Assessment of Reactive Organic Gases and Amines from a Northern California Dairy Using the USEPA Surface Emission Isolation Flux Chamber

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Purpose of the Discussion

- Present the USEPA flux chamber technology and the application for assessing air emissions from dairies
- Describe the ARB/SJV multi-phase research project and the results of the Phase 2 summer testing event (process flux, dairy emissions, pounds/cow/year)

Project Authority

- Co-Funded by ARB and SJVUAPCD
- Sponsored by the Central CA Ozone Study
- Work coordinated with other projects by the San Joaquin Valley Ag Tech Group
- Project Management by Patrick Gaffney, ARB
- Emission factors supporting SIPs/SB700

Project Scope of Work

- Developed a Site specific QAPP (Phase 1)
- Conducted a two-day field test (Phase 2) at the Merced dairy
- Over 40 flux chamber measurements were made at 11 types of emitting surfaces at a flushed lane dairy
- Analysis included speciated reactive organic gases, ammonia/amines, total organic compounds, and methane
- Empirical model developed to estimate emissions

Analytical Menu

- USEPA Method TO-15 (GC/MS) for VOCs, ROG (expressed as methane and hexane)
- NIOSH 2010 (IC) for ammonia and amines
- ASTM 3416 (GC/FID) for methane
- USEPA Method TO-11 (HPLC/UV) for aldehydes/ketones
- EAS Method (HPLC/UV) for volatile organic acids

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

Dairy Unit Processes (sources)

- Flushed lanes: pre and post-flushed
- Solids storage piles*
- Lagoon* (inlet and outlet of lagoon)
- Solids in Solids separator*
- Bedding in pile for freestall*
- Freestall area

Dairy Unit Processes (continued)

- Barn turnout and corral area*
- Manure piles in turnout*
- Heifer pens (dry cow area)*
- Open feed storage (in barn feed lanes)
- Milk parlor (wastewater effluent stream)*

Note- Process in sun* tested for diurnal emissions

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

(continued)

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
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**	

