

*14th USEPA Annual Emissions Inventory Conference
Las Vegas, Nevada, April, 2005*

**“Assessment of Reactive Organic Gases and Amines
from a Northern California Dairy Using the USEPA
Surface Emissions Isolation Flux Chamber”**

C.E. Schmidt
Environmental Consultant

Tom Card
Environmental Management Consulting

Patrick Gaffney
California Air Resources Board

Steve Hoyt
Environmental Analytical Services

Abstract

The Central California Ozone Study (CCOS) group has sponsored a field study managed by the California Air Resources Board (CARB) to evaluate the air emissions of total organic gases (TOG), reactive organic gases (ROGs) also referred to as volatile organic compounds (VOCs), and ammonia/amine compounds from flushed lane dairies in Northern California. The goal of the research is to provide process-specific dairy emissions data for use in improving emission estimates required for State Implementation Plans (SIPs) and Senate Bill 700 (Florez).

The technical approach was developed for a two-phase program to assess air emissions from ten common ‘unit process’ found at a flushed lane dairy, including: flushed lanes (pre and post water flush), solids storage piles, flush and rinse water storage lagoons, solids in solids separator, free stall areas, turnout areas (corral), heifer pens, open feed storage, and milk parlor area. The emphasis of Phase 1 of the research was to identify all major sources of air emissions, rank the emission sources, and identify all significant compound emissions from the dairy (e.g., type of compounds emitted). The area source emissions were measured using the USEPA surface emissions isolation flux chamber (flux chamber) and gas samples were collected from the flux chamber for quantitative analysis of ROG or VOCs and amine compounds. USEPA Method TO-15 was performed at all test locations for speciated ROG (VOC) emissions (gas chromatography/mass spectrometry) using an extended compound list, as well as amine compounds analyzed by NIOSH Method 2010 (ion chromatography). Some locations were selected for analysis of aldehydes and ketones (USEPA Method TO-11), volatile organic acid compounds (ultraviolet-visible spectrometry), and fixed gases by ASTM Method 3416. The testing was performed during the summer season, and those test

locations subject to solar heating were tested as a function of time of day. All unit process were tested at multiple locations over a two-day time period, and screening analysis was performed assessing spatial variability where needed in order to aid in the selection of sample location.

Flux data were collected with the intent of averaging data per unit process and generating an average or representative compound flux per process. A simple average of process data was appropriate based on the sample collection design. Flux data are reported as unit emission factors for each unit process or unique area source as well as area emission estimates per process, which were summed per test area to generate site dairy emissions per process. All process emissions data were then summed for total dairy emissions, and from this total, per cow emission rate data were obtained by dividing dairy emissions by the number of cows on the dairy. Note that these per cow emission rate estimates for study compounds do not include any air emissions directly from the cow, only from solid and liquid surfaces on the dairy. The flux data and 'per cow' emission factor data were compared to earlier studies conducted by EPA Region 9 in Northern California and the South Coast Air Quality Management District in Southern California. The results of the Phase 1 effort are discussed and the objects of the follow-on Phase 2 research effort are also presented.

Introduction

Technical Approach

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

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

The baseline data collection for each test location, other than locations screened with real time data for the purpose of selecting a baseline test location, included Method TO-15 for speciated VOCs and was summed for ROG_s or VOC_s (which is also referred to as ARB ROG), and ammonia/amines determination by NIOSH Method 2010. So long as representative full speciation data are collected for each major area source, then the baseline data set can be used to assess the spatial variability with a source and define the primary compound emissions (ROG or VOC and NH₃). A limited amount (about 1-in-3) of full speciation data was collected to assess significant contributions from the non-

primary sources. Given that project resources could not address spatial variability, the large number of major sources at a dairy and full speciation of emitted species all at the same time, the compromise of including all major sources with limited compound speciation proved to be a sound strategy.

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

Dairy Unit Process or Unique Area Source Tested at the Northern California Dairy	No. Baseline Tests- ROG and NH3	No. Full Compound Tests (Other ROG Species)	Comments
Flushed Lane- Prior to Flushing (shaded)	2- Day 1 2- Day 2	1- Day 1 1- Day 2	Stockpile of manure prior to lane flushing, half-day accumulation
Flushed Lane- Post Flushing (shaded)	2- Day 1 2- Day 2	None	Mostly clean lanes, some manure slurry
Solid Storage Piles (sun exposed)	2- Day 1 AM 2- Day 2 PM	1- Day 1 AM	Typical age and depth of manure from long term storage
Lagoon (sun exposed)	2- Day 1 AM 2- Day 2 PM	1- Day 1 AM 1- Day 2 PM	Spatial distribution of testing at inlet and outlet on primary lagoon
Solids in Solids Separator (sun exposed)	2- Day 1 AM 2- Day 2 PM	1- Day 1 AM 1- Day 2 PM	Solids material tested as daily pile material collected and moved to solids storage pile (fresh solids as opposed to aged)
Bedding in Pile for Freestall Area (sun exposed)	2- Day 1 PM	1- Day 1 PM	One day testing of bedding material in pile, one day testing of bedding in freestall
Freestall Area (shaded)	2- Day 2 AM	1- Day 2 AM	Bedding material in freestall beds
Barn Turnout and Corral Area (sun exposed)	1- Day 1 AM 2- Day 2 PM	1- Day 2 PM	Target areas included fresh manure, thin manure layer, and thick manure layer (no piles- recent corral cleaning)

Manure Piles in Turnout Areas (sun exposed)	None	None	Recent corral cleaning, no storage piles. Samples collected elsewhere.
Heifer Pens (dry cow pens- sun exposed)	1- Day 1 PM 2- Day 2 AM		Minimum testing to show similarity of source
Open Feed Storage (in freestall feed lanes- shaded)	1- Day 1 1- Day 2	1- Day 1	Typical silage only; category is variable dependent on feed type. Tested in feed lanes not store pile
Milk Parlor (wastewater effluent- sun exposed)	1- Day 1 1- Day 2		Not a significant source, similar to flushed lane.
Field Blank	2	2	Minimum QC; approx. 5%
Field Replicate	2		Minimum QC; approx. 5%
TOTAL	38	13	

Facility Description

California San Joaquin Valley dairies can generally be described a "flushed lane" dairies, meaning that the areas where milk cows are primarily kept are open barns with cement pad areas (lanes) and bedding areas where the lanes are flushed with water one or more times per day. This type of dairy is common in areas where water is available and dairies have land available for growing crops for feed. Both liquid and solid wastes are used in growing crops for silage. These dairies have open corrals or 'turnouts' where cows have free access.

