California
Air Resources Board

Dairy Air Emissions

Summary of Dairy
Emission Estimation Procedures

Report

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1. Executive Summary

The USEPA Surface Emission Isolation Flux Chamber was used to quantify air emissions from multiple unit processes at two dairies located in California's San Joaquin Valley. Samples were taken from Dairy 1 in the fall of 2004 and 2005. Samples were taken at Dairy 2 in the fall of 2005. The flux chamber data was used to estimate emissions for specific process areas. Process areas tested included turnouts (corrals), lagoons, silage piles, bunker feed, manure storage piles, and flush lanes.

The following figures present the emission estimates for both reactive organic gas (ROG) and ammonia on an annual per cow basis. The data suggest substantial variability on a dairy-to-dairy and season-to-season basis. In addition, the following facts should be considered when using or interpreting this data set:

1. Feed, and feed handling, appear to be a significant source of ROG. Because of very high variability and limited sampling of feed storage and handling compared to sampling of other dairy emission sources to date, additional research will be necessary to better quantify feed-related emissions. Identification of higher emitting components of feed and feed handling will be important for understanding how to reduce these emissions.
2. The organic gas mass emissions are reported as total reactive carbon as methane. This is the most universal method of reporting ROG emissions. However, this reporting may not be equivalent to other industries or jurisdictions so care should be taken when comparing this value to other ROG emission values.
3. Known dairy operating methods and this data set suggest that ammonia emissions could be overstated by as much as a factor of two. These dairies do not operate their turnouts in the wintertime and because of insufficient data no adjustment has been made to accommodate that fact.
4. The complete data set suggests that the ammonia emission estimate from Dairy 1 was more representative of peak emissions than of average emissions due to the turnout (corral) cleaning schedule and possible rainfall affects.

In addition, the review of this data set allows for the following recommendations:

1. Food and food handling emissions appear to be a significant source of ROG. Identification of higher emitting components of feed and feed handling will be important for understanding how to reduce these emissions.
2. For future projects, it is possible that full ROG compound speciation would only be important when a further understanding of emission mechanisms is required. The South Coast Air Quality Management District (SCAQMD) Method 25.3 has been shown to be a comprehensive ROG quantification technique and is recommended for future projects when the quantification of total ROG mass is important.
3. The important parameters for ammonia emissions variability include season-to-season and livestock turnout management. Future ammonia sampling data is needed mid-winter, in the spring (just prior to turnout use), mid-summer, and

immediately prior to end-of-turnout-season to characterize variability. In addition, emissions from various turnout management practices (scraping and harrowing) need to be quantified.

Figure ES-1 shows the total ROG emissions for Dairy 1 and Dairy 2 in year 2005. Method 25.3 data was not available from the year 2004 sampling so it is not shown in this figure. Figure ES-2 shows the total ammonia emissions for Dairy 1 in year 2004 and year 2005 as well as Dairy 2 in year 2005.

Figure ES-1 – Total ROG Emissions.

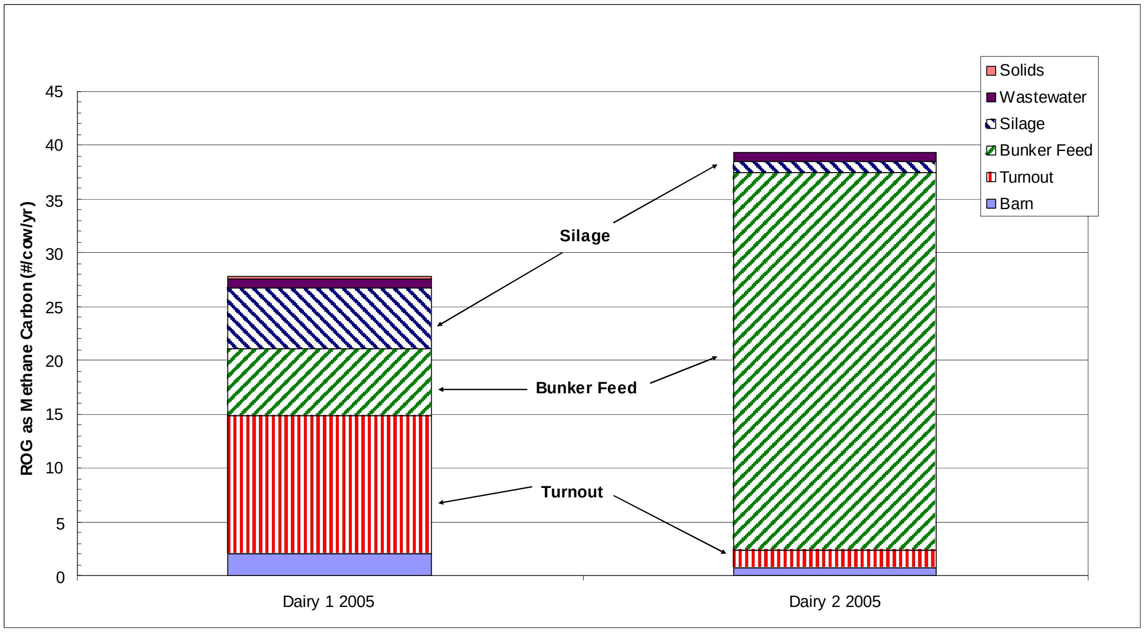
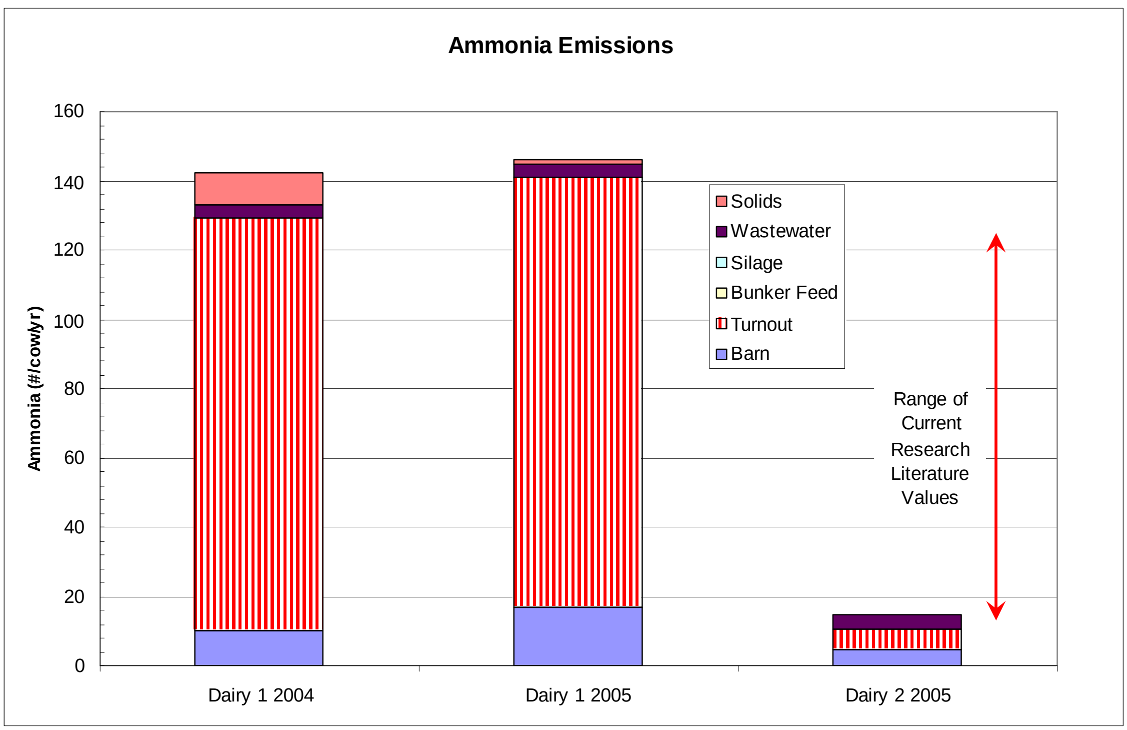


