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TECHNICAL MEMORANDUM

Results of the Dairy Emissions Evaluation Using Flux Chambers
Phase III Merced and Kings County Dairies

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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 the Phase III research is to provide process-specific (i.e., portions of dairy) dairy emission flux 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 identify key compounds emitted from the dairies, 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 solids moisture sample collection and analysis.

The flux of ROG (VOC), ammonia/amines, and other study compounds was measured at multiple locations on a total of six types of emitting surfaces found at dairies or in different unit processes over the late summer and early fall months at two Northern California dairies. The unit treatment process testing included: solids in storage piles (Merced dairy only), wastewater lagoon, barn turnout areas, pre-flushed dairy lanes, feed materials in the bunkers or feed lanes in barns, and the working face of silage storage piles. In comparison to Phase II testing conducted in 2004, this effort focused on fewer unit processes as identified in Phase II, but included an extensive species analysis list as part of the investigation. 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, and data collected during Phase II. In addition, a 24-hour diurnal emissions study was conducted at a turnout location at the Merced dairy. Repeat flux chamber testing was conducted at one location for key compounds approximately every 24-hour in order to assess diurnal variability in compound emissions. Also in support of the research, Phase III work included method verification and flux chamber technique validation of assessment capabilities for volatile fatty acids, class of compounds known to be a component of dairy emissions. In total, three field efforts and two laboratory studies were conducted during Phase III.

A robust field program was conducted during the late summer and early fall seasons 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 three flux chamber sample media blank tests (3), and replicate flux tests (3). Both laboratory and field blank data were used to establish QC criteria that were used to discriminate the data as detected and non-

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detected. In addition, performance evaluation (PE) samples were conducted for SCAQMD Method 25.3, and multiple media spike samples were conducted for VFA test methods establishing media recovery criteria. And finally, VFA verification testing and validation testing was performed demonstrating the efficacy of using the flux chamber to assess surface emissions of VFAs. The validation testing resulted in data that demonstrated the percent recovery of VFAs from the flux chamber. 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 goal of screening level testing was to select specific test locations in the field for detailed sample collection and analysis. The baseline analysis included: total hydrocarbon assessment by SCAQMD Method 25.3 for total ROG assessment; VOCs were identified by speciation methods including USEPA Method TO-15 GC/MS and USEPA Method TO-14 GC/FID; and methods were used targeting classes of compounds including VFAs by USEPA Method TO-17, aldehydes and ketones by USEPA Method TO-11, and ammonia and amines by SCAQMD 207.1. The full compound analysis provided for a more comprehensive chemical speciation of the organic gases which was needed to evaluate the photochemical reactivity of the gases produced from livestock wastes, and to confirm the compounds detected in from the baseline analysis, including: USEPA Method TO-13 for semi-volatile organic compounds (SVOCs); reduced sulfur species by USEPA Method TO-14 (GC/FPD); phenols by USEPA Method TO-8; alcohols (methanol/ethanol) by BAAQMD Method 29; and VFAs by EAS Method HPLC.

In summary, an assessment of ROG (total), ROG (VOC) species, ammonia/amine species, and other study compound air emission flux testing was conducted at two dairies located in the San Joaquin Valley (Merced dairy and Kings County dairy). Six distinct potential emission sources were tested at multiple locations and key unit processes were studied at both dairies. One location was studied over a 24-hour period in order to assess diurnal variability in emissions. Analysis of samples for these study efforts included quantitative total ROG, selected speciation VOC analysis, and ammonia/amine flux testing at all test locations with more comprehensive analytical characterization of other analytical species at a limited number of key locations. The testing was performed during the late summer and early fall seasons, and data from testing in Phase II (2004) is comparable when similar analytical methods were used, and between the two dairies tested in Phase III (2005).

Each unit process at the dairy tested showed unique emission flux characteristics, although there was some commonality in emission flux for all unit processes. Observations for each unit

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process are briefly described below. Significance in emission sources can only be determined after the flux data ($\text{ug}/\text{m}^2, \text{min}^{-1}$) are converted to unit treatment process emissions (ug/minute or pounds per day) by knowing the surface area of these sources. Flux data can be compared between sources and dairies given the fundamental nature of the measurement.

The average emission flux data presented for all unit treatment process can be used to develop emission estimates 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 by subtracting exempt compounds identified by TO-15 from the SCAQMD 25.3 total number. In addition, a summation of non-exempt compounds by TO-15 was used to generate a different total ROG (based in GC/MS) by adding all non-exempt VOCs. A TO-15 based total can be determined by adding VOCs from other methods to this number including VFAs, amines, aldehydes, ketones (except acetone), and SVOCs. The same is true for ROG determined by Method TO-14, expressed as a total detector count and reported for use in a similar fashion. Note that diurnal variation data correction was not performed on these data; all data reported are uncorrected for diurnal variability. Diurnal variability in ammonia emissions is considered in the emissions report to follow.

Separator Solids in Storage Pile

Solids from the slurry effluent stream separator unit are stored until use as field application fertilizer or are moved to the bedding storage pile. The average emissions from multiple test locations on the material stored at the Merced dairy included: comparatively high methane flux ($110,000 \text{ ug}/\text{m}^2, \text{min}^{-1}$) and 25.3 ROG flux ($140 \text{ ug}/\text{m}^2, \text{min}^{-1}$); high ammonia flux ($170 \text{ ug}/\text{m}^2, \text{min}^{-1}$), high ethylamine flux ($19 \text{ ug}/\text{m}^2, \text{min}^{-1}$), and high diethylamine flux ($27 \text{ ug}/\text{m}^2, \text{min}^{-1}$); low-level volatile organic compound species flux by TO-15; and moderate acetone levels ($2.2 \text{ ug}/\text{m}^2, \text{min}^{-1}$). Moderate alcohol levels were detected by TO-14 with isopropanol at $3.5 \text{ ug}/\text{m}^2, \text{min}^{-1}$. Detectable but lower aldehyde flux was observed by TO-11; acetone flux by TO-11 was $0.78 \text{ ug}/\text{m}^2, \text{min}^{-1}$. VFAs, phenols and acids were not detected, however, moderately high levels of dimethyl sulfide ($45 \text{ ug}/\text{m}^2, \text{min}^{-1}$) was observed with some dimethyl disulfide ($0.21 \text{ ug}/\text{m}^2, \text{min}^{-1}$). Solids storage piles were not tested at the Kings County dairy.

Treatment Lagoons

Wastewater and primarily flush lane wastewater at the Merced dairy is stored in a large treatment lagoon with mixers where water volumes are reduced by evaporation and silage crop irrigation. The lagoon is operated on an annual schedule and the lagoon was tested at the inlet, middle and outlet end of the lagoon on accessed from the shore. The Kings County dairy has a three-stage wastewater lagoon system consisting of separator vault, settling pond with aerators/mixers, and storage lagoon with aerators/mixers. The average emissions from Merced

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dairy multiple test locations (inlet, middle, and outlet) on the lagoon included: comparatively lower methane flux (4,000 ug/m²,min-1); moderate 25.3 ROG flux (110 ug/m²,min-1); moderate ammonia flux (460 ug/m²,min-1); and an extensive range of low-level to mid-level volatile organic compound species flux by TO-15/TO-14 with low ethanol flux (0.69 ug/m²,min-1). Lower levels of aldehyde flux was observed by TO-11 including formaldehyde flux (0.18 ug/m²,min-1). VFAs were not detected, and hydrogen sulfide emission was high by comparison to most species and other sources (3,200 ug/m²,min-1).