Cows at San Joaquin Valley dairies spend most of the time in flushed lane pens and most of the manure accumulates in these areas. The combined waste stream from the lanes, parlor rinse, and shower wash water flows into a separator pond where solid material is captured and the liquid waste stream is conveyed to a large liquid storage pond. Solid waste is stored temporarily until the separator solids are removed to solids storage piles. The solid waste is then used for fertilizer on the property (typically corn crop) or stored and then used eventually for bedding materials in the barns on site. The waste water is used on the crops for irrigation. Other areas where manure accumulates is in dry feed lots and manure storage areas such as storage piles.

Physical dimensions of the unit process at the tested dairy are provided below. The 'per cow' emission estimate is calculated by knowing the representative flux per unit process, the area of the process, and the number of cows. Approximately 3443 cows were reported to be at the tested dairy.

UNIT PROCESS	COMPONENT	AREA (m²)
Turnouts (corrals)	1	19,600
	2	9,100
	3	8,510
	4	10,300
	5	11,600
	6	12,100
	7	21,500
	Total Turnouts	92,700
Dry Cow Turnout		12,200
Lagoon		22,500
Manure Storage- Fresh		66
Manure Storage- Solids	Pile	1,250
Manure Storage- Bedding	In Barns	1,210
	Total Manure Storage	2,530
Active Milker Barns		
	North Barn Lanes	14,000
	Central Barn Lanes	2,960
	South Barn Lanes	15,100
	Total Barn Lanes	32,100
Dry Barn		2,548
Milking Parlor		1,254
Total Area of Dairy		167,000

Methodology

Testing was conducted using the EPA recommended Surface Isolation Flux Chamber (flux chamber) as the emission assessment tool to collect emissions data. The primary reference for this section is the document entitled "Measurement of Gaseous Emission Rates From Land Surfaces Using an Emission Isolation Flux Chamber, Users Guide" (1). The flux chamber is cylindrical (16" diameter), has a volume of 30 liters, and has a clear acrylic top with stainless steel side-walls. The chamber is portable and is designed for convenient use and decontamination. Sweep air is added to the chamber at 5 liters per minute and gas samples are collected after chamber equilibrium or five residence times. 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 surface, or liquid surface sealing the chamber for flux testing. Thermocouples were placed in order to monitor surface/air temperatures outside of the chamber.

5. The sweep air flow rate was initiated and the rotometer, which stabilizes the flow rate, was set at 5.0 liters per minute. A constant sweep air flow rate was maintained throughout the measurement for each sampling location.
6. Flux chamber data were recorded every residence interval (6 minutes) for five intervals, or 30 minutes.
7. At steady-state (assumed to be greater than 5 residence intervals), the sample collection was performed by interfacing the sample media as specified in the QAPP to the purged, sample line and collecting the sample media as appropriate.
8. After sample collection, all field data were documented on the data sheet.
9. After sampling, the flux measurement was discontinued by shutting off the sweep air, removing the chamber, and securing the equipment. The chamber was cleaned by dry wipe with a clean paper towel and the sample lines were purged with UHP air.
10. Sampling locations were recorded on the field data sheet. The equipment was then relocated to the next test location and steps 1) through 9) were repeated.

A total of five sample collection and analytical methods were used for the effort as specified in the project Quality Assurance Project Plan (QAPP) as identified below (2). 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, ROG (VOC) or ARB ROG	0.4-to-27 ug/m3 (0.04-to-4 ppbv)
	NIOSH 2010 (GC/IC)	Ammonia and other Amines	0.2 –to-0.5 ug/ml; about 0.4 mg/m3 (0.5 ppmv)
Full Compound Assessment	ASTM 3416 (GC/FID)	Fixed Gas- (CH4)	50 ppbv (30 ug/m3)

	USEPA Method TO-11 (GC/HPLC-UV/VIS)	Aldehydes/Ketones	0.04-to-0.16 ug/sample; about 0.9-to-9 ug/m3 (0.7-to-4 ppbv)
	EAS Method (GC/HPLC-UV/VIS)	Volatile Organic Acids	10 ug/sample; 290 ug/m3 (63-to-230 ppbv)

* Nominal detection limit. Each sample detection limit is based on possible dilution factors.

** Detection limit depends upon the volume of air collected through the sampling media.

GC = Gas chromatography

FID = Flame ionization detection

PID = Photoionization detection

HPLC = High performance liquid chromatography

UV-VIS = Ultraviolet-Visible Absorption Spectrophotometer

MS = Mass spectrometry

ASTM = American Society of Testing and Materials

EAS- Environmental Analytical Services

The project analytical menu included non-methane, VOC speciation analysis (USEPA Method TO-15) and summation of non-listed VOCs for an estimate of total reactive gases (ROG) and total organic gases (TOG). Rather than a 'total organic gases' method, the ROG (VOC) estimate was made by summing the known, quantitative, 'non-listed VOC compounds'. Hydrocarbon compound concentrations (ug/m3) were summed for total ROGs or VOCs. In addition to the Method TO-15 compound estimation of ROG per sample, ethyl amine and TO-11 compounds, including aldehydes and ketones (except acetone) were added to the summation of ROG as indicated by the regulatory definition of ROG. The TOG was obtained by adding methane values to the estimated ROG values as per regulatory definition.

