tests per unit process due to spatial variability, and the need to collect an adequate amount of full compound speciation data. The proposed program included a planning stage intended to identify the significant sources, evaluating key variables, and decision-making regarding data collection that will affect the usability of the emission factor data set. The technical approach included: multiple location tests for the primary area sources or unit process; and at least one full compound speciation data set for each primary emissions area.

The baseline data collection for each test location, other than locations screened with real time data for the purpose of selecting a baseline test location, included Method TO-15 for speciated VOCs or ROGs (and a total non-methane organic compound or TNMOC summation value), and ammonia/amines determination by NIOSH Method 2010. So long as representative full speciation data are collected for each major area source, then the baseline data set can be used to assess the spatial variability with a source and define the primary compound emissions (ROG or VOC/NH3 and amines). A limited amount (about 1-in-3) of full speciation data was collected to assess significant contributions from the non-primary sources. Given that project resources cannot address both spatial variability, the large number of major sources at a dairy, and full speciation of emitted species all at the same time, the compromise of including all major sources with limited compound speciation proved to be a sound strategy.

The dairy unit processes that were studied area summarized in the table below. Note that processes that were subject to solar heating (sun exposure) were sampled at different times of the day on two different days in order to assess time of day effects.

Dairy Unit Process or Unique Area Source Tested at the Northern California Dairy	***Screening Level Testing (Real time detection only)***	***Baseline Testing (ROG and NH3, amines)***	***Full Compound List (Other ROG Species)***	***Comments***
Flushed Lane- Prior to Flushing (shaded)	**1**- Day 1	**2**- Day 1 **2**- Day 2	**1**- Day 1 **1**- Day 2	Stockpile of manure prior to lane flushing, half-day accumulation

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Flushed Lane- Post Flushing (shaded)	**1**-Day 1	**2**- Day 1 **2**- Day 2	None	Mostly clean lanes, some manure slurry
Solid Storage Piles (sun exposed)	**1**- Day 1	**2**- Day 1 AM **2**- Day 2 PM	**1**- Day 1 AM	Typical age and depth of manure from long term storage
Lagoon (sun exposed)		**2**- Day 1 AM **2**- Day 2 PM	**1**- Day 1 AM **1**- Day 2 PM	Spatial distribution of testing at inlet and outlet on primary lagoon
Solids in Solids Separator (sun exposed)	**1**- Day 1	**2**- Day 1 AM **2**- Day 2 PM	**1**- Day 1 AM **1**- Day 2 PM	Solids material tested as daily pile material collected and moved to solids storage pile (fresh solids as opposed to aged)
Bedding in Pile for Freestall Area (sun exposed)	**1**- Day 1	**2**- Day 1 PM	**1**- Day 1 PM	One day testing of bedding material in pile, one day testing of bedding in freestall
Freestall Area (shaded)		**2**- Day 2 AM	**1**- Day 2 AM	Bedding material in freestall beds
Barn Turnout and Corral Area (sun exposed)	**1**- Day 1	**1**- Day 1 AM **2**- Day 2 PM	**1**- Day 2 PM	Target areas included fresh manure, thin manure layer, and thick manure layer (no piles- recent corral cleaning)
Manure Piles in Turnout Areas (sun exposed)	None	None	None	Recent corral cleaning, no storage piles. Samples collected elsewhere.
Heifer Pens (dry cow pens- sun exposed)		**1**- Day 1 PM **2**- Day 2 AM		Minimum testing to show similarity of source
Open Feed Storage (in freestall feed lanes- shaded)		**1**- Day 1 **1**- Day 2	**1**- Day 1	Typical silage only; category is variable dependent on feed type. Tested in feed lanes not store pile

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Milk Parlor (wastewater effluent- sun exposed)		**1**- Day 1 **1**- Day 2		Not a significant source, similar to flushed lane.
Field Blank		**2**	**2**	Minimum QC; approx. 5%
Field Replicate		**2**		Minimum QC; approx. 5%
TOTAL	**6**	**38**	**13**	

In addition, dairy operations information, and process specific surface area (i.e., lagoon, corrals, flush lanes, etc.) and other facility information data was collected during the field testing effort. These data are critical for data processing and process and facility emission estimation purposes, including:

a. Test location
b. Weather conditions
c. Number of animals, separated as milk cows, heifers, calves, etc.
d. Type of dairy (flush, scrape, vacuum)
e. Type of Housing (freestall, open corral)

In addition, the following information was collected for the lagoon testing effort:

a. Liquid Storage Volume, include size of lagoon (L x W x D)
b. Temperature of lagoon
c. Hydraulic Retention Time (HRT)
d. Flush frequency
e. Estimated percentage of cow manure flushed into lagoon
f. Type of solids separation (mechanical separator, settling basin)
g. Time of measurement (a.m. or p.m.)