The average emissions from Kings County dairy lagoon system included similar, lower methane flux (3,100 ug/m²,min-1), higher 25.3 ROG flux (220 ug/m²,min-1), higher ammonia flux (760 ug/m²,min-1), an extensive range of low-level to mid-level volatile organic compound species flux by TO-15/TO-14 with higher ethanol flux as compared to the Merced dairy lagoon (53 ug/m²,min-1). VFAs were not detected, and hydrogen sulfide emission was also high by comparison to most species (4,600 ug/m²,min-1) with some dimethyl sulfide emissions observed (17 ug/m²,min-1).

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 at two locations at the Merced dairy and one location at the Kings County dairy. The average emissions from the multiple test locations at the Merced dairy included: low methane flux (160 ug/m²,min-1); moderate 25.3 ROG flux (160 ug/m²,min-1); moderately high ammonia flux (960 ug/m²,min-1) and ethylamine flux (50 ug/m²,min-1); a moderately low-level volatile organic compound species flux by TO-15/TO-14 with higher ethanol flux (14 ug/m²,min-1); and some acetone flux (1.7 ug/m²,min-1). VFAs and sulfur species were not detected.

The average emissions from the multiple test locations at the Kings County dairy included: similar methane flux (170 ug/m²,min-1); lower 25.3 ROG flux (100 ug/m²,min-1); similar ammonia flux (960 ug/m²,min-1) and ethyl amine flux (46 ug/m²,min-1); moderately low-level volatile organic compound species flux by TO-15/TO-14 with lower ethanol flux (6.3 ug/m²,min-1); and higher acetone flux (3.5 ug/m²,min-1). VFAs and sulfur species were not detected.

Feed Lane and Silage Piles

Bunker feed in the barn feed lanes and the open face of the silage piles were studied at both dairies. The feed lane was refilled several times per day; feed was typically in the barn feed lanes. The open face or uncovered portion of the silage pile was tested on a freshly disturbed surface, simulating access and use of the silage in feed mixing. The average emissions from the feed (feed lanes and silage face) at the Merced dairy included: low methane flux (180

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ug/m²,min⁻¹); very high 25.3 ROG flux (19,000 ug/m²,min⁻¹); no ammonia flux; and many higher-level volatile organic compound species flux by TO-15/TO-14 including high-level ethanol flux (13,000 ug/m²,min⁻¹), carbon disulfide (250 ug/m²,min⁻¹), acetone flux (81 ug/m²,min⁻¹), other alcohols and compounds too numerous to list. Phenol was reported by Method TO-8 (890 ug/m²,min⁻¹). VFA flux levels were very high for acetic acid (1,700 ug/m²,min⁻¹) and propionic acid (66 ug/m²,min⁻¹). Sulfides were also detected including high levels of dimethyl sulfide (250 ug/m²,min⁻¹) and lower levels of dimethyl disulfide (7.3 ug/m²,min⁻¹). Silage showed the highest hydrocarbon species and total hydrocarbon flux found at the dairy.

The average emissions from the feed (feed lanes and silage face) at the Kings County dairy included: low methane flux (170 ug/m²,min⁻¹); the highest recorded 25.3 ROG flux (46,000 ug/m²,min⁻¹); very low ammonia flux (42 ug/m²,min⁻¹); and many higher-level volatile organic compound species flux by TO-15/TO-14 including high-level ethanol flux (17,000 ug/m²,min⁻¹), low-level acetone flux (8.6 ug/m²,min⁻¹), other alcohols and compounds too numerous to list. High levels of phenol were detected by Method TO-8 (480 ug/m²,min⁻¹). VFA flux levels were high for acetic acid (700 ug/m²,min⁻¹) and propionic acid (85 ug/m²,min⁻¹). Sulfides were also detected including high levels of dimethyl sulfide flux (470 ug/m²,min⁻¹) and dimethyl disulfide (210 ug/m²,min⁻¹). Silage emissions at the Kings County dairy were very similar but higher as compared to the Merced dairy showing the highest hydrocarbon species and total hydrocarbon flux found at the dairies.

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 at the Merced dairy were selected with three types of ground cover: fresh manure, thin layer of dry manure, and the thicker layers of dry manure. The Merced turnout was tested three days after a rain event and scientifically selected test locations were studied. The Kings County dairy was tested at random locations determined by constructing a transect line across three different turnouts with test locations determined by measuring out sections of the turnouts and testing at the center of equally spaced areas. The Kings County turnout data represent random test locations. The average emissions from multiple test locations at the Merced dairy in a corral for milk cows showed: moderate methane flux (780 ug/m²,min⁻¹); moderate 25.3 ROG flux (310 ug/m²,min⁻¹); high ammonia flux (12,000 ug/m²,min⁻¹) with some ethylamine (25 ug/m²,min⁻¹); and an extensive range of low-level volatile organic compound species flux by TO-15/TO-14 with higher ethanol flux (11 ug/m²,min⁻¹), and acetone flux (9.3 ug/m²,min⁻¹). VFA flux levels were moderately high for acetic acid (130 ug/m²,min⁻¹), and lower for propionic acid (2.8 ug/m²,min⁻¹), isobutyric acid (2.8 ug/m²,min⁻¹), and butyric acid (11 ug/m²,min⁻¹). Sulfides were also detected including dimethyl sulfide (1.2 ug/m²,min⁻¹) and dimethyl disulfide (16 ug/m²,min⁻¹).

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The average emissions from multiple test locations at the Kings County dairy in a corral for milk cows showed: low methane flux (71 ug/m²,min-1); lower 25.3 ROG flux (120 ug/m²,min-1); lower ammonia flux (470 ug/m²,min-1); and an extensive range of low-level volatile organic compound species flux by TO-15/TO-14 with lower ethanol flux (0.49 ug/m²,min-1), and acetone flux (1.5 ug/m²,min-1). VFA flux levels were lower for acetic acid (16 ug/m²,min-1), propionic acid (3.8 ug/m²,min-1), butyric acid (5.8 ug/m²,min-1). Sulfides 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 emission flux from unit processes at two selected dairies located in the San Joaquin Valley, California during the late summer/early fall season. Area source flux data were collected with the intention of using the flux data to generate air emission estimates from unit process at dairies and to calculate study compound emission estimates per cow at Northern California, flushed lane dairies. Field testing was conducted by Dr. C.E. Schmidt, Mr. Tom Card, and Mr. Harold Litwiler on September 26 through 29, 2005 at the Merced dairy, and October 4 through 6, 2005 at the Kings County dairy. A return trip was made to the Merced dairy for the 24-hour time-dependent testing on October 18 and 19, 2005. Representatives of the CCOS group and Fresno State were present for the testing, and representatives from ARB and members of the SJV District conducted a site visit of the field testing activities. Test locations are described in Table 1 for the Merced dairy, Table 10 for the Kings County dairy, and Table 18 for the Merced dairy 24-hour study, 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 emission flux 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- follow-on testing based on the results obtained in Phase II testing. This document reports the findings of the multiple field investigations conducted under Phase III. Other research is reported in a separate document regarding VFA compound method verification and compound validation (flux chamber recovery), and reporting of emission estimates.

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 soils moisture testing. The results from this related effort are reported herein.

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 flux 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 SCAQMD 25.3 for total hydrocarbon content, Methods TO-15 and TO-14 for speciated VOCs or ROGs (and a total non-methane organic compound or TNMOC summation value), Method TO-17 for VFAs, Method TO-11 for aldehydes and ketones, and SCAQMD 207.1 for ammonia/amines. A limited amount (about 1-in-3) of full speciation data was collected to assess other related hydrocarbon species emissions at to confirm key hydrocarbon species emissions. These methods and compounds includes: reduced sulfur species by Method TO-14, phenols by Method TO-8, SVOCs by Method TO-13, VFAs by EAS Method HPLC, and alcohols by BAAQMD 29. 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. However, for this research, the emphasis was placed on testing at fewer locations per unit process with much more comprehensive analytical sample collection and analysis. Determining the composition of dairy emissions was a major emphasis of this work.