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

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

Results

The results of the analysis of the flux samples collected from the various dairy unit processes are reported as average flux per compound per process and are provided in Table 1. Data are reported as average flux per compound (micrograms per square meter per minute or ug/m²,min⁻¹) for most of the detected compounds (very low level flux not included in Table 1). These data are above method and system blank levels.

The estimate of compound emissions from the dairy unit processes was made by multiplying the average compound flux per unit process by the surface area of the process and are reported in Table 2 as unit process emissions (mass per time) in Table 2. The emission rate data for unit process for ammonia and ROG (VOC) are displayed graphically in bar charts and are provided in Figures 1 and 2, respectively. This data presentation is useful in comparing the significance of the various unit processes in relation to the measured dairy emissions. Percentage of ammonia and ROG (VOC) emissions, broken down by type of unit process is also summarize below:

Type of Unit Process	Unit Process	% NH3	%ROG (VOC)
Milk Cow Process	Bedding in Barn	0.1	0.8
	Total Flushed Lane	4.8	11
	Feed in Barn	0.02	44
	Turnout or Corral	84	17
Dry Cow Process	Bedding in Barn	0.1	0.0
	Total Flushed Lane	0.1	0.8
	Feed in Barn	0.0	3.2
	Turnout or Corral	1.6	5.7
Solids Piles	Fresh Separator	0.008	0.0
	Aged Separator	0.2	0.0
	Bedding Pile	6.6	2.5
Lagoon	Lagoon	1.4	9.0
Milk Parlor	Effluent Stream	0.1	1.6

The annual estimate assumes that flux is a function of surface area, not volume of waste. An area source with several inches of livestock waste is assumed to have identical or similar air emissions with several feet of livestock waste (3). This estimate includes variability in source as related to spatial differences within a process (multiple spatially

oriented test locations) and diurnal variations (differences in flux during daylight hours), but it does not include seasonal variability. No seasonal data were collected.

Total dairy site emissions per compound can be obtained by summing all compound emissions from the unit process. The total compound or criteria, site-specific emissions are provided in Table 2. These summed emissions were divided by the number of cows present at the dairy on the day of testing (3442 cows) in order to obtain annual 'per cow' or 'per head' emission factors. These per cow emissions factors are provided in Table 3 in units of compound lb/cow-year units. For instance, the ROG (VOC) emission factor calculated using these site data is 1.3 lb/cow-year, and the ammonia emission factor is 135 lb/cow-year. This is compared to a similar estimate obtained from flux chamber testing for ozone precursor VOCs in Northern California (about 700 cow, flushed lane dairy) of non-methane VOC emissions (including exempt compounds) of 5.2 lb/cow-year (3), and a similar estimate from flux chamber testing for ammonia in a Southern California (over 3,000 cow, dry lot dairy) of 18 lb/cow-year (4). The high ammonia emission factor from this study is believed to be related to manure removal in the corrals prior to testing.

Using flux chamber data to represent dairy emissions or emission factors on a per cow basis that can be used to estimate air emissions from other dairies, rests on several key assumptions, including:

1. An adequate number of test locations are included in the characterization of each unit process and averaged for a representative flux per compound per process.
2. The surface area of the unit process is known with relative certainty.
3. The number of cows at the dairy is known with relative certainty.
4. The ratio of cows to surface area at a dairy covered with livestock waste is relatively constant from dairy-to-dairy.
5. Dairy operations such as frequency of lane flushing and turnout scrapping, and other factors such as feed type and type of cow are not significant factors affecting air emissions from surfaces at dairies.
6. The lagoon process is proportional to the 'as built' cow capacity at dairies.
7. The air emissions from different thickness of manure layers is relatively constant, or the air emissions is dominated by surface area and not manure layer thickness, especially in turnouts or corrals.
8. The analytical methods used for assessing VOCs adequately represents the majority of compound emissions resulting in a reasonable representation of ROG (VOC).

Characteristic compound flux was observed for each unit process. Summary information is provided below. Note that non-exempt VOC's, ROG, or ARB ROG (table nomenclature used to avoid confusion with TNMOC) all represent the same estimate of reactive hydrocarbon compounds expressed as a summation of individual compounds ($\mu\text{g}/\text{m}^3$ concentration) and used in the emission estimate

Separator Solids

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

Solids in Storage Pile

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

Bedding Pile Solids

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

Freestall Bed

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

Primary Lagoon

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

Flushed Lane; Pre-flushed

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

Flushed Lane; Post-flushed

Testing was also conducted after the barn lanes were flushed. There was very little manure in the lanes post flushing, and the source appeared to more like a dilute

wastewater stream as compared to the pre-flushed lane surface. The post-flushed barn lanes were tested with multiple locations on both test days. The average emissions from the multiple test locations included non-detect methane flux ($<1.2 \text{ ug/m}^2, \text{min}^{-1}$), moderate ARB ROG flux ($30 \text{ ug/m}^2, \text{min}^{-1}$), moderately low ammonia flux ($480 \text{ ug/m}^2, \text{min}^{-1}$) and ethylamine flux ($23 \text{ ug/m}^2, \text{min}^{-1}$), a moderately low number of low-level volatile organic compound species flux by TO-15 with moderate ethanol flux ($4.7 \text{ ug/m}^2, \text{min}^{-1}$), vinyl acetate flux ($0.40 \text{ ug/m}^2, \text{min}^{-1}$) and no aldehyde flux was observed by TO-11. Volatile organic acids were not detected.