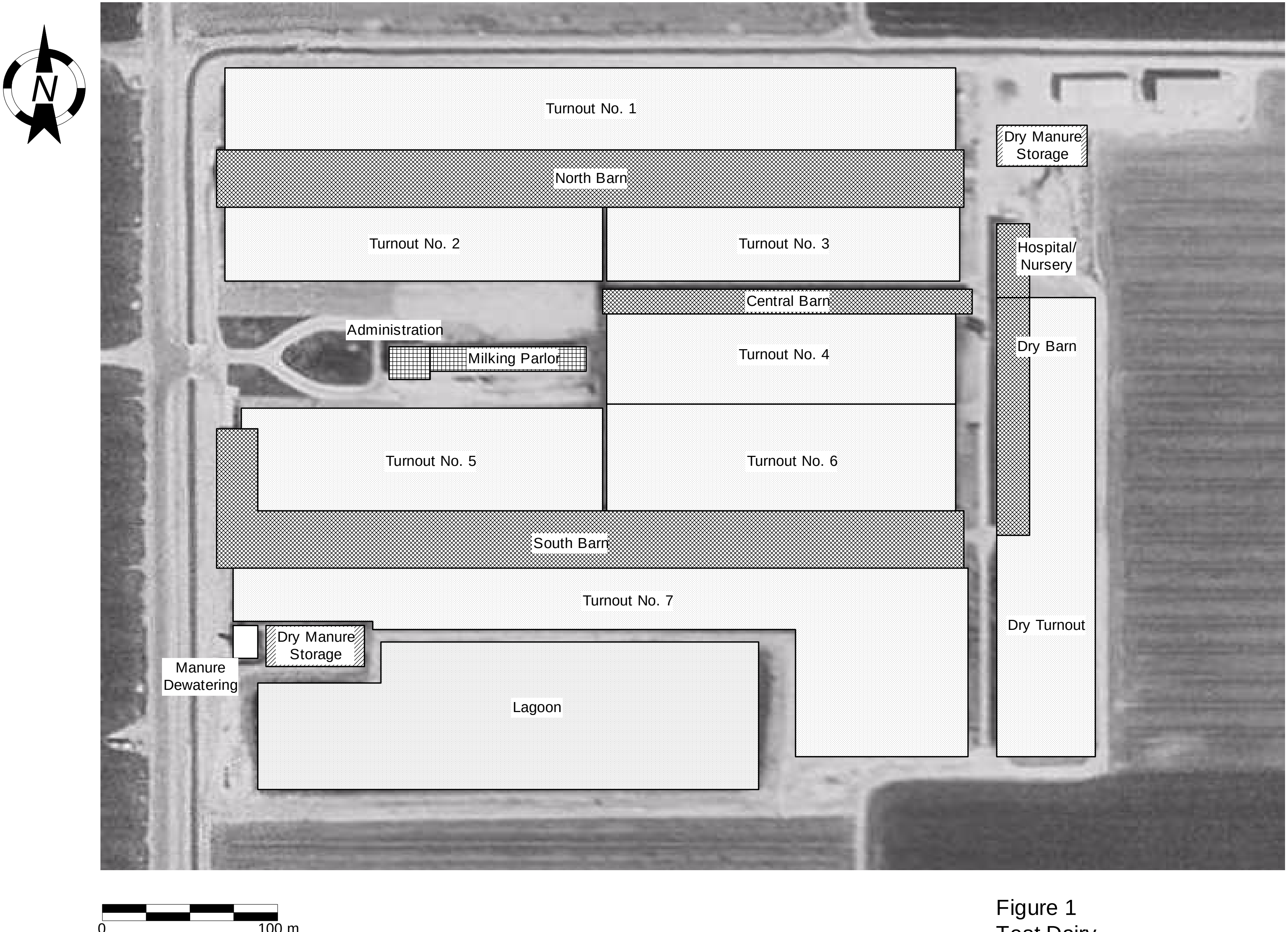
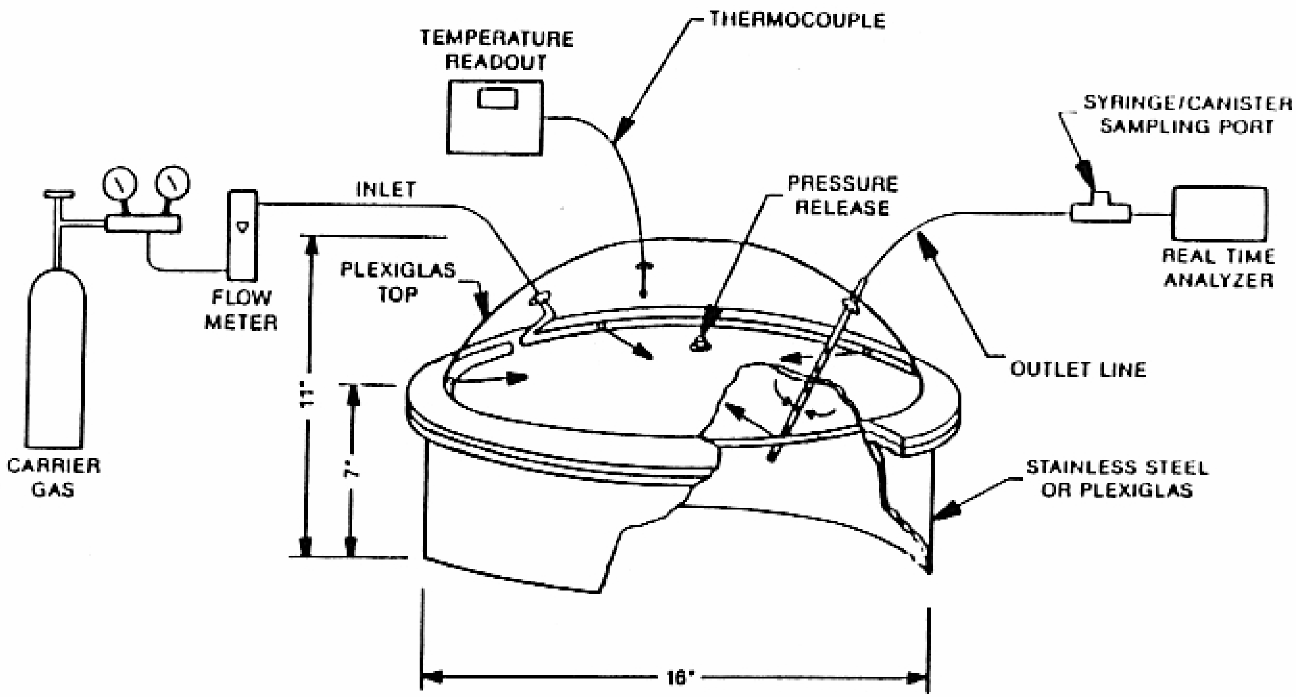


Figure 1
Test Dairy
Site Plan

What’s A Flux Chamber?