Area sources were testing using the USEPA surface emission isolation flux chamber. The flux chamber measures the flux of study compounds at a given location, and the testing effort generated 'as tested' flux data, meaning the flux was representative of the unit process tested on that given day. The operation of the surface flux chamber is given below:

1. The flux chamber equipment was decontaminated by washing with Alconox soap and water and rinsing with water prior to the equipment use. New sample lines were prepared and used for the application.

2. Flux chamber, sweep air, sample collection equipment, and field documents were located on-site. Site test locations were identified and recorded on a site plot map.

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3. The site information, location information, equipment information, date, and proposed time of testing were documented on the Emissions Measurement Field Data Sheet.

4. The exact test location was selected and placed about 1/4" into the land surface, slurry surface, or liquid surface sealing the chamber for flux testing. Thermocouples were placed in order to monitor surface/air temperatures outside of the chamber.

5. The sweep air flow rate was initiated and the rotometer, which stabilizes the flow rate, was set at 5.0 liters per minute. A constant sweep air flow rate was maintained throughout the measurement for each sampling location.

6. Flux chamber data were recorded every residence interval (6 minutes) for five intervals, or 30 minutes.

7. At steady-state (assumed to be greater than 5 residence intervals), the sample collection was performed by interfacing the sample media as specified in the QAPP to the purged, sample line and collecting the sample media as appropriate.

8. After sample collection, all field data were documented on the data sheet.

9. After sampling, the flux measurement was discontinued by shutting off the sweep air, removing the chamber, and securing the equipment. The chamber was cleaned by dry wipe with a clean paper towel and the sample lines were purged with UHP air.

10. Sampling locations were recorded on the field data sheet. The equipment was then relocated to the next test location and steps 1) through 9) were repeated.

A total of five sample collection and analytical methods were used for the effort as specified in the project QAPP as identified below. Method detection limits achieved for the testing effort are included in this information. Note that the detection limits achieved reference the media blank samples as individual sample detection limits vary depending on the amount of sample analyzed, which is a function of the level of compounds found in the sample. As the sample concentration increases, so does the detection limit of compounds not detected in the sample.

Assessment Level	Analytical Method	Species	Method Detection Limit Achieved for Testing Event (field media blank samples)

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Screening-Level Assessment	Real Time Hydrocarbons and gas tube	Total FID and PID Hydrocarbons and Ammonia	FID- 0.01 ppmv PID- 0.01 ppmv NH3- 0.1 ppmv
Baseline-Level Assessment	USEPA Method TO-15	Speciated Hydrocarbons, ROG or VOC or ARB ROG	0.4-to-27 ug/m3 (0.04- to-4 ppbv)
	NIOSH 2010	Ammonia and other Amines	0.2 –to-0.5 ug/ml; about 0.4 mg/m3 (0.5 ppmv)
Full Compound Assessment	ASTM 3416	Fixed Gas- (CH4)	50 ppbv (30 ug/m3)
	USEPA Method TO-11 (GC/HPLC-UV/VIS)	Aldehydes/Ketones	0.04-to-0.16 ug/sample; about 0.9-to-9 ug/m3 (0.7-to-4 ppbv)
	USEPA Method TO-11 (GC/HPLC-UV/VIS)	Volatile Organic Acids	10 ug/sample; 290 ug/m3 (63-to-230 ppbv)

* Nominal detection limit. Each sample detection limit is based on possible dilution factors.
** Detection limit depends upon the volume of air collected through the sampling media.