Feed Lane (pile)

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

Turnouts

Turnouts are the areas in the corral where cows travel from the covered barns to the corrals. Cows spend most of the day light hours in the barns but migrate to the corrals depending on cloud cover, temperature, and other factors. Areas of a corral were selected with three types of ground cover: fresh manure, thin layer of dry manure, and the thicker layers of dry manure. Three locations were tested in the same corral on two days and samples were collected at the highest emitting surfaces of two of the locations. The average emissions from multiple test locations in the corral for milk cows on two days included comparatively moderate methane flux ($1,700 \text{ ug/m}^2, \text{min}^{-1}$), lower ARB ROG flux ($7.0 \text{ ug/m}^2, \text{min}^{-1}$), moderately high ammonia flux ($3,600 \text{ ug/m}^2, \text{min}^{-1}$), an extensive range of low-level volatile organic compound species flux by TO-15 with higher ethanol flux ($3.8 \text{ ug/m}^2, \text{min}^{-1}$), and acetone flux ($2.2 \text{ ug/m}^2, \text{min}^{-1}$). Lower levels of aldehyde flux was observed by TO-11 including formaldehyde flux ($0.092 \text{ ug/m}^2, \text{min}^{-1}$), acetaldehyde flux ($0.25 \text{ ug/m}^2, \text{min}^{-1}$), and acetone flux ($0.85 \text{ ug/m}^2, \text{min}^{-1}$). Volatile organic acids were not detected.

Heifer Pens

Heifer pens were tested because dry cow pens were not available for testing. The heifer cows are fed a lower energy diet and the unit process is similar to the milk cow corral source (turnouts). Thicker layers of dry manure were selected for testing. Two locations were tested in the same corral on two days at different times of the day. The average emissions from multiple test locations in the corral for milk cows on two days included non-detect methane flux, moderate ARB ROG flux ($19 \text{ ug/m}^2, \text{min}^{-1}$), moderate

ammonia flux (530 ug/m²,min-1), moderate-to-low ethyl amine flux (15 ug/m²,min-1), a range of low-level volatile organic compound species flux by TO-15 with higher acetone flux (1.1 ug/m²,min-1) and m/p-xylene flux (0.91 ug/m²,min-1). Aldehyde flux was not observed by TO-11. Volatile organic acids were not detected.

Milk Parlor

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

Conclusions

Flux measurements of study compounds were measured at from various area sources at a large dairy in Northern California. The following summary statements are provided:

- Process specific flux rates of methane, VOCs, and ammonia/amines were measured at the ground surface on representative unit process on a dairy using the USEPA recommended surface isolation flux chamber technology and accepted sample collection and analytical methods. This technology quantitatively measures emission rates from an area source. TOG and ROG emissions were calculated using VOC data.
- Reported flux data can be used on a general basis or on a dairy-specific basis to estimate air emissions from the dairies or the dairy industry. Representative and compound specific flux data per process, along with surface area information, are used to calculate emission rate per process. Compounds emissions per process are summed for dairy emissions, which are then used to calculate compound per cow annual emission rate factors.
- An emission rate estimate for TOG and ROG or VOC was performed using the methane and non-methane data. ROG is defined as all non-listed VOCs including ethyl amine and aldehydes/ketones- this estimate relied on TO-15 hydrocarbon speciation data. TOG is defined as methane plus ROG- this estimate relied on ROG data and methane data.
- Emission rates for ROG or VOC and ammonia, shown graphically, illustrate the dominate sources for emissions at dairies. Given that emissions is a function of both

surface area (size) and flux (mass emitted per time per surface area), dominate source can include smaller sources with high flux rates, and large sources with moderate or even low flux rates.

- Inspection of the ROG or VOC emission rate data per process indicates that the single largest ROG or VOC source is the feed lanes in the barns. This source is dominated by ethanol from corn silage and the feed source accounts for about 44% of the dairy ROG or VOC emissions. Other key sources include turnouts (corrals), the flushed lanes, the lagoon, and bedding materials in the barns.
- Similarly, the ammonia emission rate data per process indicates that the turnout areas (corrals) account for about 84% of the dairy ammonia emissions. Other key sources include the solids storage pile (bedding materials), the flush lanes, the lagoon, and the bedding materials in the barns.
- It is possible to prorate flux or emission rate based on cattle per dairy by dividing the annual ROG or VOC emission rate by the number of milk cows (approximately 3,442) that use or contribute to the area source emissions. Air emission estimates from dairies can be made using this approach assuming that the surface area per dairy unit source is proportional to number of milk cows managed per dairy. This study determined a ROG or VOC emission factor of 1.3 lb/cow-year.
- A per cow annual emission factor for ammonia was also calculated using the ammonia flux data. The factor of 135 lb/cow-year is believed to be non-representative of because the turnouts or corrals were cleaned just prior to testing exposing soils saturated with amine compounds.

Future Research

The follow on phase to this research will include additional assessment of unit process emissions at the same or a similar dairy with the intent to improve on the compound emission factor data. Specifically, testing will be conducted to improve the emission rate data for key unit process such as the turnouts (corrals) for ammonia and feed materials, both in barn feed lanes and in silage piles. Efforts will be made to conduct testing on turnouts or corrals without manure scraping prior to testing so that the transient effects from this activity will not enter into the annual estimate of ammonia emissions. Other changes to the technical approach will include modifications to the analytical protocols used, including adding some compounds of interest by testing from the flux chamber using different sample collection and analytical methods, and in some cases deleting some analytical methods. Additionally, daytime and nighttime testing might be conducted in order to obtain information regarding the variability of diurnal emissions, especially for ammonia. The hope is that the follow on testing will generate per cow emission factors for key compounds of interest that can be used to estimate ammonia, ROG and compound emissions from other similar dairies by knowing the dairy design, operation, and number of cows per dairy.