- A flux chamber is a device used for measuring the flux of gas species from an area source
- There are a variety of ‘flux chambers’, static and dynamic
- USEPA Recommended Technology, mixed tank reactor operated at atmospheric pressure



CUT AWAY TO SHOW
SWEEP AIR INLET LINE
AND THE OUTLET LINE

Four Groups of Area Source Assessment Technologies

- Direct Measurement
- Indirect Measurement
- Predictive Modeling
- Fence line Measurement and Dispersion Modeling

So Why Use The Flux Chamber Technology Over the Others?

- Assessment does not involve predictive modeling
- All parameters of the measurement technology are controlled and an estimate of accuracy/precision is made per application
- Most cost-effective assessment technology
- Can differentiate between sources of emissions at a complex-source facility

Theory of Operation

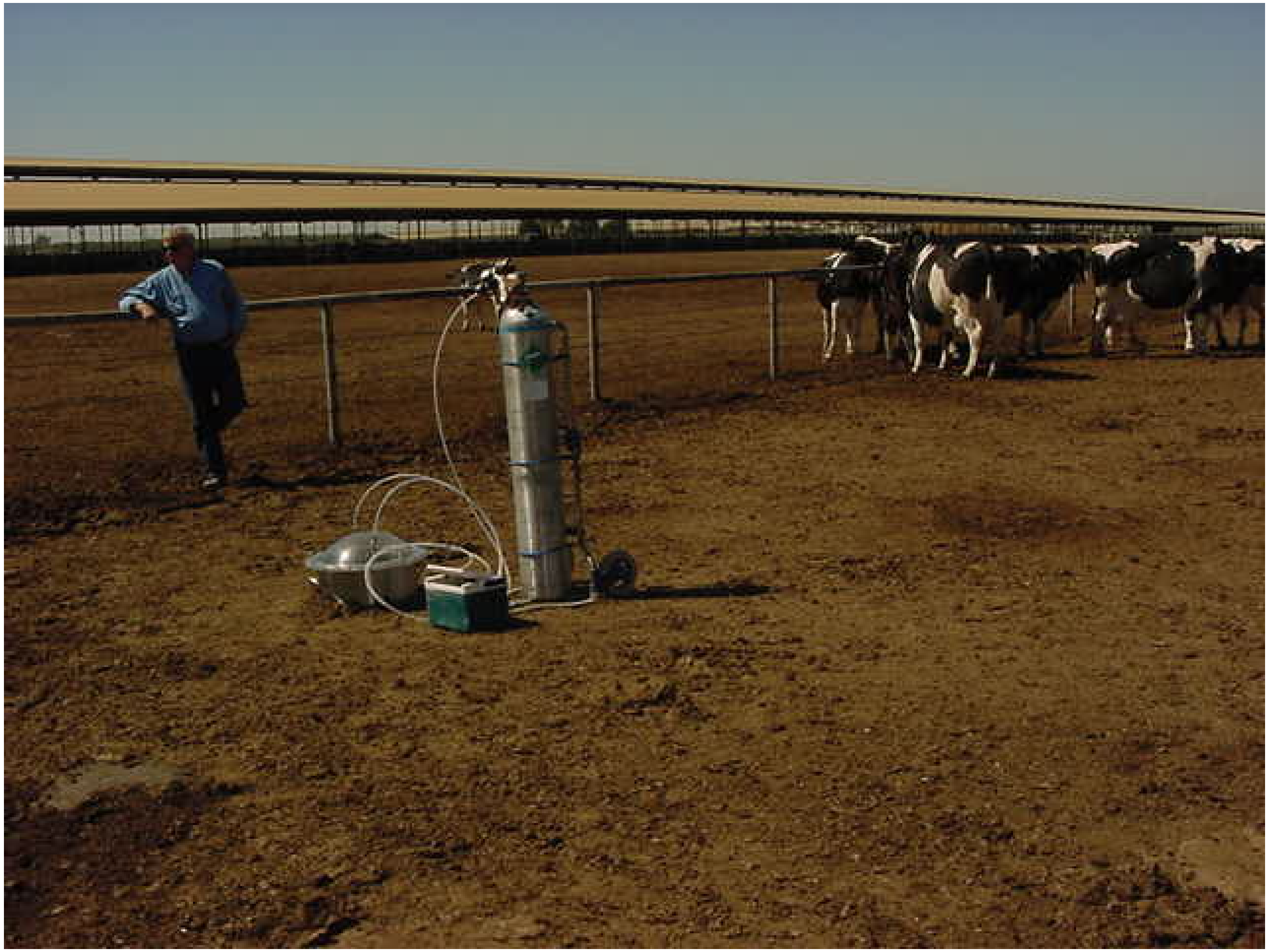
- Mixed tank reactor- CSTR
- Clean sweep air is added to the chamber
- Chamber is operated for 5 residence times
- Chamber contents come to equilibrium
- Gas sample is collected for study compounds (grab or integrated sample collection)
- Flux is calculated knowing sweep air flow rate, surface area, and concentration