GC = Gas chromatography
FID = Flame ionization detection
PID = Photoionization detection
HPLC = High performance liquid chromatography
UV-VIS = Ultraviolet-Visible Absorption Spectrophotometer
MS = Mass spectrometry
ASTM = American Society of Testing and Materials
EAS- Environmental Analytical Services

The project analytical menu included non-methane, VOC speciation analysis (USEPA Method TO-15) and summation of non-listed VOCs for an estimate of total reactive gases (ROG) and total organic gases (TOG). Rather than a 'total organic gases' method, the ROG estimate was made by summing the known , quantitative, 'non-listed VOC compounds'. Hydrocarbon compound concentrations (ug/m3) were summed per compound. This concentration is expressed as TNMOC. This total was used to generate the photochemical component or the ROG-VOC content. In addition, VOCs were summed on a molar carbon basis so that the ROG or VOC could be expressed as methane, like workings of SCAQMD Method 25.3 (all carbon atoms are oxidized to carbon dioxide, reduced to methane, and detected as methane). The TO-15, ROG or

VOC estimate amounts to a numerical simulation of ROG gases expressed as a total ROG concentration assayed at low method detection limits, but with the advantage of collecting compound-specific data, which is useful data to the project in understanding the type of compounds emitted from each unit process tested. The difference in this approach is that a 'total organic gases' analysis method like SCAQMD Method 25.3 will detect and count all measured VOCs in the 'ROG' total including VOCs listed as non-reactive ROG compounds (ROG exempt compounds). In addition to the Method TO-15 compound estimation of ROG per sample, ethyl amine was converted on a molar basis like the TO-15 VOC compounds and added to the summation of ROG as indicated by the regulatory definition of ROG. Since amines were sampled at each location, and the detection limit for ethyl amine was relatively high compared to the TO-15 detection limits, non-detection for ethyl amine was taken as zero in the average ROG calculation. Method TO-11 aldehyde and ketone compounds were also included in the estimation of ROG or VOC, including formaldehyde, acetaldehyde, crotonaldehyde, and butyaldehyde). The TOG was obtained by adding methane values to the estimated ROG values as per regulatory definition.

All laboratory data are reported as delivered from the laboratory without background or blank subtraction. Compound concentration data found below detection limit are reported by the laboratory as less than method detection by reporting the detection limit with a qualifying flag **'U**'. This indicates that the compound was not detected, or is below the minimum reported detection limit (same as 'ND' or not detected). Compound concentration data found above the detection limit but below the reporting limit are qualified with a **'J'** flag. The reporting limit is established by the laboratory and is based on the detection limit and the variability in analysis near the detection limit. The reporting limit is a multiple of the detection limit (i.e., like 5 times detection limit) and data reported above this level are greater than the 'region of less certainty', or outside of the range near the detection limit where is greater imprecision, a higher occurrence of false positive detections, and a higher occurrence of false negative detection. Another way to say this is that data reported above the reporting limit are reported with greater confidence or the highest level of confidence as compared to the 'J' flagged data. It is important to note that all data have value above the method detection limit, and this system of data qualification is used to assist in understanding data quality and assessing data for various data uses and applications.

In addition to the laboratory data qualification, project QC criteria have been established for all quantitative methods, and these data can also be used to qualify the field data. QC criteria have been established that represent the sensitivity of the method, specifically in reference to the laboratory and field blank data. The project included laboratory method blank QC samples and field media blank QC samples. Compounds appearing in either method or field media blank were summarized and the highest occurrence of a compound in either the method blank or the field blank data sets were used as the QC criteria. The logic here is that since a compound can occur in the laboratory method blank or the field media blank, reported levels below this level

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can be false positive detections or unrelated to the source. As such, data reported above the QC criteria limit are reported in bold and are taken to be related to the area source tested. Level found below the QC criteria are reported and can be used, however, it should be recognized that a given compound reported at or below the QC criteria may be related to another source or may not be a valid number, and may not related to the area source tested. Also, on occasion, a sample will have a detection limit that is greater than the QC reporting limit determined by QC data. This happens when a sample has a high detect of one or more compounds and a smaller sample volume is used to properly analyze the sample. This results in a higher detection limit ('U') that may exceed the QC criteria. In this case, the detection limit value above QC criteria is not taken as sample value.

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III. QUALITY CONTROL

Control procedures that were used to assure that data of sufficient quality resulted from the flux chamber study are listed and described below. The application and frequency of these procedures were developed to meet the program data quality objectives as described in the project work plan (Schmidt, C.E., February 2004).

Field Documentation -- A field notebook containing data forms, including sample chain-of-custody (COC) forms, was maintained for the testing program. Attachment A contains the Emission Measurement Data Sheets.

Chain-of-Custody -- COC forms were not used for field data collection. Field data were recorded on the Flux Chamber Data Forms provided in Attachment A.