Acknowledgements

We would like to acknowledge the support of the Central California Ozone Study (CCOS) group and the dairy that participated in the study.

References

- 1) US EPA. "Measurement of Gaseous Emission Rates From Land Surfaces Using an Emission Isolation Flux Chamber, Users Guide." EPA Environmental Monitoring Systems Laboratory, Las Vegas, Nevada, EPA Contract No. 68-02-3889, Radian Corporation, Work Assignment No. 18, February 1986.
- 2) Card, T.R., and C.E. Schmidt, Quality Assurance Project Plan, Revision #2, "Dairy Emissions Evaluation Using the USEPA Surface Emissions Isolation Flux Chamber," California Air Resources Board, August 11, 2004.
- 3) Schmidt, C.E., John Ungvarsky, Eric Winegar, "Assessment of Ozone Precursor Emissions from the Dairy Industry", 97-MP74.01, 90th Annual Meeting of the Air and Waste Management Association, Toronto, Canada, June, 1997.
- 4) "Results of the Measurement of PM10 Precursor Compounds (PM10PCs) from Dairy Industry Livestock Waste: Summer Testing Event (09/26/95-10/07/95) and Winter Testing Event (12/11/95-12/14/95)", Technical Report, South Coast Air Quality Management District, Dr. Julia Lester, June, 1996.

Key Words- dairy emissions, ROG air emissions, amine emissions, area source emissions factors for dairies, per cow air emission estimates.

Contact Information- For additional information or questions, please contact Patrick Gaffney (pgaffney@arb.ca.gov) or CE Schmidt (schmidtce@aol.com).

Table 1. Summary of Average Flux Data per Dairy Unit Process (ug/m2,min-1).

COMPOUNDS	AVE FLUX	AVE FLUX	AVE FLUX	AVE FLUX	AVE FLUX	AVE FLUX	AVE FLUX	AVE FLUX	AVE FLUX	AVE FLUX	AVE FLUX
	Sep Solids	Lagoon	Turnout	Bedding Pile	Freestl Bed	Flush L Pre	Flush L Post	Feed (pile)	Milk P Efflu	Solids Pile	Heifer Pens
	ug/m2,min-1	ug/m2,min-1	ug/m2,min-1	ug/m2,min-1	ug/m2,min-1	ug/m2,min-1	ug/m2,min-1	ug/m2,min-1	ug/m2,min-1	ug/m2,min-1	ug/m2,min-1
Ammonia	650	250	3600	22000	830	2400	480	31	340	630	530
Ethylamine	29					19	23		29		15
Methane*	15,000	2300	1700	64	24	430		29		220,000	
TNMOG	25	13	10	110	22	23	7.8	910	21	4.3	4.7
ARB ROG (VOC)	48	16	7.0	75	16	34	30	890	47	3.4	19
ARB TOG	15,000	2300	1700	140	42	460	30	940	47	220,000	19
Chloromethane	0.071	0.037	0.027	4.3	0.050	0.0054	0.010		3.7	0.49	0.0092
Chloroethane				0.15					3.0		
Ethanol	13	0.39	3.8		3.7	10	4.7	870	1.3	0.45	0.31
Acetone*	2.5	0.90	2.2	35	6.7	0.92	0.47	13	1.4	2.4	1.1
2-propanol	0.14	0.12	0.23	0.75	0.39	0.29	0.092	5.8	0.10	0.072	0.0087
Carbon disulfide*	2.9	0.47	0.59	4.2	0.15	0.02	0.13		2.3	0.61	0.31
Propionitrile		0.069	0.041	1.1		0.027			0.025		
2-Butanone	0.53	0.22	0.76	330	0.65	0.12	0.072		0.10	0.30	0.22
Hexane	0.67	0.035	0.012	1.0			0.0079	10		0.10	
Tetrahydrofuran	0.040	0.035	0.037	0.46	0.10	0.016			0.061		0.073
Isobutyl alcohol	0.051	0.13	0.16		0.25	0.058			0.14		
Chloroform	0.59								2.5		
1,2-Dichloroethane		0.016									
Cyclohexane	0.49	0.065	0.27		9.4	0.079	0.057		0.20		0.10
Benzene	0.057	0.046	0.045	1.1		0.027	0.020		0.0082	0.12	0.0049
n-Heptane	0.15			1.1						0.13	
1,4 Dioxane	0.10	0.20	0.12	6.2	0.10	0.23	0.015		0.058		
Trichloroethene		0.090									
Methyl methacrylate		0.077									
Methyl Isobutyl Ketone	0.050	0.090	0.065	5.1	0.13		0.031				0.12
cis-1,3-Dichloropropene		0.039	0.0089								
Toluene	1.3	0.20	0.10	0.94	0.30	0.10	0.27	0.33	4.6	0.48	0.50
2-Hexanone	0.053	0.21	0.071	2.0		0.059			0.040		0.068
Octane	1.2	0.16	0.14	2.8		0.033	0.14			0.31	
Chlorobenzene	0.043	0.10	0.024	0.60		0.037	0.0064		0.16		
Ethylbenzene	0.11	0.12	0.044	0.58		0.046	0.10		0.020	0.21	0.10
m & p-Xylene	0.25	0.27	0.12	1.4		0.11	0.46		0.053	0.059	0.91
Styrene	0.039	0.13	0.03	1.1					0.028	0.15	
o-Xylene	0.10	0.14	0.060	0.63		0.051	0.15		0.026		0.26
sec-butylbenzene		0.13									
1,3-Dichlorobenzene		0.39							0.085		
1,2-Dichlorobenzene		0.52							0.10		
1,2-Dibromo-3-chloropropane		1.4							0.32		
Tetraethyl lead		0.42									
1,2,4-Trichlorobenzene		3.3									
Napthalene	0.16	1.5				0.13	0.063		0.17		
Hexachlorobutadiene		1.6									
Formaldehyde	0.076	0.13	0.092	1.1	0.21	0.15				0.19	
Acetaldehyde	0.20	0.25	0.25	6.9	0.69	6.1				0.25	
Acetone*	1.1	0.52	0.85	2.8	3.9	1.2				0.92	
Crotonaldehyde				0.92	0.37						
Butyraldehyde	0.12			1.1	0.25						
Total TO-11 less Acetone	0.46	0.37	0.34	10	1.5						
25.3 Equivalent	18	12	6.8	80	19	9.0	5.7	630	13	4.3	4.1
25.3 ROG Equivalent	16	11	5.4	61	15	8.4	5.4	620	11	2.9	3.4