Goal of the Assessment Using the Flux Chamber

- Measure the compound (or odor) flux from the area source without disturbing the flux and without predictive modeling
- Provide a data set that represents the area source emissions (flux times surface area is emissions in mass/time)
- Report the range, average, and maximum compound flux as a function of the area source (i.e., spatial, process, chemical/physical source changes as a function of time)

Advantages of Using the Direct Measurement/Flux Chamber

- Only EPA recommended in-depth assessment technology applicable for most area sources
- Known accuracy and precision
- Very low sensitivity using appropriate sample collection and analysis
- Spatially specific technology; defines unique emission sources
- Can differentiate the sources of ubiquitous compounds
- Provides the preferred input for dispersion assessment and compliance reporting



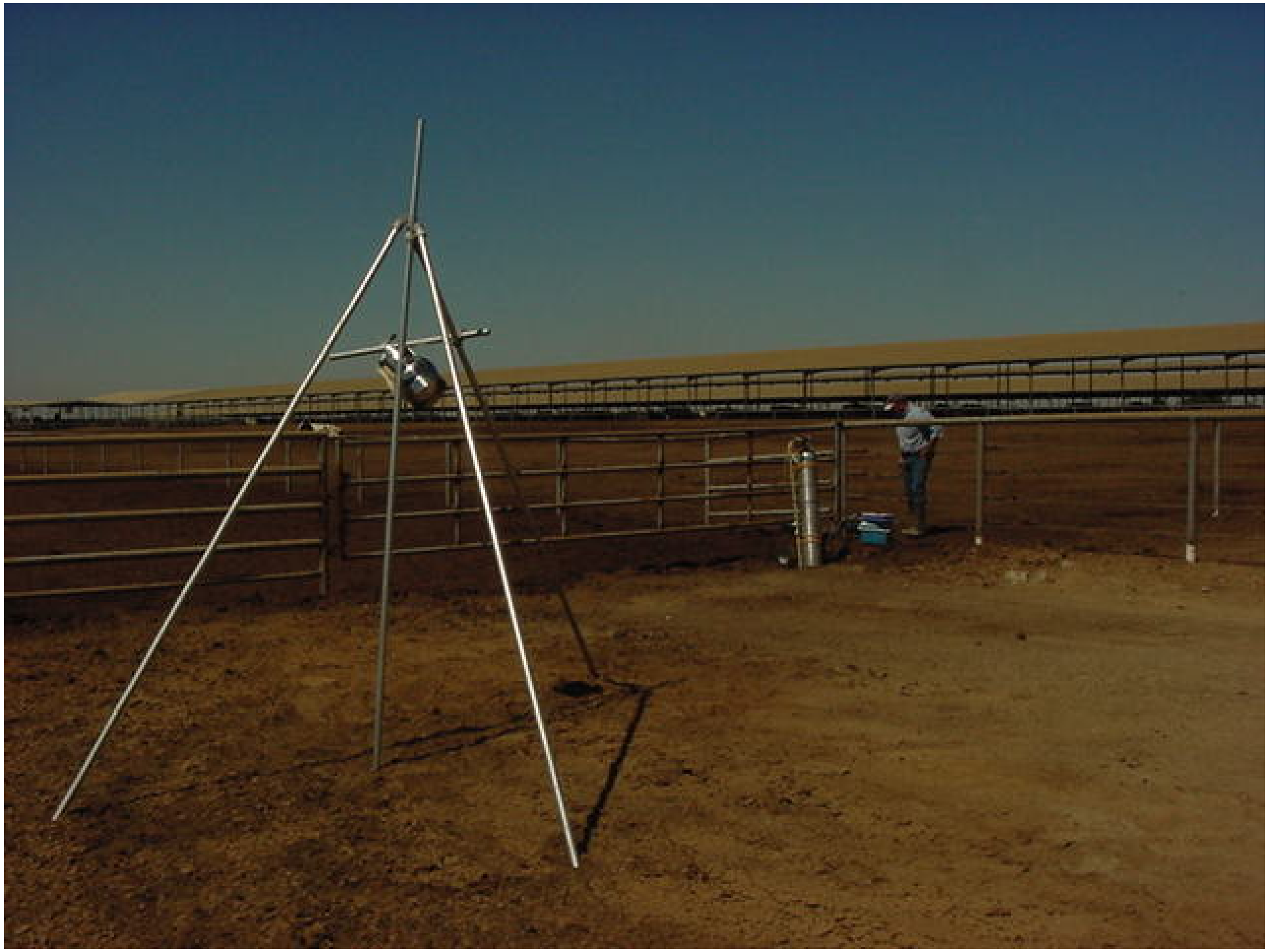


Figure 1. - Dairy Ammonia Emissions (As Tested)