The dairy unit processes that were studied area summarized in the table below. Note that identical unit processes were tested at two different dairies in order to determine the dairy-to-dairy variability in air emissions.

DAIRY UNIT PROCESS	MERCED DAIRY	KINGS COUNTY DAIRY
Pre-Flush, Flushed Lanes	2 Locations	1 Location
Turnouts (Corrals)	6 Locations	9 Locations, 8 with samples
Lagoon	3 Locations	3 Locations

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Solids from Separator Storage	2 Locations, 2 with samples	None
Feed in Barn Bunkers	2 Locations	1 Location
Working Face of Silage Piles	2 Locations	1 Location

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.
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

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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 up to 11 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)
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 (GC/MS)	Speciated Hydrocarbons	0.6-to-1 ug/m3 (0.1- to-0.5 ppbv)

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	SCAQMD 207.1 (GC/IC)	Ammonia and other Amines	0.2 –to-0.5 ug/ml; about 0.4 mg/m ³ (0.5 ppmv)
	SCAQMD 25.3 (GC/FID)	Total Hydrocarbons	1.3 mg/m ³ Total (2 ppmv)
	USEPA Method TO-14 (GC/FID)	Speciated Hydrocarbons	1.6-to-24 ug/m ³ (0.7- to-20 ppbv)
	USEPA Method TO-11 (HPLC-UV/VIS)	Aldehydes and Ketones	0.04-to-0.16 ug/sample; about 0.9-to-9 ug/m ³ (0.7-to-4 ppbv)
	USEPA Method TO-17 (GC/MS)	Volatile Fatty Acids	0.1 ug/sample; 36.7 ug/m ³ (8.5-to-15 ppbv)
Full Compound Assessment	BAAQMD Method 29 (GC/FID)	Methanol and Ethanol	600 ug/sample; 10,000 ug/m ³
	USEPA Method TO-13 (HPLC-UV/VIS)	Semi Volatile Organic Compounds	0.3-to-0.7 ug/sample; about 0.4-to-0.7 ug/m ³
	USEPA Method TO-8 (GC/MS)	Phenols	15 ug/sample; 500 ug/m ³
	USEPA Method TO-14	Reduced Sulfur Compounds	1.4-to-5.2 ug/m ³ (1 ppbv)
	EAS HPLC-UV/VIS Method	Volatile Organic Acids	10 ug/sample; 290 ug/m ³ (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

EAS- Environmental Analytical Services

The project analytical menu included non-methane, VOC analysis as a total hydrocarbon method (SCAQMD 25.3, and methane) and speciation of VOCs (USEPA Method TO-15 and TO-14) which also provided for an estimate of total reactive gases (ROG) by summation. Hydrocarbon compound summations were performed by calculating the carbon equivalents per molecule, summing carbon and expressing total hydrocarbon as methane. This provide for a comparison of 25.3 total to summation totals by TO-15 and TO-14. In addition to the Method TO-15/TO-14 compound estimation of ROG per sample, ethyl amine and other compounds detected by other

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methods were 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. Method TO-11 aldehyde and ketone compounds were also included in the estimation of ROG or VOC, as well as Method TO-13 SVOCs, Method TO-8 phenols, and Method TO-17 VFAs. The TOG can be 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 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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Summary data are presented both with and without correction to the QC criteria, however, data use is recommended only for corrected data (i.e., data above QC criteria).

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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.

SCAQMD Method 25.3 Total Non-Methane and Non-Ethane Organic Compounds; GC/FID Method Quality Control –Method quality control included duplicate analysis of all samples, method blank determinations, and method response to four-point calibration curves. All method QC testing was with method specifications, and these data indicate acceptable method performance.

Laboratory Duplicate Sample Analysis- All samples were analyzed in duplicate, and these data show acceptable method precision with methane (tank) and NMNEO from the trap less than 20% area count difference and 30% difference from the mean, with the exception of 9 of 38 samples. In these samples, and exceedance of these criteria was recorded. The coefficient of variation for replicate trap analyses were less than criteria at 10 coefficient of variation (COV) for all samples except for one (37 replicate samples within COV of 10). These data indicate acceptable method performance.

Field Media Blank – Three media (field) blank samples (L/G-106, L/G-307, L/G-804, and L/G-914, one or more per three trips) were analyzed as field samples (blind QC sample). The blank data are summarized below:

<u>Sample ID.</u>	<u>CH4 (ppmv)</u>	<u>Tank (ppmv)</u>	<u>Trap (ppmv)</u>	<u>Total (ppmv)</u>
L/G-106	<2	<2	1.23	1.23
L/G-307	<2	<2	<1	<2
L/G-804	<2	0.66J	3.23	3.89
L/G-914	<2	<2	1.18	1.18

Methane was non-detect as was NMNEO compounds in the tank (volatile fraction) above the detection limits of 2 ppmv. The trap (condensable fraction) showed a NMNEO concentration of 1.18 ppmv, 1.23 ppmv, and 3.23 ppmv (MDL 1 ppmvC) with total blank levels of from non-detect to up to 3.89. The blank occurrence in the one trap sample is not uncommon and is less than two and

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three times the MDL for TNMNEO (2 ppmv MDL). These data are considered typical and no data flagging is recommended, however, these data were used in developing the QC criteria per field test. The QC criteria were used to correct the data; both uncorrected and corrected data were produced. These data indicate acceptable method performance.

Field Replicate Sample – All field samples were collected and analyzed in replicate. Summarized field data for key compounds are presented below. Typical precision for field replicate samples is less than 50 RPD.

<u>Sample ID.</u>	<u>CH4 (ppmv)</u>	<u>Tank (ppmv)</u>	<u>Trap (ppmv)</u>	<u>Total (ppmv)</u>
L/G-402	3,920	0.90J	3.67	4.57
L/G-403	7,645	2.05	4.97	7.02
<i>RPD</i>	<i>64</i>	<i>78</i>	<i>26</i>	<i>42</i>
L/G-702	2.36	1.18J	2.53	3.71
L/G-703	1.70	1.16J	2.80	3.96
<i>RPD</i>	<i>16</i>	<i>1.7</i>	<i>9.8</i>	<i>6.5</i>
L/G-904	13.1	<2	4.05	4.05
L/G-915	14.5	1.10J	6.25	7.35
<i>RPD</i>	<i>10</i>	<i>NA</i>	<i>43</i>	<i>57</i>

Three of 12 comparisons exceeded precision criteria. Precision, especially at the levels near the MDL in the region of less certainty is variable, and these data are typical for the method. These data indicate acceptable method precision and performance.

Performance Evaluation (PE) Samples – Two audit samples were submitted to the laboratory as blind QC samples in order to evaluate method precision. Two canisters were prepared and certified by a different laboratory containing varying amounts of a standard consisting of acetone (trap compound) and hexane (tank compound). The results of the analysis are given below expressed as methane as per the reporting unit:

<u>PE ID</u>	<u>Acetone (ppmvC)</u>	<u>Hexane (ppmvC)</u>	<u>Total (ppmvC)</u>
#1- STD.	65.1	129	194
Response	40	134	174
% Recovery	<i>61</i>	<i>104</i>	<i>90</i>
#2- STD.	35.5	70.3	106
Response	16.9	56.6	72.5
% Recovery	<i>48</i>	<i>81</i>	<i>68</i>

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The QC criteria for the TNMNEO or total response is $\pm 50\%$ of the standard. These data, although one tank response and one trap response exceeded criteria, both TNMNEO responses were within the accuracy criteria for the method. These data indicate acceptable method performance.

TO-15 Volatile Organic Compounds; GC/MS

Laboratory Control Spike Recovery Analysis and Duplicate – Nine 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 four compounds in one spike recovery sample. In addition, these nine control spike samples were analyzed in duplicate, and the relative percent difference (RPD) for the samples were within the QC criteria of ± 30 RPD for all compounds in all samples. These data represent acceptable method performance for the data set.