Compounds with asterisk are listed, non-ROG compounds

Flux = (ug/m3)(0.005 m3/min)/(0.13 m2) = (ug/m3)(0.0385)(ug/m2.min-1)

TNMOG- Summation of VOCs reported as ug/m3

ARB ROG (VOC)- Summary of non-except VOCs by TO-15 plus ethyl amine plus aldehydes/ketone

ARB TOG- Summary of methane plus ARB ROG

Table 2. Dairy Emissions Per Unit Process (lb/year) for Dairy with 3442 Cows.

Component	Active Milking				Dry Cows				Solids				Milk Parlor	Total	Total/H/d	Tot/H/d/yr
	Barn Emissions				Barn Emissions				Solids							
	Bed	Fish Lane	Feed	Turnout	Bed	Fish Lane	Feed	Turnout	Fresh	Aged	Bedding	Lagoon				
Fraction	0.3	0.42	0.06		0.3	0.42	0.06									
Area (m ²)	9,617	13,464	1,923	92,739	764	1,070	153	12,218	65,813	1250.4	1209.375	22,478	1,254			
	Milker Barn Bed	Milker Barn Flush Lane	Milker Barn Feed	Milker Turnout	Dry Barn Bedding	Dry Barn Flush Lane	Dry Barn Feed	Dry Barn Turnout	Solids - Fresh	Solids - Aged	Solids - Bedding Storage	Lagoon	Milk Parlor			
Ammonia	25.3	61.6	0.2	1,060.0	1.3	1.8	0.0	20.6	0.1	2.5	84.5	17.8	1.4	1,277.0	0.371	135.4
Ethylamine	0.0	0.9	0.0	0.0	0.0	0.1	0.0	0.6	0.0	0.0	0.0	0.0	0.1	1.7	0.0005	0.18
Methane*	0.7	9.2	0.2	500.5	0.0	0.0	0.0	0.0	3.1	873.4	0.2	164.1	0.0	1,551.6	0.451	164.5
TNMOG	0.7	0.7	5.6	2.9	0.0	0.0	0.4	0.2	0.0	0.0	0.4	0.9	0.1	11.9	0.003	1.27
ARB TOG (VOC)	0.5	1.4	5.4	2.1	0.0	0.1	0.4	0.7	0.0	0.0	0.3	1.1	0.2	12.3	0.004	1.30
ARB TOG	1.3	10.5	5.7	500.5	0.0	0.1	0.5	0.7	3.1	873.4	0.5	164.1	0.2	1,560.7	0.453	165.5
Chloromethane	0.002	0.000	0.000	0.008	0.000	0.000	0.000	0.000	0.000	0.002	0.017	0.003	0.015	0.046	0.00001	0.005
Chloroethane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.012	0.013	0.00000	0.001
Ethanol	0.113	0.314	5.313	1.119	0.001	0.001	0.422	0.012	0.003	0.002	0.000	0.028	0.005	7.332	0.00213	0.777
Acetone*	0.205	0.030	0.079	0.648	0.003	0.004	0.006	0.043	0.001	0.010	0.134	0.064	0.006	1.231	0.00036	0.131
2-propanol	0.012	0.008	0.035	0.068	0.000	0.000	0.003	0.000	0.000	0.000	0.003	0.009	0.000	0.139	0.00004	0.015
Carbon disulfide*	0.005	0.003	0.000	0.174	0.001	0.001	0.000	0.012	0.001	0.002	0.016	0.034	0.009	0.257	0.00007	0.027
Propionitrile	0.000	0.001	0.000	0.012	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.005	0.000	0.022	0.00001	0.002
Vinyl acetate	0.000	0.009	0.079	0.000	0.000	0.000	0.006	0.002	0.000	0.001	0.000	0.000	0.001	0.099	0.00003	0.010
2-Butanone	0.020	0.004	0.000	0.224	0.001	0.001	0.000	0.009	0.000	0.001	1.267	0.016	0.000	1.542	0.00045	0.163
Hexane	0.000	0.000	0.061	0.004	0.000	0.000	0.005	0.000	0.000	0.000	0.004	0.002	0.000	0.076	0.00002	0.008
Tetrahydrofuran	0.003	0.000	0.000	0.011	0.000	0.000	0.000	0.003	0.000	0.000	0.002	0.002	0.000	0.022	0.00001	0.002
Isobutyl alcohol	0.008	0.001	0.000	0.047	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.009	0.001	0.066	0.00002	0.007
Chloroform	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.010	0.00000	0.001
1,2-Dichloroethane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.00000	0.000
Cyclohexane	0.287	0.003	0.000	0.079	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.005	0.001	0.379	0.00011	0.040
Benzene	0.000	0.001	0.000	0.013	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.003	0.000	0.023	0.00001	0.002
n-Heptane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.004	0.000	0.000	0.005	0.00000	0.001
1,4-Dioxane	0.003	0.005	0.000	0.035	0.000	0.000	0.000	0.000	0.000	0.000	0.024	0.014	0.000	0.082	0.00002	0.009
Trichloroethene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.000	0.006	0.00000	0.001
Methyl methacrylate	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.000	0.005	0.00000	0.001
Methyl Isobutyl Ketone	0.004	0.001	0.000	0.019	0.000	0.000	0.000	0.005	0.000	0.000	0.020	0.006	0.000	0.055	0.00002	0.006
cis-1,3-Dichloropropene	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.005	0.00000	0.001
Toluene	0.009	0.008	0.002	0.029	0.001	0.002	0.000	0.019	0.000	0.002	0.004	0.014	0.018	0.109	0.00003	0.012
2-Hexanone	0.000	0.001	0.000	0.021	0.000	0.000	0.000	0.003	0.000	0.000	0.008	0.015	0.000	0.048	0.00001	0.005
Octane	0.000	0.004	0.000	0.041	0.000	0.000	0.000	0.000	0.000	0.001	0.011	0.011	0.000	0.069	0.00002	0.007
Chlorobenzene	0.000	0.001	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.007	0.001	0.018	0.00001	0.002
Ethylbenzene	0.000	0.003	0.000	0.013	0.000	0.000	0.000	0.004	0.000	0.001	0.002	0.009	0.000	0.032	0.00001	0.003
m & p-Xylene	0.000	0.012	0.000	0.035	0.002	0.003	0.000	0.035	0.000	0.000	0.005	0.019	0.000	0.113	0.00003	0.012
Styrene	0.000	0.000	0.000	0.009	0.000	0.000	0.000	0.000	0.000	0.001	0.004	0.009	0.000	0.024	0.00001	0.003
o-Xylene	0.000	0.004	0.000	0.018	0.001	0.001	0.000	0.010	0.000	0.000	0.002	0.010	0.000	0.046	0.00001	0.005
t-1,4-Dichloro-2-butene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.039	0.001	0.040	0.00001	0.004
sec-butylbenzene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.009	0.000	0.009	0.00000	0.001
1,3-Dichlorobenzene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.028	0.000	0.028	0.00001	0.003
1,2-Dichlorobenzene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.037	0.000	0.038	0.00001	0.004
1,2-Dibromo-3-chloropropane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.100	0.001	0.101	0.00003	0.011
Tetraethyl lead	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.030	0.000	0.030	0.00001	0.003
1,2,4-Trichlorobenzene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.235	0.000	0.235	0.00007	0.025
Naphthalene	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.107	0.001	0.112	0.00003	0.012
Hexachlorobutadiene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.114	0.000	0.114	0.00003	0.012
Formaldehyde	0.006	0.003	0.000	0.027	0.000	0.000	0.000	0.000	0.000	0.001	0.004	0.009	0.000	0.051	0.00001	0.005
Acetaldehyde	0.021	0.130	0.000	0.074	0.000	0.000	0.000	0.000	0.000	0.001	0.026	0.018	0.000	0.270	0.00008	0.029
Acetone*	1.191	0.026	0.000	0.250	0.000	0.000	0.000	0.000	0.000	0.004	0.011	0.037	0.000	1.518	0.00044	0.161
Crotonaldehyde	0.011	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.015	0.00000	0.002
Butyraldehyde	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.012	0.00000	0.001