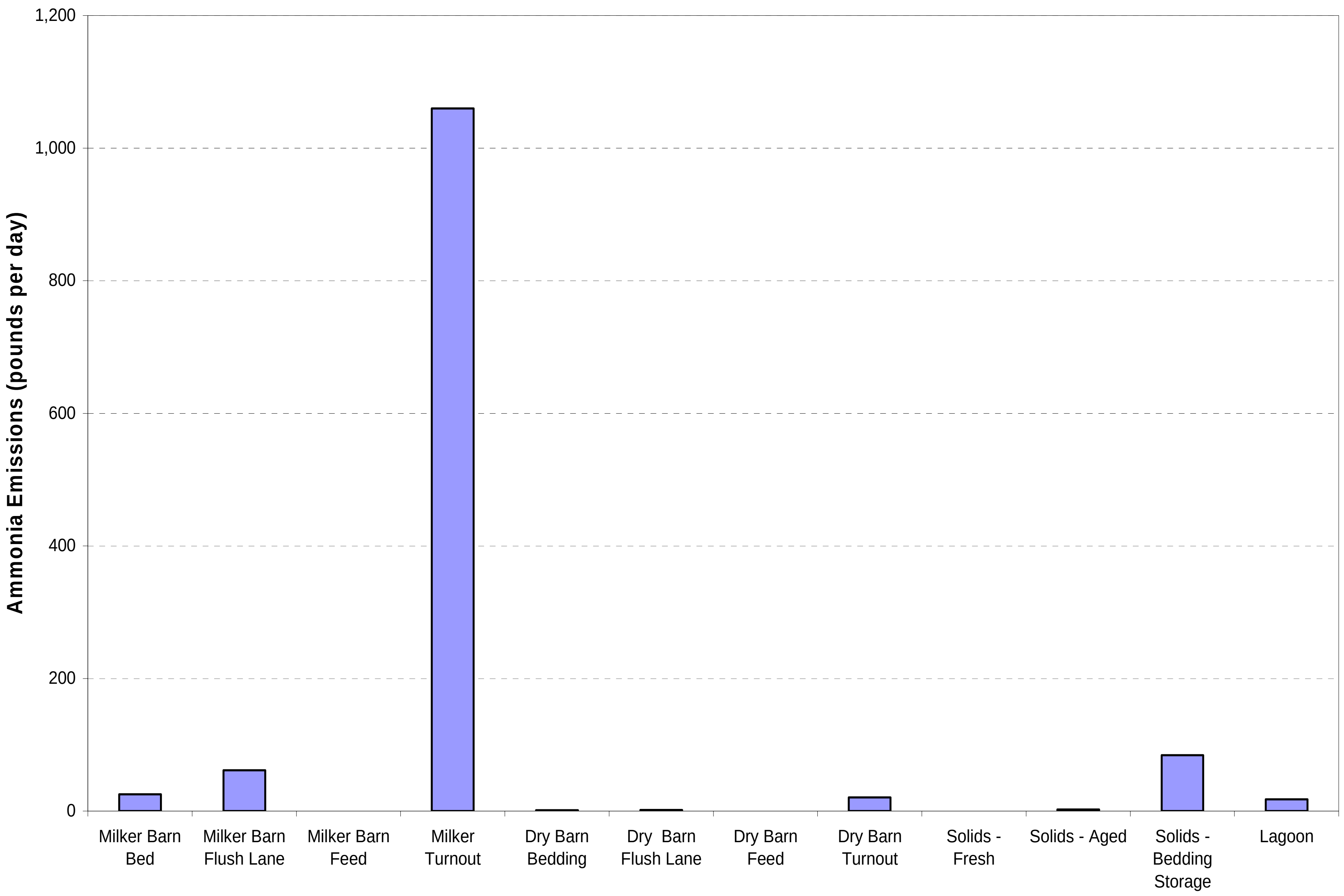
