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TECHNICAL MEMORANDUM

Results of the Dairy Emissions Evaluation Using Flux Chambers
Phase III Volatile Fatty Acids (VFAs) Verification and Validation Tasks

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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 emissions data for use in improving emission estimates required for State Implementation Plans (SIPs) and Senate Bill 700 (SB700).

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 in 2005 at two Northern California dairies.

Volatile fatty acids (VFAs) are a class of compounds known to exist at dairies. In support of the research, Phase III work included method verification and flux chamber technique validation of VFA recovery or assessment capabilities for volatile fatty acids. To accomplish this task, a laboratory verification, method detection limit study, and flux chamber validation study were conducted during Phase III.

VFA verification testing and validation testing was performed demonstrating the efficacy of using the flux chamber to assess surface emissions of VFAs. The verification testing demonstrated the functionality of the technologies, and 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.

As part of the method development work, EAS labs conducted a method detection limit study in order to establish the empirically determined detection limit for the selected VFA analytical methodologies. As per EPA protocol, low level standards were introduced into the GC/MS instrument multiple times (7). The method detection limit is determined by taking three times the standard deviation value from the multiple test analysis of the low-level standard and adding this value to the baseline signal from the instrument for the target compounds. The detection limits were determined uniquely for the target species as given below, and ranged from 5 to 10 ppbv as anticipated.

VOLATILE FATTY ACID	MDL (ppbv)
Acetic acid	6.9
Propionic Acid	5.3
Isobutyric Acid	7.2
Butyric Acid	7.3

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Isovaleric Acid	9.6
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These detection limits were more than sufficient for the field testing effort given that the flux chamber technology is a source assessment technology at levels higher than ambient air levels of VFAs. A report from EAS laboratory documenting this procedure and all analytical data is provided in Attachment B.

The analytical Method TO-17 verification of VFA testing was a demonstration of the recovery of VFA compounds from the carbopack sorbent material from both primary liquid standards and gas standards generated from by the permeation generator. Percent recovery data are provided below demonstrating acceptable spike recovery of target compounds.

VOLATILE FATTY ACID LIQUID PRIMARY STD.	AVERAGE % RECOVERY
Acetic acid	108
Propionic Acid	86
Isobutyric Acid	110
Butyric Acid	80
Isovaleric Acid	110

VOLATILE FATTY ACID PERMEATION GAS STD	AVERAGE % RECOVERY
Acetic acid (30 Deg C)	102
Acetic Acid (50 Deg C)	88
Butyric Acid (50 Deg C)	117

These data demonstrate that sorbent media (carbopack solid sorbent) can be spiked in the laboratory and efficiently transferred from the media to the GC/MS as per the analytical method requirements. These QC data provide for the qualification of analytical method accuracy (not related to the flux chamber) or, simply said, validate the performance of the analytical method by using primary standards.

The VFA verification task was conducted prior to the field testing program, and the purpose of the testing was to: demonstrate the effectiveness of using the USEPA flux chamber to assess VFA emission in the field; demonstrate proficiency of laboratory methods prior to field testing; and to collect empirical data on the correlation between liquid dairy sources containing VFAs (such as lagoon unit processes) and measured VFA flux. Three liquid solutions were prepared in the laboratory with target levels of VFAs determined by Henry's Law Constant literature data

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which describes the volatilization potential of compounds from liquid solutions. Liquid solutions were sampled and analyzed confirming the stock solution concentrations, and flux chamber testing was conducted on the test solutions following the standard testing protocols. Replicate samples were collected from the flux chamber and from an 8' Teflon line (or longer), and both USEPA Method TO-17 and EAS/HPLC methods were used (emphasis on TO-17). In addition, a limited amount of SCAQMD Method 25.3 testing was conducted in order to assess total hydrocarbon emissions from the test solutions. The results showed no VFA flux by TO-17 and low and variable total hydrocarbon flux from the test solutions. A comparison of field data from the 2005 Merced and Kings County dairy testing to these data indicated that higher concentrations of VFAs in the stock solutions are necessary in order to generate measurable levels of VFAs, even with MDL values of between 5-to-10 ppbv in the flux chamber. This is explained by the affinity that VFAs have in aqueous solutions to water (hydrogen bonding). The VFA verification testing did, however, accomplish the task goals: the VFA analytical methods and sample collection proficiency was demonstrated prior to the field test; and the VFA flux level from sources of known VFA content was 'bench-marked' supporting data from other studies that indicated low VFA flux from dairy sources. Note that the literature values regarding VFA flux from liquid solutions can be updated using these data; the literature values are based on theoretical behavior and not empirical data.