Note: Total process emissions = Unit Flux Rate (ug/m²/min)*Area (m²) * 1 g / 1000000 ug * 1 pound / 453.56 g * 1440 min / day

Table 3. Summary of Dairy Emissions per Head/Year.

Component	Total	Total/Hd	Tot/Hd/yr
Ammonia	1,277.0	0.37	135.4
Ethylamine	1.69	0.0005	0.18
Methane*	1,551.6	0.45	164.5
TNMOC	11.94	0.0035	1.27
ARB ROG (VOC)	12.27	0.0036	1.30
ARB TOG	1,560.7	0.45	165.5
Ethanol	7.332	0.00213	0.777
2-Butanone	1.542	0.00045	0.163
Acetone*	1.518	0.00044	0.161
Acetone*	1.231	0.00036	0.131
Cyclohexane	0.379	0.00011	0.040
Acetaldehyde	0.270	0.00008	0.029
Carbon disulfide*	0.257	0.00007	0.027
1,2,4-Trichlorobenzene	0.235	0.00007	0.025
Tetrachloroethene*	0.180	0.00005	0.019
2-propanol	0.139	0.00004	0.015
Hexachlorobutadiene	0.114	0.00003	0.012
m & p-Xylene	0.113	0.00003	0.012
Napthalene	0.112	0.00003	0.012
Toluene	0.109	0.00003	0.012
1,2-Dibromo-3-chloropropane	0.101	0.00003	0.011
Vinyl acetate	0.099	0.00003	0.010
1,4 Dioxane	0.082	0.00002	0.009
Hexane	0.076	0.00002	0.008
Octane	0.069	0.00002	0.007
Isobutyl alcohol	0.066	0.00002	0.007
Methyl Isobutyl Ketone	0.055	0.00002	0.006
Formaldehyde	0.051	0.00001	0.005
2-Hexanone	0.048	0.00001	0.005
o-Xylene	0.046	0.00001	0.005
Chloromethane	0.046	0.00001	0.005
1,2,4-Trimethylbenzene	0.043	0.00001	0.005
t-1,4-Dichloro-2-butene	0.040	0.00001	0.004
1,2-Dichlorobenzene	0.038	0.00001	0.004
Ethylbenzene	0.032	0.00001	0.003
Tetraethyl lead	0.030	0.00001	0.003
1,4-Dichlorobenzene	0.030	0.00001	0.003
1,3-Dichlorobenzene	0.028	0.00001	0.003
Styrene	0.024	0.00001	0.003
Benzene	0.023	0.00001	0.002
Tetrahydrofuran	0.022	0.00001	0.002
Propionitrile	0.022	0.00001	0.002
1,1,2,2-Tetrachloroethane	0.019	0.00001	0.002
1,2-Dibromoethane	0.019	0.00001	0.002
1,3,5-Trimethylbenzene	0.019	0.00001	0.002
Chlorobenzene	0.018	0.00001	0.002
Benzyl chloride	0.018	0.00001	0.002
Isopropyltoluene	0.017	0.00001	0.002
Methylstyrene	0.015	0.00000	0.002
Crotonaldehyde	0.015	0.00000	0.002
Carbon tetrachloride	0.015	0.00000	0.002
tert-butyl benzene	0.014	0.00000	0.001
Acrylonitrile	0.013	0.00000	0.001
Isopropylbenzene	0.013	0.00000	0.001
Chloroethane	0.013	0.00000	0.001
1,1,2-Trichloroethane	0.012	0.00000	0.001
n-Butylbenzene	0.012	0.00000	0.001
Butyraldehyde	0.012	0.00000	0.001
Dichlorodifluoromethane*	0.011	0.00000	0.001
Chloroform	0.010	0.00000	0.001
Bromoforn	0.010	0.00000	0.001
sec-butylbenzene	0.009	0.00000	0.001
1,2,3-Trichloropropane	0.009	0.00000	0.001
trans-1,3-Dichloropropene	0.008	0.00000	0.001
4-Ethyltoluene	0.007	0.00000	0.001
Trichloroethene	0.006	0.00000	0.001
n-Propylbenzene	0.006	0.00000	0.001
Methyl methacrylate	0.005	0.00000	0.001