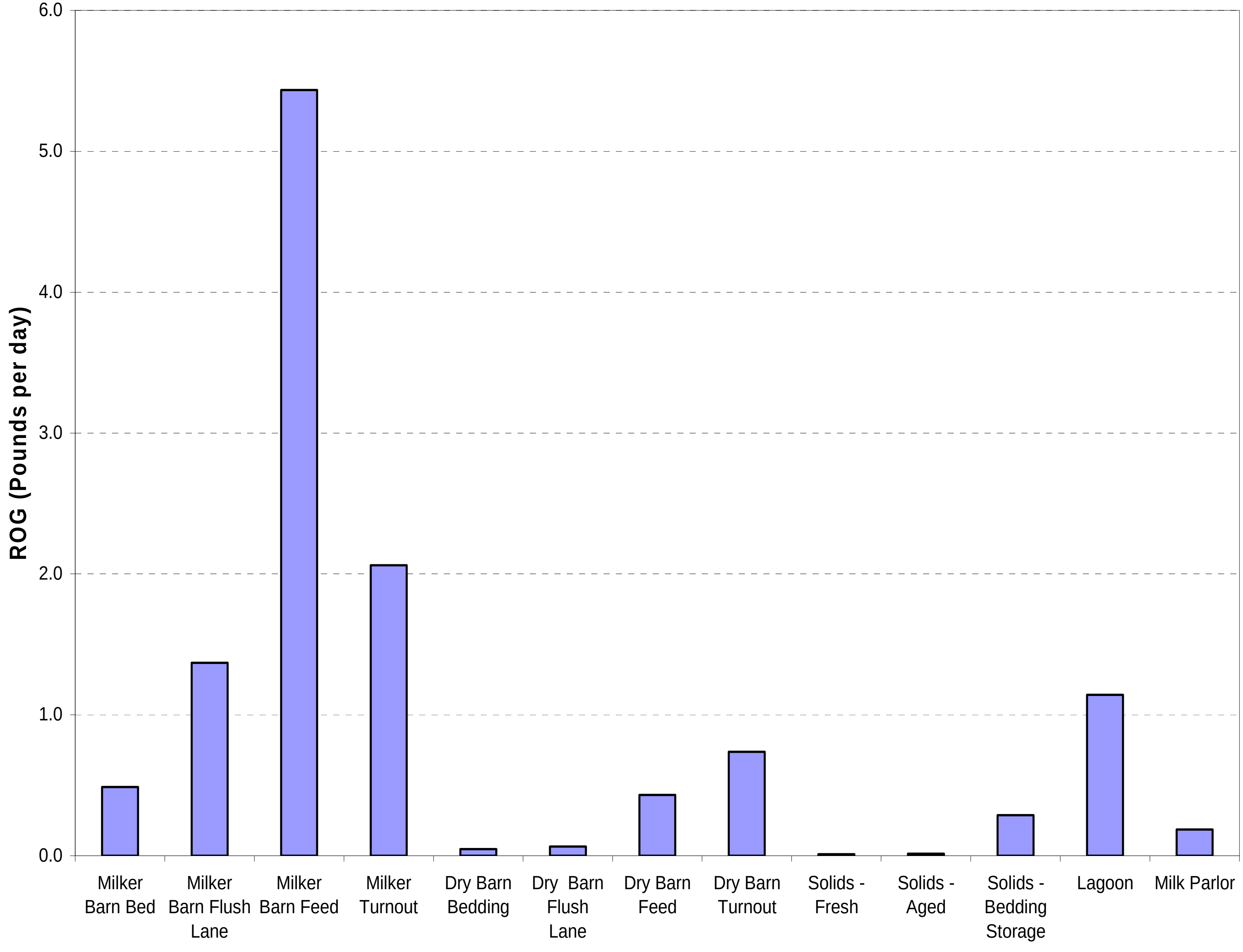