The final testing that was conducted in support of the efficacy of using the USEPA flux chamber technique for assessing VFAs from dairy sources was the VFA flux chamber recovery study. This was accomplished by designing, building, testing, and calibrating a VFA gas generator. A VFA gas generator calibrated to fixed operating conditions, was necessary for this task given that primary gas standards of VFAs are not available. As such, EAS labs constructed and tested a permeation tube device and documented the VFA gas stream generation under operating conditions for project purposes (i.e., target species concentrations). The goal was to generate three different concentrations of VFA standards (50 ppbv, 150 ppbv, and 300 ppbv) for acetic acid, propionic acid, and butyric acid at a fixed flow rate of about 200 ml/minute. This research is document in a separate report that is included as Attachment D. This task was made more difficult given that in order to conduct the flux chamber recovery study as described in the QAPP, the flowrate of the VFA generator needed to be fixed (approximately 200 ml/minute) keeping the characteristics of the artificial 'VFA source' constant for all recovery measurements. Given these demands on the VFA source, a compromise was made so that acetic acid levels would be preserved and the other acid source levels would vary or deviate from the target levels. Acetic acid is the dominant VFA at dairies, and this decision provided for recovery data reflecting the project needs. As such, some data was lost for the other target acids. Said another way, with VFA generator conditions optimized for acetic acid, we could not, during the same test, generate the levels of propionic acid and butyric acid in all test cases that would meet our sampling requirements. If you cannot measure an inlet VFA concentration at levels that meet the method detection limits of the test, given that the ratio of flux chamber sweep air gas to VFA

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generator flow rate is about 26, then the recovery test will not result in levels that are measurable in the flux chamber thus limiting the assessment of VFA recovery assessment.

Recovery testing was performed by introducing a known concentration of VFAs into the flux chamber at a low and controlled flowrate (200 ml/minute), conducting a flux chamber test as per protocol (equilibrating for five residence times), and collecting replicate VFA samples directly from the chamber, and from a purged 8' Teflon line. Sample collection on the test surface (Teflon sheet with inlet ports connected to the VFA generator) was performed exactly as samples are collected in the field. Testing was conducted on the inlet stream using both the EAS/HPLC method, which is better for high concentration gas streams, and TO-17. Flux chamber and 8' line testing was conducted with replicate the TO-17 method. All testing was conducted in replicate, each target concentration was tested twice with complete repeat testing efforts, and each repeat test was 'bracketed' before and after testing by measuring VFA source flowrates and VFA source concentration. Target concentration of VFAs was 50 ppbv, 150 ppbv, and 300 ppbv. The focus was on determining recovery efficiencies at the low end of the VFA flux range from dairy sources (e.g., turnouts and flushed lanes) rather than the expected higher sources (bunker feed and silage).

The results of the VFA recovery testing indicated that the flux chamber was capable of assessing VFA emissions from dairy sources. Variable recoveries were observed, especially for propionic acid and butyric acid, however this was related to generating and maintaining a standard source from the VFA generator under conditions that were optimized for acetic acid, the key VFA compound of concern. Essentially, in order to provide data for all three acids for the three target concentrations as was the goal, a permeation tube generator would have to be designed, constructed, and used for each acid, and testing would have to be repeated for each acid separately rather than conducting the test for the 'mixture' of VFAs of interest.

The recoveries were calculated in several ways, given that two methods were intentionally used for assessing the VFA inlet concentrations whereas one method, TO-17 was the preferred field test method. The EAS/HPLC is better suited for assessing higher level VFA levels from the inlet gas stream as compared to the TO-17 method, and, as such, the most representative chamber recovery data came by data where the VFA generator inlet stream into the chamber was measured with the EAS/HPLC method. Some baseline adjustment was required for the TO-17 as blank levels on occasion (e.g., 50 ppbv target levels) were above detection. The results showed that the recovery of acetic acid over the target concentrations ranged from 98% to 171% in the chamber (direct sample collection from the chamber), and 82% to 94% from the 8' Teflon line (QC criteria $\pm 50\%$ recovery). These data show acceptable recoveries from the chamber and also from the 8' Teflon sample line. Note that recoveries greater than 100% can be a result of: a distribution of analytical response around a number (i.e., analytical method accuracy $\pm 30\%$ around a true value); an error in either assessing the VFA inlet gas stream concentrations or the

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VFA inlet gas flowrate; or generating an insufficient and unreliable source stream of VFAs for the test. Discussions with the lab director have indicated that the major source for these high, positive response recovery values is related to the limitations of the VFA generator.