TO-15 Volatile Organic Compounds; GC/MS

Laboratory Control Spike Recovery Analysis and Duplicate – Eleven laboratory control spike samples were analyzed using a standard containing 17 of the TO-15 study compounds. All compounds were reported for all spike samples within the QC criteria of 70%-to-130% with the exception of the following compounds: vinyl chloride- 65% recovery on one of 17 QC samples. In addition, these 11 control spike samples were analyzed in duplicate, and the relative percent difference (RPD) for the samples were within the QC criteria of $\pm$30 RPD except for the following: 1,1-dichloroethane- 30 RPD and 37 RPD; 1,2-dibromoethane- 30 RPD; and chlorobenzene- 30 RPD. With these four exceptions, all other compounds were within criteria for all other QC samples. These data represent acceptable method performance for the data set.

Laboratory Control Duplicate – Eleven QC samples with 17 of the study compounds (around 1 ppbv level standard) were analyzed in duplicate. All data was found within the precision criteria of 30% recovery for the spiked compounds with the following exceptions: 1,1-dichloroethane- 66% and 67 %; and vinyl chloride- 69%. With these three exceptions, all other compounds were within criteria for all other QC samples. These data indicate acceptable method performance.

Laboratory Method Blank – Eleven laboratory method blank samples were analyzed and the TO-15 study compounds and no compounds were found above the reporting limits in any samples. The detection limits ranged from as 0.07 ppbv to 65 ppbv. These data were used along with field blank data to qualify the field data. These method blank data indicate acceptable method performance.

Field Media Blank -- Two media blank samples (T-118 and T-220) were collected by filling sample containers with ultra high purity air and submitting the samples for analysis. Several compounds were detected above method detection limits (J flagged) but no compounds were reported above method detection limits. The media blank data were included in developing data qualifiers that

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indicate system sensitivity and represent acceptable method performance.

Replicate Sample -- Two field replicate samples were collected for the flux testing program. The flux replicate sample was collected by sampling the chamber contents after the flux sample was collected. Sample T-115/T-116 had four compound pairs that were not replicated and nine replicate pairs with a range of RPD of 0 to 140 and seven of nine pairs exceeding (criteria is 50 RPD) the average RPD was 81. The other sample, T-201/T-202 had 27 compound not replicated and five compound pairs with a range of RPD values of 47 to 95 with four pairs exceeding criteria. These data indicate poor but it is likely that the source tested was not the best selection for replicate testing. The goal was to select a low level emitting surface, which was taken to be the milk parlor effluent. However, the waste stream was highly variable and a true test of method variability is provided with replicate testing on a low-level, stable source. Given the variability of the source and the low level of study compounds, as well as the good laboratory precision shown with laboratory replicate analysis, these data indicate poor field precision but acceptable method performance. These observations do not limit data usage.

ASTM D-3416 Methane; GC/FID

Laboratory Control Spike Recovery Analysis and Duplicate – One laboratory control spike sample was analyzed using a standard of methane at 1.75 ppmv. Methane was reported within the QC criteria of 70%-to-130% at 104%. In addition, this control spike sample was analyzed in duplicate, and the RPD for the sample was within the QC criteria of $\pm$30 RPD at 13. These data represent acceptable method performance for the data set.

Laboratory Method Blank – One laboratory method blank sample was analyzed and methane was not found above the method detection limit of 50 ppbv. These data were used along with field blank data to qualify the field data. These method blank data indicate acceptable method performance.

Field Media Blank -- One media blank sample (T-118) was collected by filling sample container with ultra high purity air and submitted for methane analysis. Methane was not detected above the method detection limit of 50 ppbv. The media blank data were included in developing data qualifiers that indicate system sensitivity and represent acceptable method performance.

TO-11 Aldehydes; GC/HPLC-UV/VIS

Laboratory Control Spike Recovery Analysis and Duplicate – One laboratory control spike sample was analyzed using a standard containing all 15 of the TO-11 study compounds. All compounds were reported for all spike samples within the QC criteria of 70%-to-130. In addition, the duplicate analysis of this QC sample had all compound pairs within the QC criteria for RPD (30 RPD). These data represent acceptable method performance for the data set.

Laboratory Control Duplicate – One QC sample with 15 of the study compounds (around 0.3

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ug/sample) were analyzed in duplicate. All data was found within the precision criteria of 30% recovery for the spiked compounds with the exception of p-tolualdehyde at 67% recovery. These data indicate acceptable method performance.

Laboratory Method Blank – One laboratory method blank sample was analyzed and no TO-11 study compounds were found above the reporting limits in any samples. The detection limits ranged from as 0.04 ppbv to 0.40 ppbv. These data were used along with field blank data to qualify the field data. These method blank data indicate acceptable method performance.