Laboratory Control Duplicate – Nine 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 exception of three compounds in one sample and two compounds in a second sample. With these exceptions, all other compounds were within criteria for all other QC samples. These data indicate acceptable method performance.

Laboratory Method Blank – Nine laboratory method blank samples were analyzed and the TO-15 study compounds ranging from 0.1 ml to 500 ml injection volumes. Several compounds were detected in many samples which is typical for the method, depending on the injection volumes used in the analysis. 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 – Four media blank samples (T15-106, T15-307, T15-804 and T-914) 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 only one compound, acetone in one sample (18.6 ug/m³), was detected above reporting limits. No other compounds were reported above method detection limits. The media blank data were included in developing QC criteria or data qualifiers that indicate system sensitivity and represent acceptable method performance.

Replicate Sample -- Four 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 T15-103/T15-104 had six compounds that were not replicated and 13 replicate pairs with a range of RPD of 3.3-to-71 and two of 13 pairs exceeding (criteria is 50 RPD). Sample T15-402/T15-403 had two compounds that were not replicated and 11 replicate pairs with a range of RPD of 3.1-to-78 and two of 11 pairs exceeding (criteria is 50 RPD). Sample T15-

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702/T15-703 had five compounds that were not replicated and five replicate pairs with a range of RPD of 39-to-150 and three of five pairs exceeding (criteria is 50 RPD). And finally, sample T15-904/T15-915 had six compounds that were not replicated and 10 replicate pairs with a range of RPD of 0-to-140 and four of 10 pairs exceeding (criteria is 50 RPD). These data indicate acceptable but poor precision. This is probably related to the types of compounds (i.e., oxygenated compounds) and levels of compounds in the samples since good laboratory precision was shown with the laboratory replicate analysis of spike samples. These observations do not limit data usage.

TO-14 Volatile Organic Compounds; GC/FID (note- same canister as TO-15)

Laboratory Control Spike Recovery Analysis and Duplicate – Nine laboratory control spike samples were analyzed using a standard containing five of the TO-14 study compounds. All compounds were reported for all spike samples within the QC criteria of 70%-to-130%. In addition, these nine control spike samples were analyzed in duplicate, and the relative percent difference (RPD) for the samples were within the QC criteria of ± 30 RPD for all compounds in all samples. These data represent acceptable method performance for the data set.

Laboratory Control Duplicate – Nine QC samples with five of the study compounds (around 80 ppbv level standard) were analyzed in duplicate. All data was found within the precision criteria of 30% recovery for the spiked compounds. These data indicate acceptable method performance.

Laboratory Method Blank – Nine laboratory method blank samples were analyzed and the TO-15 study compounds ranging from 10 ml to 200 ml injection volumes. Very few compounds were detected in the blank samples which is typical for the method given these injection volumes. 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 – Four media blank samples (T15-106, T15-307, T15-804 and T-915) were collected by filling sample containers with ultra high purity air and submitting the samples for analysis. A few compounds were detected above method detection limits (J flagged) but no compounds were detected above reporting limits. The media blank data were included in developing QC criteria or data qualifiers that indicate system sensitivity and represent acceptable method performance.

Replicate Sample -- Four 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 T15-103/T15-104 had over 20 compound pairs and many compounds that were not replicated, most of which grossly exceed criteria (criteria is 50 RPD). The total ion count had a RPD of 190 indicating that this sample and replicate pair indicated no precision. A sample mislabeling is possible. However, all TO-14 field precision data indicates unacceptable precision. Sample T15-402/T15-403 had 10 compounds that were not replicated and 10 replicate pairs with a

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range of RPD of 16-to-180 and nine of 10 pairs exceeding (criteria is 50 RPD). Sample T15-702/T15-703 had 12 compounds that were not replicated and five replicate pairs with a range of RPD of 47-to-130 and four of five pairs exceeding (criteria is 50 RPD). And finally, sample T15-904/T15-915 had nine compounds that were not replicated and three replicate pairs with a range of RPD of 110-to-150 and all three pairs exceeding (criteria is 50 RPD). These data indicate unacceptable precision. This is most likely related to the types of compounds (i.e., oxygenated compounds) and levels of compounds in the samples since good laboratory precision was shown with the laboratory replicate analysis of spike samples. These observations do not limit data usage, especially since the TO-14 were only used to: confirm the identification of alcohols, and generated a 'total hydrocarbon count' by a detector (flame ionization) that emulates carbon counting. As such, the total ion count was used to support the utilization of SCAQMD for quantitative ROG estimation. The TO-14 data were not used for quantitative emission estimate analysis.

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

Laboratory Control Spike Recovery Analysis and Duplicate – Five laboratory control spike samples were 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 with the exception of : p-tolualdehyde in one sample (57% recovery), and valeraldehyde in two samples (53% and 63% recovery). All duplicate analysis were within precision criteria (RPD 30). These data represent acceptable method performance for the data set.

Laboratory Control Duplicate – Fiver QC samples with 15 of the study compounds (around 0.3 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, valeraldehyde at 60% and 67% recovery, formaldehyde at 67% recovery, acetaldehyde at 67% recovery, and butyraldehyde at 67% recovery. In total, only 6 exceedances in 60 spike duplicate pairs exceeded criteria. These data indicate acceptable method performance.

Laboratory Method Blank – Five laboratory method blank samples were analyzed and four TO-11 study compounds were found above the reporting limits in one or more samples at low levels. The detection limits ranged from as 0.03-to-0.16 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 – Four media blank samples were collected by opening a sampling cartridge for TO-11, sealing the cartridge, and then submitting the samples for analysis. Acetone was found in two of the four samples above method detection limits, and these data were used to establish the QC criteria for acetone by this method. The criteria are field project specific. These data represent acceptable method performance.

Replicate Sample -- Four field replicate samples were collected for the flux testing program. The

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flux replicate sample was collected by sampling the chamber contents after the flux sample was collected. Sample T11-103/T11-104 had one compound that was not replicated and one replicate pair with a RPD of 88 exceeding (criteria is 50 RPD). Sample T11-402/T11-403 had no compounds that were not replicated and one replicate pair with a RPD of 56 exceeding (criteria is 50 RPD). Sample T11-702/T11-703 had two compounds that were not replicated and no replicate pairs. And finally, sample T11-904/T11-915 had no compound that were not replicated and one replicate pair with a RPD of 36, within criteria (criteria is 50 RPD). These data indicate poor but acceptable precision. This is probably related to the types of compounds (i.e., oxygenated compounds) and levels of compounds in the samples since good laboratory precision was shown with the laboratory replicate analysis of spike samples. These observations do not limit data usage.

TO-17 Volatile Fatty Acids; GC/MS

Laboratory Method Blank – Four laboratory method blank samples were analyzed and no volatile fatty acid study compounds were found above the method detection limits or the reporting limits in any samples. The detection limits were as low as 0.1 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 – Four media blank samples (T17-106, T17-307, T-804, and T17-914), were collected by submitting the samples for analysis. Detections were observed for acetic acid and isobutyric acids in one or more of the samples. The media blank data were included in developing QC criteria or data qualifiers that indicate system sensitivity and represent acceptable method performance. Analytical system carry over was suspected based on these and other data. Given the properties of VFAs, this was not unexpected. Data above the established QC criteria are believed to be unrelated to this problem.