Figure 2. - Dairy ROG (VOC) Emissions (as tested condition)



Type of Unit Process	**Unit Process**	**% NH3**	**%ROG**
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

Dairy Emissions- Phase 2 Summer Emissions			
Compounds Sorted by Compound Mass		(Continued)	
Component	**Lbs/cow/year**	**Component**	**Lbs/cow/year**
Ammonia	135		
Ethylamine	0.18	Carbon Disulfide*	0.027
		1,2,4-Trichlorobenzene	0.025
Methane	165	Tetrachloroethene*	0.019
TNMOHC as Methane	1.27	2-propanol	0.015
ROG (ppbvC reported as methane)	1.30	Hexachlorobutadiene	0.012
TOG	166	m/p-Xylene	0.012
Ethanol	0.78	Napthalene	0.012
2-Butanone	0.16	Toluene	0.012
Acetone* (ROG exempt compound)	0.16	1,2-Dibromo-3-chloropropane	0.011
Acetone* (ROG exempt compound)	0.13	Vinyl Acetate	0.010
Cyclohexane	0.040	1,4-Dioxane	0.009
Acetaldehyde	0.029	Hexane	0.008

Preliminary Phase 2 ROG (VOC) Results

- Schmidt: 1.3 lb ROG (VOC) lbs/cow/year based on flux chamber measurement
- Current Emission Factors: 12.8 lbs ROG/cow/head base on 1938 chamber study (VOC or ROG?)
- Region 9 EPA (Schmidt): 5.2 lbs VOC/cow/year based on flux chamber measurement
- ROG (VOC) by TO-15 summation calculated as SCAQMD 25.3 on carbon basis would be 0.83 lb/cow/year

Preliminary Phase 2 NH_3 Results Based on 3442 Cow/Dairy

- Schmidt: 135 lbs NH_3/cow/year based on summer flux chamber measurement at one flushed lane dairy (note- turnout scraping conducted the day prior)
- Schmidt/SCAQMD: 18 lbs NH_3/cow/year based on winter/summer flux chamber measurement at two, dry lot dairies

Literature Dairy NH3 EFs	Low	High
Source	**Lb/cow/yr**	**Lb/cow/yr**
NOAA 1999	50.38	
Pinder et al	28.82	122.1
Sutton et al 1995	48	72
Corsi 2000	43	101
USEPA 2001	51	
USEPA 2002	55	
EEA 2001	54.2	
Groot Koerkup 1998	9.1	26.8
Dutch Ag	9.5	24.2
Pedersen et al 2004	15.3	
Max is 122 lb/cow/yr; Min is 9.1 lb/cow/yr		
Average is 46, st.dev. 34		

Gross Conclusions

- Barn feed source dominates ROG (VOC) process emissions
- ROG (VOC) emissions less that TNMOC emissions
- The dominate ROG species is ethanol
- Ammonia is the dominate amine, but ethyl amine is significant (ROG compound; time dependent)
- Freshly scraped turnouts dominate ammonia emissions
- ROG and ammonia emissions relatively low from the wastewater lagoon

Summary

- Process specific flux and emission estimates for a representative Northern California dairy were generated for total and speciated ROG (VOC) speciated emissions
- Facility-wide emissions were calculated
- Estimate of ROG (VOC), TOG (total), ROG species, and amine species per cow emission factors were generated

Future Research

- Phase 3 research may include:
  - **Option A**: More testing at the same dairy to evaluate seasonal emissions at significant sources (winter season) and diurnal variability (NH_3 and ROG)
  - **Option B**: Testing at a different dairy to evaluate within day and dairy-to-dairy variability
  - **Approach Modifications**: lab method for ROG, emphasis on ethyl amines, diurnal testing, focus on major sources, operations and facility utilization consideration