Field Media Blank -- Two media blank samples (K-107 and K-206) were collected by opening a sampling cartridge for TO-11, sealing the cartridge, and then submitting the samples for analysis. No compounds were reported above method detection limits. These data represent acceptable method performance.

TO-11 Organic Acids; GC/HPLC-UV/VIS

Laboratory Method Blank – One laboratory method blank sample was analyzed and no volatile organic acid study compounds were found above the reporting limits in any samples. The detection limits were 10 ug/sample. These data were used along with field blank data to qualify the field data. These method blank data indicate acceptable method performance.

Field Media Blank -- Two media blank samples (V-107 and V-206) were collected by filling a clean impinger with impinger solution, transferring the solution into the sample bottle, sealing the bottle, and then submitting the samples for analysis. No compounds were reported above method detection limits. These data represent acceptable method performance

NIOSH Method 2010 Ammonia/Amines; IC

Laboratory Spike Recovery Analysis – One laboratory spike sample was analyzed using a standard containing ammonia. Ammonia was reported within the QC criteria of 70%-to-130. for the spike recovery (117%) and the duplicate spike recovery (111%). The precision was 4 RPD. These data represent acceptable method performance for the data set.

Laboratory Control Duplicate – One QC sample with ammonia (3 ug/ml) was analyzed in duplicate. All data was found within the precision criteria of 30% recovery for the spiked compound at 0 RPD. These data indicate acceptable method performance.

Laboratory Spike Recovery Analysis – One laboratory control spike sample was analyzed using a standard addition of 20 ug/ml containing ammonia. Ammonia was reported within the QC criteria of 70%-to-130. for the spike recovery (100%) and the duplicate spike recovery (94%). The precision was 6.2 RPD. Additional recovery of spike samples was also conducted at 10 ug/ml and these recoveries as well as the duplicate analysis of these recoveries was within method QC criteria. These

data represent acceptable method performance for the data set

Field Media Blank -- Two media blank samples (A-118 and A-204) were collected by filling a clean impinger with impinger solution, transferring the solution into the sample bottle, sealing the bottle, and then submitting the samples for analysis. No compounds were reported above method detection limits. These data represent acceptable method performance

IV. RESULTS AND DISCUSSIONS

Field sampling information and real time field data for all testing activities are reported in Table 1. QC data and QC criteria for TO-15 VOC analyses are presented in Table 2. These QC criteria data are used to qualify all Method TO-15 field data which are shown in Table 3. QC qualification includes field data exceeding method detection limits ('U' values) and those levels per compound exceeding levels found in the laboratory method blank samples and the media field blank samples. As such, data found above the QC criteria (shown in BOLD) are taken to be related to the area source tested and are not related to laboratory artifacts or other sources. All flux data are reported in flux units per square meter of exposed surface (ug/m2,min-1).

All field for Method TO-5 aldehydes and ketones analysis, including QC criteria are reported in Table 4. All field for Method TO-5 volatile organic acids, including QC criteria are reported in Table 5. And all field for NIOSH Method 2010 ammonia and amines analysis, including QC criteria are reported in Table 5.

In addition to data reported by analytical method (Tables 2 through 7), all compound flux data are reported in Tables 7 through 17 by unit process tested as follow:

Table 7- Separator Solids
Table 8- Lagoon
Table 9- Turnout (milk cow corral)
Table 10- Bedding Pile
Table 11- Freestall Bed
Table 12- Flushed Lane; Pre-Flushed
Table 13- Flushed Lane; Post-Flushed
Table 14- Feed (in barn feed lane)
Table 15- Milk Parlor Effluent
Table 16- Solids Pile
Table 17- Heifer Pen (dry cow corral)

And finally, data from each of the unit process tables (Tables 7 through 17) were averaged per compound and reported by unit process in Table 18. Method detection limits were not used in the generation of average flux per unit process; a zero value was used. The highest measured, average flux per compound has been shaded for identification. Data per compound found in Table 18 can be used to represent emissions from these unit treatment processes.