Recoveries of propionic acid and butyric acid showed similar but more variable response, most of which is related to the generation of VFAs and not 'loss' or variability in the recovery test. Propionic acid showed a chamber recovery range over the three tests of 58% to 90%, and a 24% to 63% recovery range from the 8' line. These data suggest some line loss, which might be the case for heavier or more reactive acids. Note that all TO-17 VFA samples for the 2005 dairy testing were collected directly from the flux chamber and not the 8' sample line. Similar but more variable recoveries were observed for butyric acid. The range of butyric acid from the chamber was 73% to 406%, and 105% to 551%. Clearly, some of these data are affected by the demands placed on the VFA generator.

In summary, the VFA validation study demonstrated that VFAs can be assessed in the field by using the USEPA flux chamber and EPA Method TO-17. Some line loss is possible, given these data, and VFA samples should be taken from the chamber when possible in order to avoid this potential problem. Given the low level range TO-17 attainable by this method and the species positive identification by GC/MS, the TO-17 analytical method is well suited for low level source assessment at dairies. Likewise, the EAS/HPLC method is preferred for higher level sources. Establishing the VFA recovery from the flux chamber demonstrates the efficacy of using this area source for assessing VFAs from area sources found at dairies.

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I. INTRODUCTION

This technical memorandum describes the laboratory testing that was conducted in order to assess the efficacy of using the USEPA surface mission isolation flux chamber and various analytical methods, to assess VFA emissions from unit process at Northern California dairies. Laboratory testing was conducted by Dr. Steve Hoyt with Environmental Analytical Services (EAS), Dr. C.E. Schmidt, and Mr. Harold Litwiler on September 22, 2005 (verification test), and on December 20 through 23, 2005 (validation test) at the EAS laboratory facility located in San Luis Obispo, California.

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

VFA verification and validation testing was conducted using the USEPA surface emission isolation flux chamber. The flux chamber measures the flux of study compounds from a given source in either the laboratory or the field. 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 at the test surface in the laboratory. Lab test conditions were identified and recorded in a notebook.
3. The lab test information, equipment information, date, and proposed time of testing were documented on the Emissions Measurement Field Data Sheet.
4. The experimental test surface was generated in order to simulate field conditions. Test surfaces included vats of aqueous solutions containing VFAs, and a Teflon working surface equip with multiple tube inlet ports. Note that the VFA inlet gas stream was samples before and after each flux test in order to establish the source of VFAs introduced into the flux 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. Flow rates of the sweep air and inlet gas stream (VFA generator) were measured using a primary gas standard (Altech Digital Flow meter for VFA inlet stream assessment and a DC Lite primary standard for sweep air flowrate assessment.)
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/task Program Instructions to the purged, sample line and collecting the sample media as appropriate. Sample collection was conducted in replicate from both the flux chamber and from the 8' Teflon line. Sample collection was performed using the same protocol as was used in the field.
8. After sample collection, all field data were documented on the data sheet.

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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. Laboratory testing was recorded on the field data sheet. The equipment was then prepared for the next verification or validation test, and steps 1) through 9) were repeated.

A total of up to three 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)
In-Depth	USEPA Method TO-17 (GC/MS)	Volatile Fatty Acids	0.1 ug/sample; 36.7 ug/m ³ (5-to-10 ppbv)
In-Depth	EAS HPLC-UV/VIS Method	Volatile Organic Acids	10 ug/sample; 290 ug/m ³ (63-to-230 ppbv)
In-Depth	SCAQMD 25.3 (GC/FID)	Total Hydrocarbons	1.3 mg/m ³ Total (2 ppmv)

* 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
 HPLC = High performance liquid chromatography
 UV-VIS = Ultraviolet-Visible Absorption Spectrophotometer
 MS = Mass spectrometry
 EAS- Environmental Analytical Services

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

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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.

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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 within method specifications with the exception of variable precision; these data generally indicate acceptable method performance.

Laboratory Duplicate Sample Analysis- All samples were analyzed in duplicate, and these data show variable method precision with methane (tank) and NMNEO from the trap less than 20% area count difference and 30% difference from the mean; 4 of 7 samples exceed criteria. The coefficient of variation for replicate trap analyses were less than criteria at 10 coefficient of variation (COV) for all samples. These data indicate variable 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>
HH-C-25.3	3.62	<2	1.86	3.79
HH-C-25.3-R	2.75	<2	1.59	2.95
<i>RPD</i>	<i>27</i>	<i>NA</i>	<i>16</i>	<i>25</i>

These data indicate acceptable method precision and performance.