Note: Total process emissions = Unit Flux Rate (ug/m²/min)*Area (m²)
 * 1 g / 1000000 ug * 1 pound / 453.56 g * 1440 min / day

Figure 1. - Dairy Ammonia Emissions (As Tested)

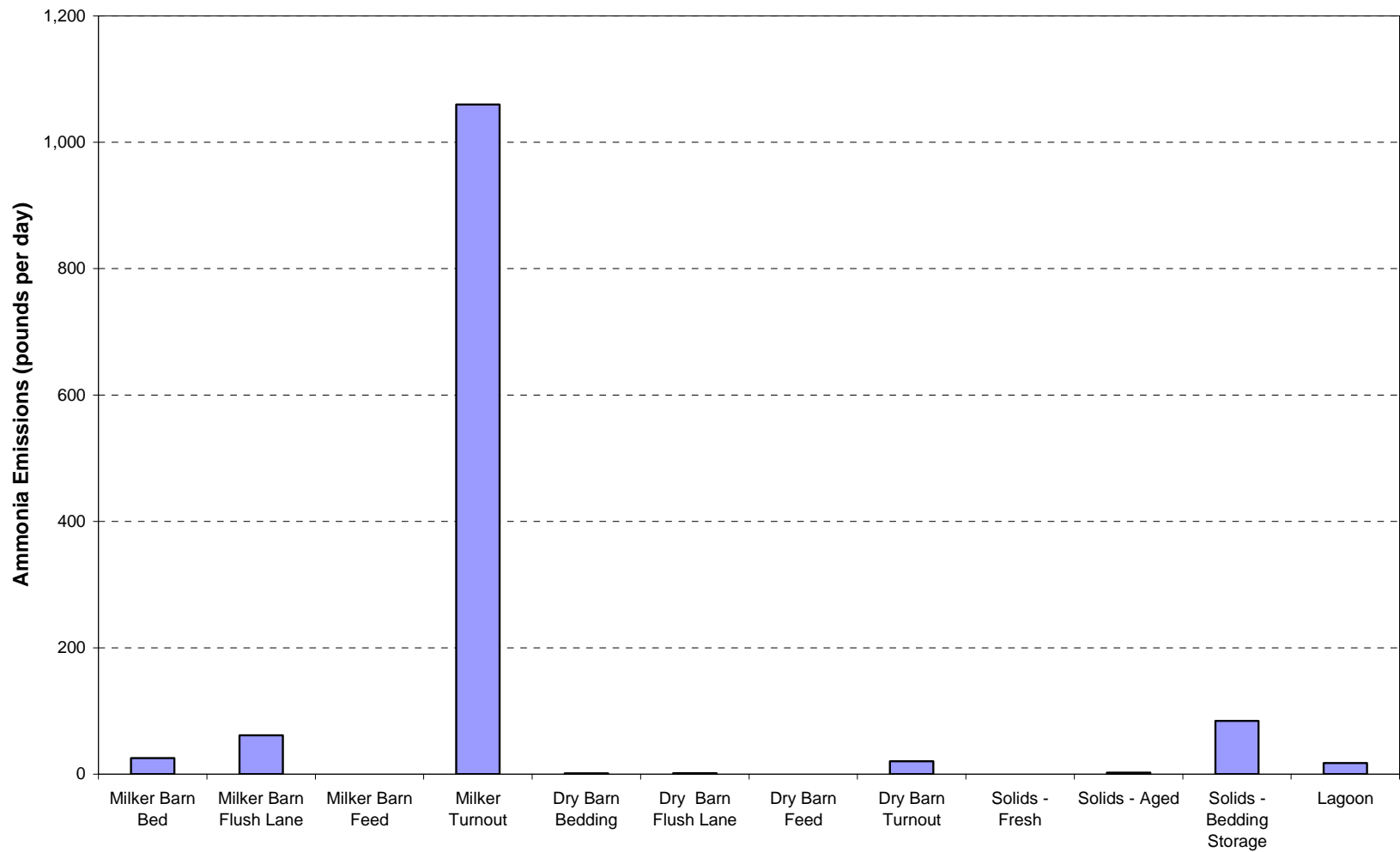


Figure 2. - Dairy ROG (VOC) Emissions (as tested condition)