Surface flux data for a surface area source are calculated using measured target compound concentrations and flux chamber operating parameter data (sweep air flow rate of 5.0 liters per

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minute [L/min], surface area 0.13 square meters). The site emissions per area can be calculated by multiplying the flux by the surface area of the source. The flux is calculated from the sweep air flow rate Q (cubic meters per minute [m^3/min]), the species concentration Yi (micrograms per cubic meter [mg/m^3)], and exposure to the chamber surface area (square meters [m^2]), as follows:

$$Fi = \frac{(Q)\,(Yi)}{(A)}$$

Quality control field blank data were collected and these data were used to qualify the field data. All field data above the higher of the blank QC criteria (qualifying data shown in grey shade) are reported in **bold**. Field data below these limits are reported, however, these data are reported as 'less certain' and should be used only with the appropriate QC qualification. All field data were qualified using method blank, field blank, and field background data. A review of the project QC data indicated acceptable laboratory and method performance for the assessment, with the exception of poor field precision, which is unfortunately commonly observed at the low levels of detection achieved with the analytical method.

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V. SUMMARY

Surface flux measurements were made at multiple locations on a total of 11 unit process at a northern California dairy in order to assess dairy emission of ROG or VOC (ARB ROG in summary tables), ammonia/amine compounds, and other study compounds. The following is a summary of activities and results associated with this objective:

- Surface flux measurements of study compounds were measured at multiple outdoor, locations on the selected unit process at a dairy using the USEPA recommended surface flux chamber technology. This technology quantitatively measures vapor fluxes at the test surface (solid, slurry, sludge, liquid) due to the presence of volatile organic an inorganic compounds.

- Laboratory and field quality control data indicated acceptable sampling method performance. Poor precision for field replicate samples was observed, however, this is common for low level samples using this analytical method. Data above the reporting limits are indicted as those without a 'J' flag as provided on the laboratory sheets and summary tables (J flag values are above method detection but below reporting limit, less than method detection limits are 'U' flagged values).

- ***Separator Solids***
  Solids from the slurry effluent stream separator unit are stored for up to a day at the unit and moved to solids separator pile where they are stored unit application to fields off site or moved to the bedding storage pile. The age of the material tested was less than a day (fresh solid waste). The solid waste is sun exposed and was tested on two consecutive days at different time of the day. The average emissions from multiple test locations on the material included comparatively high methane flux (15,000 ug/m2,min-1) and ARB ROG flux (48 ug/m2,min-1), high ammonia flux (650 ug/m2,min-1) and high ethylamine flux (29 ug/m2,min-1), a wide range of low-level volatile organic compound species flux by TO-15 with high ethanol flux (13 ug/m2,min-1), acetone flux (2.5 ug/m2,min-1), carbon disulfide flux (2.9 ug/m2,min-1), toluene flux (1.3 ug/m2,min-1), and octane flux (1.2 ug/m2,min-1). Significant aldehyde flux was observed by the TO-11 including formaldehyde flux (0.076 ug/m2,min-1), acetaldehyde flux (0.2 ug/m2,min-1), acetone flux (1.1 ug/m2,min-1), and butyraldehyde flux (0.12 ug/m2,min-1). Volatile organic acids were not detected.

- ***Solids in Storage Pile***
  Solids from the solids separator unit are stored for weeks or longer until the material is used for on site applications such as bedding material or application to crop fields off site. The age of the material tested was more than a week (aged solid waste). The solid waste

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is sun exposed and was tested on two consecutive days at different times of the day. The average emissions from multiple test locations on the material included comparatively high methane flux (220,000 ug/m2,min-1- note highest methane flux detected), low ARB ROG flux (3.4 ug/m2,min-1), high ammonia flux (630 ug/m2,min-1) but no ethylamine flux, a moderate range of low-level volatile organic compound species flux by TO-15 with higher acetone flux (2.4 ug/m2,min-1), and detectable but lower aldehyde flux was observed by TO-11 including formaldehyde flux (0.19 ug/m2,min-1), acetaldehyde flux (0.25 ug/m2,min-1), and acetone flux (0.92 ug/m2,min-1). Volatile organic acids were not detected.

- ***Bedding Pile Solids***
  Solids (from the solids separator) are stored in the bedding pile for several months and then used for bedding material in the freestall beds. The age of the material tested was not know exactly but was from one-to-three months old. The solid waste pile is sun exposed and was tested on one day. The average emissions from multiple test locations included comparatively low methane flux (65 ug/m2,min-1), high ARB ROG flux (75 ug/m2,min-1), very high ammonia flux (22,000 ug/m2,min-1- note highest ammonia emissions detected), a large number of low-level volatile organic compound species flux by TO-15 with high oxygenated compound and chlorinated compound flux, including 2-butanone flux (330 ug/m2,min-1), acetone flux (35 ug/m2,min-1), and 15 other compounds over 1 ug/m2,min-1. Significant aldehyde flux was observed by TO-11 including formaldehyde flux (1.1 ug/m2,min-1), acetaldehyde flux (6.9 ug/m2,min-1), acetone flux (2.8 ug/m2,min-1), crotonaldehyde flux (0.92 ug/m2,min-1) and butyraldehyde flux (1.1 ug/m2,min-1). Volatile organic acids were not detected.