Performance Evaluation (PE) Samples – Two audit samples were submitted to the laboratory during the field testing 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

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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	61	104	90
#2- STD.	35.5	70.3	106
Response	16.9	56.6	72.5
% Recovery	48	81	68

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 with the accuracy criteria for the method. These data indicate acceptable method performance.

TO-17 Volatile Fatty Acids; GC/MS

Laboratory Method Blank – Six laboratory method blank samples were analyzed and various levels of VFAs were found above the method detection limits or the reporting limits these samples. The data were reported in data tables and use to correct test data as appropriate.\

Replicate Sample – All test samples were collected in duplicate or triplicate. Outliers were eliminated by the laboratory and average data were reported in the data sheets. Method precision was typically within QC criteria (criteria is 50 RPD), however since average data were used for project purposes, limited precision in the cases of exceedances was reported and used for the various studies. The variability is, in part, the data quest for these verification and validation studies.

Liquid and Gas Phase Spike Recovery – An additional QC test was performed for VFAs in this phase of the research; liquid and gas phase spike recovery of VFAs from the sorbent media. Liquid standards were spike on sorbent media, and 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 liquid phase and gas phase standards is reported below.

VOLATILE FATTY ACID PERMEATION GAS STD	AVERAGE % RECOVERY
Acetic acid (30 Deg C)	102
Acetic Acid (50 Deg C)	88
Butyric Acid (50 Deg C)	117

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VOLATILE FATTY ACID PERMEATION GAS STD	AVERAGE % RECOVERY
Acetic acid (30 Deg C)	102
Acetic Acid (50 Deg C)	88
Butyric Acid (50 Deg C)	117

These data clearly demonstrate acceptable recovery of VFA standards from carboxpack 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 – Eight laboratory method blank samples were analyzed and various levels of VFAs were found above the method detection limits or the reporting limits these samples. The data were reported in data tables and use to correct test data as appropriate.

Replicate Sample – Test samples were usually collected in duplicate. Outliers were eliminated by the laboratory and average data were reported in the data sheets. Method precision was typically within QC criteria (criteria is 50 RPD), however since average data were used for project purposes, limited precision in the cases of exceedances was reported and used for the various studies. The variability is, in part, the data quest for these verification and validation studies.

Gas Phase Spike Recovery -- Recovery of gas phase VFA standards from distilled water were also determined like the recovery of VFAs from carboxpack 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

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when an exceedance of calibration was observed for three TO-17 samples.

IV. RESULTS AND DISCUSSIONS

Laboratory testing information for the VFA verification study is reported in Table 1. A summary of data from the verification study, showing liquid stock solution concentrations and corresponding flux data are presented in Table 2. A similar data table is provide showing field data from the 2005 dairy testing effort comparing lagoon VFA concentration data and VFA flux data Table 3). The data in these tables shows that test source levels of VFAs used in the VFA verification study (VFA flux from aqueous solutions) are below levels of detection for VFA flux. The field data confirm the laboratory data.

Laboratory testing information for the VFA validation is reported in Table 4. A testing program was designed in order to establish the recovery efficiency of three target VFAs from the flux chamber at three different target concentrations. VFA source generator inlet concentrations and flowrate into the flux chamber were measured before and after each recovery test that was conducted as replicate samples. All testing was repeated, and average sample replicates and average test runs were reported for each VFA source strength. VFA recovery efficiency for acetic acid, propionic acid, and butyric acid are presented in Tables 5, 6, and 7, respectively. These tables show the spread sheets where recovery efficiencies were calculated. Four recovery values were calculated per concentration range: average VFA recovery from the flux chamber using HPLC inlet concentration data; average VFA recovery from the flux chamber using TO-17 inlet concentration data; average VFA recovery from the 8' sample line using HPLC inlet concentration data; and average VFA recovery from the 8' sample line using TO-17 inlet concentration data. Further, most estimates were performed using uncorrected data and baseline corrected data for Method TO-17. From these various estimates of recovery efficiency, one recovery value per VFA species was selected that best represented the performance of the VFA generator. The selection criteria was dependent on the test condition and specific method. For all test cases and species at the 50 ppbv target level, the recovery data using TO-17 inlet data, corrected for blank levels (if detected), was used with chamber and 8' line TO-17 data. This is because the TO-17 method at these levels agreed best with the VFA generator calibration data, understandably given that the mass loading for TO-17 is lower significantly lower for this method as compared to the EAS/HPLC method. The selected estimate is shown on Tables 5,6, and 7 in a bold highlighted box. Similarly, the selection of recovery data for the 150 ppbv and 300 ppbv target levels was based on using the HPLC method given that the mass loading was higher making the HPLC method preferred over the TO-17 method given that the higher levels were more difficult for the TO-17 method to achieve. As such, the HPLC (uncorrected for blank data) were selected for all species for the 150 ppbv and 300 ppbv test levels. Regardless of the compound, this selection process was used in order to keep the comparison of VFA recovery efficiency equivalent.