Replicate Sample -- Four 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 T17-103/T17-104 had two compounds that were not replicated and two replicate pairs with a range of RPD of 52-to-130 and both of the pairs exceeded (criteria is 50 RPD). Sample T17-402/T17-403 had one replicate pair with a RPD of 170 exceeding (criteria is 50 RPD). Sample T17-702/T17-703 had one compound that was not replicated and two replicate pairs with a range of RPD of 84-to-100 both exceeding (criteria is 50 RPD). And finally, sample T17-904/T17-915 had one replicate pair with a RPD of 80 exceeding (criteria is 50 RPD). These data indicate poor precision with all compound replicate pairs exceeding criteria. This is probably related to the nature of VFAs and the wide range of observed concentrations. These observations do not limit data usage, however, given the variability in replicate sample data and the documented blank levels in method and field blank samples, data use above QC criteria is recommended.

Gas Phase Spike Recovery – An additional QC test was performed for VFAs in this phase of the

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research; gas phase spike recovery of VFAs from the sorbent media. A permeation tube VFA gas generator was built and tested in order to establish the recovery of VFAs from the flux chamber. This work is reported in a separate Technical Memorandum. As part of the VFA flux chamber recovery testing, the recovery efficiency of VFAs from carbopack sorbent media was determined. The results of the media recovery from gas phase standards is reported below. Back up data for this QC test is reported elsewhere.

SPIKE RECOVERY TEST	Acetic Acid (ppbv)	Acetic Acid % Recovery	Butyric Acid (ppbv)	Butyric Acid % Recovery
TO-17	1,378	143	NA	NA
TO-17	1,378	141	NA	NA
TO-17	1,378	91	NA	NA
TO-17	1,378	60	NA	NA
TO-17	1,378	68	NA	NA
TO-17	6,253	100	430	123
TO-17	6,253	71	430	73
AVERAGE		96		98

These data clearly demonstrate acceptable recovery of VFA standards from carbopack sorbent. It also provides for an explanation regarding the marginal performance of the method for assessing field blank and field recovery (precision). Since the analytical method and recovery of VFA gas standards is acceptable, it is likely that the field QC data (blanks and replicate analysis) show a matrix effect from the complex mixture of compounds found in gases emitted from unit processes at dairies.

TO-11 Volatile Fatty Acids; GC/HPLC-UV/VIS

Laboratory Method Blank – Four laboratory method blank samples were analyzed and no volatile fatty acid study compounds were found above the method detection limits or the reporting limits in any samples. The detection limits were as low as 9 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 – Three media blank samples (V-106, V-307, and V-804, same impinger sample as BAAQMD 29) were collected by filling sample impingers and then sample containers with impinger solution (distilled water) and submitting the samples for analysis. No compounds were detected above method detection limits except for acetic acid. The media blank data were included in developing QC criteria or data qualifiers that indicate system sensitivity and represent acceptable method performance.

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Replicate Sample -- Three 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 V-103/V-104 had one compound and replicate pair, and the RPD was 5.7 (QC criteria of 50 RPD). Sample VA-402/V-403 had no compounds detected as well as sample V-702/V-703. These data indicate acceptable precision and indicate acceptable method performance.

Gas Phase Spike Recovery -- Recovery of gas phase VFA standards from distilled water were also determined like the recovery of VFAs from carbopack solid sorbent. These data are presented below.

SPIKE RECOVERY TEST	Acetic Acid (ppbv)	Acetic Acid % Recovery	Butyric Acid (ppbv)	Butyric Acid % Recovery
HPLC	1,379	112	88	<MDL
HPLC	1,379	105	88	<MDL
HPLC	6,250	94	430	154
AVERAGE		104		154

These data demonstrate acceptable recovery for acetic acid and near criteria data for butyric (QC criteria ± 50 % recovery). HPLC data were used to confirm TO-17 VFA data and benchmark levels when an exceedance of calibration was observed for three TO-17 samples.

SCAQMD 2007.1 Ammonia/Amines; IC

Method Blank Analysis—Three method blank samples were performed for target species, and all samples showed non-detect for all samples. These data indicate acceptable method performance.

Laboratory Spike Recovery Analysis and Duplicate – Three laboratory spike sample were analyzed using a standard containing ammonia, methyl amine, and ethyl amine. These amines were reported within the QC criteria of 70%-to-130% for three spike samples except for one methyl amine sample (138% recovery) in exceedance of criteria. The RPD for the duplicate spike recovery samples was within criteria for all samples (criteria 25 RPD). These data represent acceptable method performance for the data set.

Laboratory Control Duplicate – Three QC samples with ammonia and method target amines were analyzed in duplicate. All data was found within the recovery criteria (± 30 % recovery) and precision criteria of 25 RPD. These data indicate acceptable method performance.

Laboratory Duplicate Analysis – Three laboratory analyses were analyzed using a standard for ammonia, methyl amine, and ethyl amine. These amines were reported within the QC criteria of RPD 25 for the duplicate analyses. These data represent acceptable method performance for the data set.

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Field Media Blank – Four media blank samples (A-106, A-307, A-804 and A-914) were collected by filling sample impingers and then sample containers with impinger solution (0.1 N hydrogen sulfide) and submitting the samples for analysis. No compounds were detected above method detection limits. The media blank data were included in developing QC criteria or data qualifiers that indicate system sensitivity and represent acceptable method performance.

Replicate Sample -- Four 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 A-103/A-104 had no compounds detected in the sample or the replicate sample.

Sample A-402/A-403 had three compounds that were not replicated and no replicate pairs. Sample A-702/A-703 had one compound pair with a range of RPD of 13 with none exceeding (criteria is 50 RPD). And finally, sample A-904/A-905 had one replicate pair with a RPD of 41 and no pairs exceeding (criteria is 50 RPD). These data indicate acceptable precision but poor repeatability in sample/replicate pair A-402/A403. These data indicate acceptable method performance.

BAAQMD Method 29 Methanol/Ethanol; GC/FID

Method Blank Analysis—One method blank sample was performed for target species and target species were not detected above method detection limits. These data indicate acceptable method performance.

Laboratory Spike Recovery Analysis and Duplicate – One laboratory spike sample was analyzed using a standard containing methanol and ethanol. The target species were reported within the QC criteria of 70%-to-130% for three spike samples. The RPD for the duplicate spike recovery samples was within criteria for all samples (criteria 30 RPD). These data represent acceptable method performance for the data set.

Laboratory Control Duplicate – One QC sample with target species was analyzed in duplicate. All data was found within the recovery criteria ($\pm 30\%$ recovery) and precision criteria of 30 RPD. These data indicate acceptable method performance.

Laboratory Duplicate Analysis – Three laboratory analyses were analyzed using a standard for ammonia, methyl amine, and ethyl amine. These amines were reported within the QC criteria of RPD 25 for the duplicate analyses. These data represent acceptable method performance for the data set.

Field Media Blank – Three media blank samples (V-106, V-307, and V-804) were collected by filling sample impingers and then sample containers with impinger solution (distilled water) and submitting the samples for analysis. Ethanol was detected in two of the three samples, and these

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data were used to develop the QC criteria. The QC criteria or data qualifiers indicate system sensitivity and represent acceptable method performance. Note that the Method 29 data were used to confirm the presence of alcohols and not for quantitative purposes.

Replicate Sample – Three 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 V-103/V-104 had one compound detected in the sample and the RPD for the replicate pair was 5.2 (criteria 50RPD). Sample V-402/V-403 had no compounds detected. And sample V-702/V-703 had one compound pair with a RPD of 33. All detected pairs were within QC criteria. These data indicate acceptable method performance.

TO-8 Phenols; GC/HPLC

Method Blank Analysis—Two method blank sample were performed for target species and target species were not detected above method detection limits. These data indicate acceptable method performance.

Laboratory Spike Recovery Analysis and Duplicate – One laboratory spike sample was analyzed using a standard containing methanol and ethanol. The target species were reported within the QC criteria of 70%-to-130% for three spike samples. The RPD for the duplicate spike recovery samples was within criteria for all samples (criteria 30 RPD). These data represent acceptable method performance for the data set.

Laboratory Control Duplicate – Three QC samples with target species were analyzed and all data was found within the recovery criteria ($\pm 30\%$ recovery). These data indicate acceptable method performance.