- ***Freestall Bed***
  Solids (from the bedding pile solids pile) are taken into a corral where they are further aged and mechanically broken-down by cow traffic, and then used for bedding material in the freestall beds. The age of the material tested was not know exactly but is likely older that three months old. The freestall beds are located in the covered barns and two beds were tested with one measurement per bed on one day. The average emissions from the multiple bed test locations included low methane flux (24 ug/m2,min-1), moderate ARB ROG flux (16 ug/m2,min-1) and ammonia flux (830 ug/m2,min-1), a moderately low number of low-level volatile organic compound species flux by TO-15 with higher cyclohexane flux (9.4 ug/m2,min-1), acetone flux (6.7 ug/m2,min-1), and ethanol flux (3.7 ug/m2,min-1). Notable aldehyde flux was observed by the TO-11 including formaldehyde flux (0.21 ug/m2,min-1), acetaldehyde flux (0.69 ug/m2,min-1), acetone flux (39 ug/m2,min-1), crotonaldehyde flux (0.37 ug/m2,min-1) and butyraldehyde flux (0.25 ug/m2,min-1). Volatile organic acids were not detected.

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- ***Primary Lagoon***
  Wastewater, primarily flush lane wastewater, is stored in a large lagoon where water volumes are reduced by evaporation and wastewater is used for silage crop irrigation. The lagoon in operated on an annual schedule and the lagoon was tested at the inlet and outlet ends of the lagoon on two consecutive days at different times of the day. The average emissions from multiple test locations (inlet and outlet) on the lagoon included comparatively lower methane flux (2,300 ug/m2,min-1), moderate ARB ROG flux (16 ug/m2,min-1), moderate ammonia flux (250 ug/m2,min-1), an extensive range of low-level volatile organic compound species flux by TO-15 with higher trans-1,4-dichloro-2-butene flux (0.55 ug/m2,min-1), 1,2-dichlorobenzene flux (0.52 ug/m2,min-1), tetraethyl lead flux (0.42 ug/m2,min-1), 1,2,4-trichlorobenzene flux (3.3 ug/m2,min-1), and naphthalene flux (1.5 ug/m2,min-1). Lower levels of aldehyde flux was observed by TO-11 including formaldehyde flux (0.13 ug/m2,min-1), acetaldehyde flux (0.25 ug/m2,min-1), and acetone flux (0.52 ug/m2,min-1). Volatile organic acids were not detected.

- ***Flushed Lane; Pre-flushed***
  Solid waste from the barn lanes are flushed several times per day and directed to the solid/liquid waste stream separator. The barn lanes accumulate fresh manure and manure layers range up to several inches over a six to eight hour time period. The pre-flushed barn lanes were tested with multiple locations on both test days. The average emissions from the multiple test locations included moderate methane flux (430 ug/m2,min-1), moderate ARB ROG flux (34 ug/m2,min-1), moderately high ammonia flux (2,400 ug/m2,min-1) and ethylamine flux (19 ug/m2,min-1), a moderately low number of low-level volatile organic compound species flux by TO-15 with higher ethanol flux (10 ug/m2,min-1), and some aldehyde flux by TO-11 including formaldehyde flux (0.15 ug/m2,min-1), acetaldehyde flux (6.1 ug/m2,min-1), and acetone flux (1.2 ug/m2,min-1). Volatile organic acids were not detected.

- ***Flushed Lane; Post-flushed***
  Testing was also conducted after the barn lanes were flushed. There was very little manure in the lanes post flushing, and the source appeared to more like a dilute wastewater stream as compared to the pre-flushed lane surface. The post-flushed barn lanes were tested with multiple locations on both test days. The average emissions from the multiple test locations included non-detect methane flux (<1.2 ug/m2,min-1), moderate ARB ROG flux (30 ug/m2,min-1), moderately low ammonia flux (480 ug/m2,min-1) and ethylamine flux (23 ug/m2,min-1), a moderately low number of low-level volatile organic compound species flux by TO-15 with moderate ethanol flux (4.7 ug/m2,min-1), vinyl acetate flux (0.40 ug/m2,min-1) and no aldehyde flux was observed by TO-11. Volatile organic acids were not detected.