Finally, the selected VFA recovery efficiency data for all tests, reported as average test values, are given in Table 8. The footnotes provided indicate the data treatment and selection on inlet gas

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stream characterization used in the data evaluation process.

Note that flux data were not calculated or reported for the recovery study. The estimate of flux chamber recovery was performed by measuring the inlet gas concentration (ppbv), calculating the idea flux chamber concentration given the measured flowrates of VFA source as stream (about 0.2 liters per minute) and the flux chamber sweep air flow rate (about 5.0 liters per minute), and comparing the theoretical flux chamber VFA concentration to the actual, measured concentration. The equation for this calculation is as follows:

Flux Chamber Percent Recovery =

$$\frac{(\text{Measured VFA, ppbv})}{(\text{Inlet VFA, ppbv})} \left(\frac{\text{VFA flowrate}}{\text{Total flowrate}} \right) 100$$

Note- the dilution factor referred to is the ratio of total flowrate to VFA flowrate or (5.2 lpm/0.2 lpm, or a ratio of about 26).

Data collected by SCAQMD 25.3 for total hydrocarbon assessment as part of the VFA verification study produced no useful data. QC data indicated limitations in the method performance that may be related to the low levels of total hydrocarbon emissions generated by the aqueous VFA stock solutions.

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V. SUMMARY

Laboratory studies were designed and conducted to demonstrate the efficacy of using the USEPA flux chamber for assessing VFA emissions from area sources at dairies in Northern California. The following is a summary of activities and results associated with this objective:

- Surface flux measurements of VFA study compounds were measured during a method verification study and a method validation study using the USEPA recommended surface flux chamber technology. This technology quantitatively measures vapor fluxes at the test surface (aqueous test solutions, Teflon inlet systems) as in field applications.
- 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).
- Laboratory studies were performed in order to establish the method detection limits of Method TO-17. The MDLs for the full list of target compounds ranged from 5-to-10 ppbv.
- Spike recovery of primary liquid phase and gas phase standards of VFAs from sorbent media was within method specifications for all species (QC criteria $\pm 30\%$).
- A demonstration was performed for VFAs that showed that the analytical methods used on the project were suitable for the quantitation of VFAs. The VFA verification study showed that the analytical method performed within method specifications, and that higher levels of VFA aqueous stock solutions were necessary in order to reach gas phase MDL flux levels. This observation was confirmed by comparing liquid sources at dairies to gas phase flux levels. VFAs have a high affinity for water and stay in aqueous solution.
- A demonstration was performed for VFA recovery from the flux chamber for three VFAs and at three target concentrations. Emphasis was placed on acetic acid given that acetic acid is the dominant VFA found at dairy sources. Testing demonstrated that the flux chamber was a viable area source assessment approach given that acceptable recoveries from the flux chamber were documented. Acetic acid showed no loss in an 8' sample line, however, sample line loss is indicated for propionic acid at higher concentrations. Recovery testing was limited, especially for butyric acid given the need to customize the operation of the VFA source generator for acetic acid. Insufficient amounts of butyric acid were generated and introduced into the flux chamber for an accurate assessment at the 50 ppbv and 150 ppbv

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level. Regardless of these limitations, the study demonstrated an acceptable recovery efficiency for target VFAs from the flux chamber.

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REFERENCES

Schmidt, C.E., Tom Card. **QUALITY ASSURANCE PROJECT PLAN- DAIRY EMISSIONS EVALUATION USING SURFACE ISOLATION FLUX CHAMBERS; PHASE III- Retesting of Merced Dairy, Second Dairy Testing, 24-Hour Test REVISION 1.** Prepared for the California Air Resources Board, September 22, 2005.

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ATTACHMENT A

EMISSION MEASUREMENT DATA SHEETS

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ATTACHMENT B

LABORATORY NOTEBOOK NOTES

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ATTACHMENT C

EAS METHOD VALIDATION STUDY- DATA PACKAGE

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ATTACHEMENT D

EAS PROJECT REPORT- FLUX CHAMBER VALIDATION STUDY
ORGAINC ACIDS

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ATTACHMENT E

LABORATORY REPORTS