Laboratory Duplicate Analysis – One laboratory analysis was analyzed in duplicate, and the sample reported phenol within the QC criteria of RPD 25 for the duplicate analysis. These data represent acceptable method performance for the data set.

Field Media Blank – Three media blank samples (T8-106, T8-307, and T-804) were collected by filling sample impingers an then sample containers with impinger solution (0.1 N sodium hydroxide) and submitting the samples for analysis. Phenol was not detected in the field blank samples, and these data were used to develop the QC criteria. The QC criteria or data qualifiers indicate system sensitivity and represent acceptable method performance.

Replicate Sample – Three 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 T8-103/T8-104 had no compounds detected. Sample T8-402/T8-403 had one compound detected with no detection in the replicate. And sample T8-702/T8-703 had non

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compounds detected. Insufficient data are available for assessing precision. These data indicate acceptable method performance.

TO-13 Semi-Volatile Organic Compounds; GC/MS

Method Blank Analysis—Two method blank samples were performed for target species and target species were detected above method detection limits for three compounds, all below reporting limits. These data were used to develop the QC criteria data. These data indicate acceptable method performance.

Laboratory Spike Recovery Analysis and Duplicate – One laboratory spike sample was analyzed using a standard containing five SVOC compounds. The target species were reported within the QC criteria of 50%-to-150% for the five target compounds. The RPD for the duplicate spike recovery sample was within criteria for all compounds samples (criteria 30 RPD). These data represent acceptable method performance for the data set.

Laboratory Control Duplicate –. Like the spike recovery samples, the target species were reported within the QC criteria of 50%-to-150% for the duplicate spike sample. These data indicate acceptable method performance.

Field Media Blank – Three media blank samples (T13-106, T13-307, and T13-804) were collected by submitting the sorbent media cartridges as samples for analysis. Phthalate compounds were detected above method detection limits, as anticipated, and the levels of these compounds were used to develop the QC criteria. Data below the project specific QC criteria are considered to be related to media or laboratory method sources. QC corrected data are provided for data use. These data indicate acceptable method performance.

Replicate Sample – Three 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 T13-103/T13-104 had four compound replicate pairs, and the RPD values were within criteria at 5.7-to-30 (criteria 50RPD). Sample T13-402/T13-403 had one compound detected in the sample but not the replicate pair, and one compound and replicate pair with the RPD value of 5.4. And sample T13-702/T13-703 had no compounds detected. All detected pairs were within QC criteria. These data indicate acceptable method performance.

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IV. RESULTS AND DISCUSSIONS

Field sampling information and real time field data for the testing activities at the Merced dairy for the assessment program are reported in Table 1. QC data and QC criteria for all species are presented in Table 2. These QC criteria data are used to qualify all field data which are shown in Tables 3-9 for the Merced dairy. 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. Data found above the QC criteria are shown in corrected data tables and 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 ($\text{ug}/\text{m}^2, \text{min}^{-1}$).

Field data collected at the Merced dairy are reported by unit process (and not by analytical method as was done in Phase II). All compound flux data are reported in Tables 3 through 7 by unit process tested as follows. General field observations about these sources are noted.

Table 3- Flush Lane

Two locations in a flush lane were tested prior to lane flush; one location selected was thicker manure, the other location was a thin liquid manure layer area. These two locations represented the majority of the flush lane surface.

Table 4- Bunker Feed/Silage

Two random locations were selected and tested on feed in the bunker lane located in the barn. The feed had been in the bunker for at least two hours or longer, and was eaten down to about half the amount presented in the bunker. Two types of silage were tested in the silage storage area; summer corn silage and winter hay silage. Testing was performed by peeling back the plastic cover, digging a shelf in the feed pile about five feet off the ground, and testing on freshly uncovered and disturbed silage.

Table 5- Lagoon

The lagoon was tested at three locations accessed by a boom arrangement from the bank of the lagoon. The distance from the bank edge to the test location was approximately six feet in all cases (avoiding lagoon edge effects). The lagoon was tested at the inlet end, the middle, and the outlet end of the lagoon at about six feet from the bank. Fine bubble aeration was noticed in all test areas as related to microbial action.

Table 6- Turnout (milk cow)

A turnout was tested at six locations, all of which were selected scientifically and not randomly. The goal was to determine the range of emissions as a function of type of surface in the turnout. The test areas included: thick, wet manure in a 'social area'; fresh urine area on dry manure; fresh manure

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(freshly disturbed manure that was about one hour old); turnout representative dry manure about 6" thick; representative dry manure about 4"-to-6" thick; and representative dry manure about 1" thick that was a common traffic area or path of travel. Most of the surface area in the turnout was dry manure from 1"-to-6" thick. Note that the first rainfall even of the season occurred three days prior to testing. It is likely that the added moisture had an effect on air emissions from the turnout. It is likely that ammonia emissions were significantly affected, however this was not quantified. Note that at this dairy, the manure is removed annually, and the manure in this turnout represents the accumulation for the year. Manure removal was performed after this testing event.

Table 7- Separator Solids Pile

Four areas in the separator solids storage pile were tested (two locations on the top of pile, one location at the mid-height of pile, and one location at the foot of pile) and screened using the real time instruments. The two locations with the highest air emissions were tested using sample collection and off site analysis. The top of the pile test location and middle-height of the pile test locations were sampled for off site analysis.

And finally, data from each of the unit process tables (Tables 3 through 7) were averaged per compound and reported by unit process in Table 8 for all compounds, and in Table 9 for all detected compounds. Data in Tables 8 and 9 are average flux data per unit process. Method detection limits were not used in the generation of average flux per unit process; a non-detect cell is ignored in the software program. Average data per compounds detected found in Tables 8 and 9 can be used to represent emissions from these unit treatment processes.

Field sampling information and real time field data for all testing activities at the Merced dairy are reported in Table 10. QC data and QC criteria for all species are presented in Table 11. These QC criteria data are used to qualify all field data which are shown in Tables 12-15 for the Kings County dairy. 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. Data found above the QC criteria are shown in corrected data tables and 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).

Field data collected at the Kings County dairy are reported by unit process like the Merced dairy data. All compound flux data are reported in Tables 12 through 15 by unit process tested as follows. General field observations about these sources are noted.

Table 12- Turnout (milk cow)

Six test locations were randomly selected along a transect across two turnouts for testing; one turnout was a scrapped turnout with little manure, the other was a harrowed turnout with some manure. The random locations were determined by dividing the turnout into three equal size blocks,

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and testing the center of each block. The random sample locations were intended to generate representative average emissions data for the turnout source. Two locations were also tested (random selection) in a turnout that had not recently been scrapped or harrowed. Note that the turnout management practice at this dairy was different than that used at the Merced dairy. The Kings County dairy scraped and removed manure about once every 7 to 10 days, and harrows the turnouts. There was very little manure in these turnouts.

Table 13- Flush Lane

One location in the barn flush lane was tested prior to and during the lane flush. Flushing occurred during the end of the test and flush water entered and cycled through the flux chamber. These data could be used to represent the flush as it enters the flush lane effluent treatment system.

Table 14- Bunker Feed/Silage

One random location was selected and tested on feed in the barn bunker. The feed had been delivered to the bunker just prior to testing. Corn silage was tested in the silage storage area. Testing was performed by peeling back the plastic cover, digging a shelf in the feed pile about five feet off the ground, and testing on freshly uncovered and disturbed silage.

Table 15- Lagoon

The flush lane effluent treatment system was tested at three locations accessed by a boom arrangement from the bank. The distance from the bank edge to the test location was approximately six feet in all cases (avoiding lagoon edge effects). The system was tested at the solids separator vault (freshly filled and vigorously mixed), the settling pond (2"-to-3" scum layer), and the storage lagoon (mixed and aerated) at about six feet from the bank. Fine bubble aeration was noticed in the settling pond and the storage lagoon as related to microbial activity.