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- ***Feed Lane (pile)***
  The original unit process of interest regarding feed was feed storage, however, feed storage was housed off site and feed storage consisted of many large piles of feed stock materials that are blended into the feed material presented to the cows in the barns. The feed lane was refilled several times per day, and there was always a piled feed in the barn feed lanes. The feed was tested at one location per day. The average emissions from the testing on multiple days included low methane flux (29 ug/m2,min-1), high ARB ROG flux (890 ug/m2,min-1), low ammonia flux (31 ug/m2,min-1), and many higher-level volatile organic compound species flux by TO-15 including high-level ethanol flux (870 ug/m2,min-1), vinyl acetate flux (13 ug/m2,min-1), acetone flux (13 ug/m2,min-1), hexane flux (10 ug/m2,min-1- highest hexane flux detected), and 2-propanal flux (5.8 ug/m2,min-1- highest 2-propanal flux detected) and no aldehyde flux was observed by TO-11. Volatile organic acids were not detected.

- ***Turnouts***
  Turnouts are the areas in the corral where cows travel from the covered barns to the corrals. Cows spend most of the day light hours in the barns but migrate to the corrals depending on cloud cover, temperature, and other factors. Areas of a corral were selected with three types of ground cover: fresh manure, thin layer of dry manure, and the thicker layers of dry manure. Three locations were tested in the same corral on two days and samples were collected at the highest emitting surfaces of two of the locations. The average emissions from multiple test locations in the corral for milk cows on two days included comparatively moderate methane flux (1,700 ug/m2,min-1), lower ARB ROG flux (7.0 ug/m2,min-1), moderately high ammonia flux (3,600 ug/m2,min-1), an extensive range of low-level volatile organic compound species flux by TO-15 with higher ethanol flux (3.8 ug/m2,min-1), and acetone flux (2.2 ug/m2,min-1). Lower levels of aldehyde flux was observed by TO-11 including formaldehyde flux (0.092 ug/m2,min-1), acetaldehyde flux (0.25 ug/m2,min-1), and acetone flux (0.85 ug/m2,min-1). Volatile organic acids were not detected.

- ***Heifer Pens***
  Heifer pens were tested because dry cow pens were not available for testing. The heifer cows are fed a lower energy diet and the unit process is similar to the milk cow corral source (turnouts). Thicker layers of dry manure were selected for testing. Two locations were tested in the same corral on two days at different times of the day. The average emissions from multiple test locations in the corral for milk cows on two days included non-detect methane flux, moderate ARB ROG flux (19 ug/m2,min-1), moderate ammonia flux (530 ug/m2,min-1), moderate-to-low ethyl amine flux (15 ug/m2,min-1), a range of low-level volatile organic compound species flux by TO-15 with higher acetone flux (1.1 ug/m2,min-1) and m/p-xylene flux (0.91 ug/m2,min-1). Aldehyde flux was not observed

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by TO-11. Volatile organic acids were not detected.

- ***Milk Parlor***
  Wastewater from the milk parlor and cow washing area was tested at the process effluent channel at one location on two days. The level and type of emissions was similar to the post-flush lane source. The average emissions from multiple test days at one location in the milk parlor effluent channel included non-detect methane flux (<1.2 ug/m2,min-1), moderately high ARB ROG flux (47 ug/m2,min-1), moderately high ammonia flux (340 ug/m2,min-1) and ethylamine flux (29 ug/m2,min-1), an range of low-level volatile organic compound species flux by TO-15 with higher chloroethane flux (3.0 ug/m2,min-1), chloromethane flux (3.7 ug/m2,min-1), toluene flux (4.6 ug/m2,min-1), chloroform flux (2.5 ug/m2,min-1), carbon disulfide flux (2.3 ug/m2,min-1), acetone flux (1.4 ug/m2,min-1), ethanol flux (1.3 ug/m2,min-1), and 1,2-dibromo-3-chloropropane flux (0.32 ug/m2,min-1). Aldehyde flux was not observed by TO-11. Volatile organic acids were not detected.

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ATTACHMENT A

EMISSION MEASUREMENT DATA SHEETS

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ATTACHMENT B

CHAIN OF CUSTODY

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ATTACHMENT C

LABORATORY REPORTS

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ATTACHMENT D

PHOTOS FROM SUMMER TESTING EVENT- MERCED DAIRY