And finally, data from each of the unit process tables (Tables 12 through 15) were averaged per compound and reported by unit process in Table 16 for all compounds, and in Table 17 for all detected compounds. Data in Tables 16 and 17 are average flux data per unit process. Method detection limits were not used in the generation of average flux per unit process; a non-detect value is ignored in the software program. Average data per compound found in Tables 16 and 17 can be used to represent emissions from these unit treatment processes.

Field sampling information and real time field data for all testing activities related to the 24-hour variability study (diurnal variability) that was conducted at the Merced dairy are reported in Table 18. QC data and QC criteria for all species are presented in Table 19. These QC criteria data are used to qualify all field data which are shown in Table 19. 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. Data found above the QC criteria are shown in corrected data tables and are taken to be related to the area source tested

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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). And finally, data from the 24-hour study were averaged per compound and reported in Table 21 for all compounds, and in Table 22 for all detected compounds. Method detection limits were not used in the generation of average flux per unit process; a non-detect value is ignored in the software program. Average data per compound found in Tables 21 and 22 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 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 [m³/min]), the species concentration Yi (micrograms per cubic meter [mg/m³]), and exposure to the chamber surface area (square meters [m²]), as follows:

$$F_i = \frac{(Q)(Y_i)}{(A)}$$

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 data columns labeled 'QC Corrected' data. Note that both corrected and uncorrected data are presented for data use on the unit process data tables and the corrected data are summarized and presented on the unit process summary tables (Tables 8 and 9, Tables 16 and 17, and Tables 21 and 22). Field data below these QC 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 occasional poor field precision which, is unfortunately and commonly observed at the low levels of detection achieved with the analytical method.

One goal of the Phase III program was to collect data by various analytical methods and establish a total hydrocarbon ROG emission flux from the unit treatment processes and total hydrocarbon emissions per cow per year. SCAQMD Method 25.3 was used for this purpose (25.3 ROG) and, by design, the method captures all hydrocarbon compounds (condensable and non-condensable hydrocarbon compounds). Hydrocarbon compounds are collected, analyzed, and reported as methane. This is because the method reduces all hydrocarbons to carbon but detected as methane. By design, this is the best method for a total hydrocarbon count, but it does not represent the

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individual compounds that generated the total count. The representation (carbon atoms per molecule) and reporting/use of these data (mass of total carbon detected) are needed in order to properly represent these data. Total hydrocarbon emissions by SCAQMD Method 25.3 should be adjusted to photo-chemically active compounds by subtracting the exempt compounds expressed as methane from the reported total. Exempt compounds are identified in the data tables, and exempt compounds identified by EPA Method TO-15 are recommended for this purpose. Note that a provision for this has been made as indicated in the data spread sheets; these data sheets were formatted as direct input for the emissions report. As such, these cells are left blank for future use.

Other ways to approach the total hydrocarbon ROG emission flux is to sum various other methods constructing a total hydrocarbon emissions estimate. This can be accomplished by taking the non-exempt compounds identified by EPA Method TO-15 on a molar basis, and adding to this summation non-exempt compounds identified by the numerous other methods. This TO-15 based total can be used and reported like the 25.3 ROG total. Likewise, the same can be done with the TO-14 data. But in this case, the detector reports a total detector count that can be used in place of a summation of the individual compounds on a molar basis. A TO-14 based total can likewise be used and reported like the 25.3 ROG total.

Several key groups of compounds were studied by using concurrent sample collection and analytical methods, in particular: VFAs- EPA Method TO-17 and EAS HPLC Method; alcohols- EPA Method TO-15, EPA Method TO-14, and BAAQMD Method 29; acetone- EPA Method TO-11, EPA Method TO-15, EPA Method TO-14; phenols- EPA Method TO-8, EPA Method TO-13, carbon disulfide- EPA Method TO-14 (GC/FPD), EPA Method TO-14, and other compounds detected by both EPA Method TO-15 and EPA Method TO-14. For most comparisons by multiple analytical methods, the second or third method supported or confirmed the detection of a selected compound that was quantified by the preferred method. In all most all cases, positive compound identification by GC/MS is preferred over other GC methods. For VFAs, USEPA Method TO-17 was the preferred method given that the method is positive identification by GC/MS, and the method has been modified specifically for this family of compounds. Alcohols are similar in that the detection and quantitation by EPA Method TO-15 (GC/MS) is valued over TO-14 and even the specific alcohol method, since the BAAQMD method is subject to interference by other, similar oxygen containing compounds (note- dairy emissions are dominated by oxygenated compounds). Decisions regarding data use are identified in the data tables. For instance, the subtraction of exempt compounds from the 25.3 ROG total relies on EPA Method TO-15 for all exempt compounds, even acetone, where other credible methods were used. One instance occurred where very high levels of VFAs were observed from the bunker feed and silage samples at the Kings County Dairy. VFAs were found in gross exceedance of the method calibration and know to be overestimated. Concurrent HPLC VFA data collected for the source was used to normalize the TO-17 VFA data since the reported data for the HPLC analysis was within method calibration for the HPLC method. This type of data correction is common in situations where a few samples are grossly higher than

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other samples, which was the case for VFAs at this source. In summary, confirmatory analysis showed the presence of key compounds like VFAs, alcohols, ketones, and phenols supporting the presence and relative abundance of these compounds as part of the dairy emissions. Given that total hydrocarbon emissions were appropriately determined by the 25.3 ROG total emissions measurement, the speciation data have only two uses since all compounds with carbon atoms (VFAs, alcohol compounds, aldehyde compounds, ketone compounds, aliphatic compounds, aromatic compounds, reduced sulfur compounds, SVOCs, and amine compounds) are quantified as carbon by SCAQMD 25.3: 1) identify the types of compounds counted in the total and calculate a ‘percent of total’ for compounds or types of compounds; and 2) identify exempt compounds that can be subtracted from the 25.3 ROG total allowing for an estimate of ROG.

One ambient air sample (T17-309) was collected in the turnout at the Merced dairy for VFAs by USEPA Method TO-17. The purpose of this sample was to support the investigation as to whether or not VFAs were being lost in the flux chamber during the sample collection event. If VFAs were detected in an ambient air sample collected a few inches above the manure in a turnout and not detected in the chamber, then chamber loss could be demonstrated. Likewise, if VFAs were detected in both the ambient air sample and the chamber, then recovery data from the chamber would be verified (note- validation only happens when a known amount is added as in the validation study). This sample showed moderate-to-low levels of acetic acid at 144 ug/m³ (MDL 11 ug.m³) demonstrating that low levels of acetic acid as expected from manure in turnouts. Given that VFA recovery from the flux chamber was demonstrated (see VFA recovery Technical Memorandum), and VFAs were quantified from several sources at dairies at expected levels and high levels in feed/silage sources, these data provide confirmation or parallel evidence as to the efficacy of using these analytical sampling methodologies to quantify VFA and other hydrocarbon compound emissions.

Ethanol was measured quantitatively by EPA Method TO-15 and EPA Method TO-14. As mentioned earlier, the TO-15 data were recommended as the preferred method for ethanol reporting, however, it should be noted that in three cases, ethanol was reported at higher levels by TO-14 as compared to the data from TO-15. Those samples are: T15-204, T15-305, and T15-801. Although this does not effect the ROG emissions, data users may wish to evaluate both the TO-14 and TO-15 data sets when assessing speciated data sets, especially for ethanol.

Variability in the data set has been considered in Section III- Quality Control; analytical variability, sample collection variability/source variability is described fully in the discussion of the precision of laboratory replicate samples and the precision of field replicate samples. Generally, most methods met the quality control specifications of $\pm 50\%$ precision and $\pm 50\%$ accuracy, and a general ‘uncertainty’ of $\pm 50\%$ can generally be applied to the data set. Method-specific precision can be used for each analytical method employed if desired. However, an uncertainty analysis has not been performed on these data. One reason for this is that the

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program was not designed with this purpose in mind, but rather to generate a representative data set for a wide range of study compounds intended to define the range of potential emissions from key sources found at dairies. There were limited data sets collected, however, that lend themselves to statistical analysis. These are listed below.

24-Hour Turnout Study (Merced Dairy- one location)

COMPOUNDS	Average (ug/m2,min-1)	Std Deviation	Relative Percent Diff
25.3 Total ROG (CH4)	150	45	30
EPA TO-14 Total	8.3	5.1	60
EPA TO-15 Total	5.8	5.8	100
SCAQMD 207.1 (NH3)	720	580	81
TO-17 Acetic Acid	6.3	6.3	100

Merced Dairy Turnout Study (Six locations)

COMPOUNDS	Average (ug/m2,min-1)	Std Deviation	Relative Percent Diff
25.3 Total ROG (CH4)	140	37	26
EPA TO-14 Total	12	2.4	20
EPA TO-15 Total	14	5.7	41
SCAQMD 207.1 (NH3)	170	N/A	N/A
TO-17 Acetic Acid	7.5	8.9	120

Kings County Dairy Turnout Study (Nine locations)

COMPOUNDS	Average (ug/m2,min-1)	Std Deviation	Relative Percent Diff
25.3 Total ROG (CH4)	120	31	26
EPA TO-14 Total	12	5.5	46
EPA TO-15 Total	4.3	2.7	63
SCAQMD 207.1 (NH3)	470	319	68
TO-17 Acetic Acid	22	13	81

A subset of key compound/criteria average data for three data sets are presented along with the respective standard deviation and relative percent difference information. All data represent flux from turnouts, and a comparison of average flux per compound/criteria and deviation provides information regarding data set uncertainty. Higher uncertainty is observed for the VFA compounds (acetic acid) and ammonia, where lower uncertainty is observed for total ROG by SCAQMD Method 25.3. The flux of hydrocarbon compounds as determined by the summation of compounds by Methods TO-15 and TO-14 indicates similar or lower variability as compared to VFAs, but higher variability as compared to total ROG by SCAQMD 25.3. Considering the differences in the sample design of these data sets (diurnal variability study versus area source

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assessment using scientific data collection at the Merced Dairy and random data collection at the Kings County Dairy) and the differences in turnout management between the dairies (annual manure removal at the Merced Dairy and routine and frequent manure removal at the Kings County Dairy), these data indicate that average data generated in this study are representative of the emission sources and data variability generally met the QC specifications given in the QAPP. An analysis of variability in the data provides an insight into the uncertainty of the results of the investigation.

One anomaly that was discovered in the data set had to do with ROG as determined by SCAQMD Method 25.3. Total non-methane non-ethane organic carbon in the trap fraction is determined by testing for total carbon, inorganic carbon, and then calculating organic carbon. If inorganic carbon is introduced into the sample collection or analytical system at comparable levels, organic carbon in the trap will not be detected. Apparently this happened for one turnout sample (Merced Dairy sample G-304) where ROG was reported as non-detect, yet moderately high levels of other hydrocarbons were detected. This isolated incidence does not significantly affect the data set since the other multiple data points (five) were averaged to represent turnout emissions from the Merced dairy. It is difficult to keep all particulate matter away from sampling equipment, especially in an environment such as a turnout location. A very small amount of particulate matter containing inorganic carbon (elemental carbon or a carbonate compound) in a trap sample can easily account for the gas phase organic carbon emitted from a turnout test location.

Research scientists from the University of California, Fresno collected solid samples from the Merced dairy turnout (12 samples) and the Kings County dairy (13 samples) for percent moisture content analysis. The results of this effort are reported in Attachment C.

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V. SUMMARY

Surface flux measurements were made at multiple locations on a total of six unit process at a two Northern California dairies in order to assess dairy emission flux of ROG, 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 two study dairies 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 and inorganic compounds.
- Laboratory and field quality control data indicated acceptable sampling method performance. Poor precision for field replicate samples was observed for measurements near method detection limits, however, this is common for low level samples. Data above the reporting limits are indicated 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).
- Field data were collected for selected unit process at two Northern California dairies with the intent of providing data on compound emission flux and developing improved emission estimates for unit process and per cow annual emission estimates. The data collected and reported herein can be used for this purpose. Data tables have been prepared for use in developing the improved unit process emission estimates and the annual per cow emissions. The emission estimate data are reported in a separate document.
- An emphasis was placed on assessing VFAs and alcohols, as well as other less commonly identified compounds. The extensive analytical work demonstrated the presence of VFAs, alcohols, and other compounds such as reduced sulfur compounds (from some sources), carbonyl compounds, and phenolic compounds on occasion. The speciation data can be used to illustrate the relative importance of these different classes of compounds as part of the total dairy emissions. The speciation data such as VFAs, amines, sulfur compounds, oxygenated compounds, etc. provide useful information related to understanding dairy emissions, however, total quantitation of ROG is best realized by the SCAQMD Method 25.3 with the total count adjusted for exempt compounds.
- A demonstration was performed for VFAs, reported under separate cover, that showed that the analytical methods used on the project were suitable for the quantitation of VFAs, and that an acceptable recovery efficiency was achieved from the flux chamber.

- The 24-hour diurnal variability study generated useful data related to understanding how compound emissions vary over a daily cycle. These data showed significant variability in flux and a cyclic emissions pattern for ammonia as was reported in prior ammonia emission studies. Ammonia emissions will be normalized for ‘time of day’ as part of the emission estimate development work. However, the lack of time-dependency in the hydrocarbon emissions data set suggests that the normalization of ROG data is not warranted.
- A review of the analytical methods used in the Phase III suggests that hydrocarbon species assessment at this level of detail (10 methods) is not necessary for future dairy emissions assessment programs. As always, specific analytical methods are required for the assessment specific compounds or classes of compounds of interest. But for total ROG, this work suggests that a total hydrocarbon method such as SCAQMD 25.3, combined with EPA Method TO-15 for the removal of carbon derived from exempt species, provides for both a comprehensive and cost-effective assessment of photochemical ROG. The assessment of amines, other than ammonia, is not needed since carbon from amines is counted by Method 25.3. Likewise, carbon from non-exempt compounds such as reduced sulfur species, VFAs, SVOCs, and carbonyl compounds along with all condensable and non-condensable hydrocarbon compounds, are counted by Method 25.3. As such, future work related to assessing differences in dairy emissions (dairy-to-dairy variability), improvement in ROG emission flux, seasonal differences (seasonal variability), variability related to spatial differences in area sources, differences in dairy operation effecting ROG emissions, and dairy emission as a function of feed type and feed handling can be achieved with a more focused list of analytical methods.
- The two dairies tested proved to be very different dairy operations. The Merced dairy used an annual turnout manure removal schedule where the Kings County dairy removed manure and conditioned turnouts on a weekly schedule. Bedding material was produced differently at each dairy. The Merced dairy stockpiled separator solids at different locations, then returned the aged solids to unscrapped turnouts for drying. The Kings County dairy avoided separator solids piles and dried solids for bedding directly in scrapped turnouts. The treatment and storage lagoon at Merced is one large, mixed lagoon operated essentially on an annual ‘use’ schedule, and the Kings County dairy lagoon system consists of three parts, each of which is designed for different treatment goals. And finally, the silage production, management, and dietary schedules at the two dairies are very different. Differences in unit flux data from these two dairy sources are a function of these design and process differences. Variability in dairy emissions is dominated by these design and operational differences. Seasonal variability has not been investigated, however, seasonal differences are also expected to be significant.

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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