Figure ES-2 – Total Ammonia Emissions.



2. Introduction

2.1. Background

This project was undertaken to better understand the sources, quantity, and types of airborne emissions from at two dairies in the San Joaquin Valley in Central California. The first dairy (referred to as Dairy 1 in this report) is located in the Northern portion of the valley and was sampled in September 2005 at multiple emission points such as the turnouts (corrals), lagoon, silage piles, flush lanes, bunker feed, and manure piles. The dairy was again sampled in November 2005 to evaluate the variability of emissions from a corral (turnout) area over a 24-hour period. Dairy 1 was also previously sampled in September 2004 as part of a separate study. The second dairy (referred to as Dairy 2 in this report), was located south of Dairy 1 and multiple emission points were sampled in October 2005.

This report focuses on the overall emissions results for the project. Detailed information regarding test protocols, field test plans, laboratory results, quality assurance procedures, and other documents related to this study are available through the California Air Resources Board (CARB) staff.

2.2. Report Conventions

Gas phase organic compounds are referred to in several different ways in this report. The following are the definitions used in this report:

1. **Reactive Organic Gas (ROG) –** This represents all measured gas dispersed organics with methane, ethane, and CARB listed non-photoreactive compounds (e.g. acetone) specifically subtracted. It is reported as a mass value in methane equivalents unless otherwise noted (total moles of carbon multiplied by 16 g/g-mole). In addition, this value is always based on South Coast Air Quality Management District (SCAQMD) Method 25.3 unless otherwise noted.
2. **Total Non-methane, Non-ethane Organic Gas (TNMNEOG) –** This is the reported value in the laboratory analysis report for the South Coast Air Quality Management District (SCAQMD) Method 25.3. It represents all measured gas dispersed organic carbon except methane and ethane. It is reported as a mass value in methane equivalents unless otherwise noted (total moles of carbon multiplied by 16 g/g-mole).
3. **Organic Gas –** This refers to the generic, non-specific, organic emissions.
4. **Speciated ROG –** This represents a ROG value that was developed by summing individual speciated organic compounds. In most cases, this value will be less than the actual ROG because it is impossible to speciate all organic compounds. The compound speciation is usually based on the results of a TO-14 or TO-15 analysis, plus additional non-canister species analysis. The largest contributors to this value in the non-canister analysis were normally carboxylic acids.

3. Dairy Configurations

3.1. Dairy 1

Figure 3.1 shows the arrangement of components of Dairy 1. Dairy 1 had an off-site feed storage and mixing area that served multiple dairies. The component areas of Dairy 1 are shown in Table 3.1. The areas for the interior barn were calculated based on the fraction of the barn cross-section devoted to each component. In addition to the areas listed on Table 3.1, the open face of both of the silage piles (corn and hay) were estimated to be 10 x 25 meters each. These piles also served other dairies but at this time there was no attempt to pro-rate the surface areas to Dairy 1.

The barn cross section is shown in Figure 3.2. Dairy 1 had 3443 cows on site during the first event and 3412 cows on site for the second event. All cow counts were reported by the dairies based on the dairy records of cow inventories. Matt Beene, a researcher at Fresno State University who has monitored these dairies for years, provided the sampling team with the cow count inventory data.

Figure 3.1 – Process Area Plan for Dairy 1

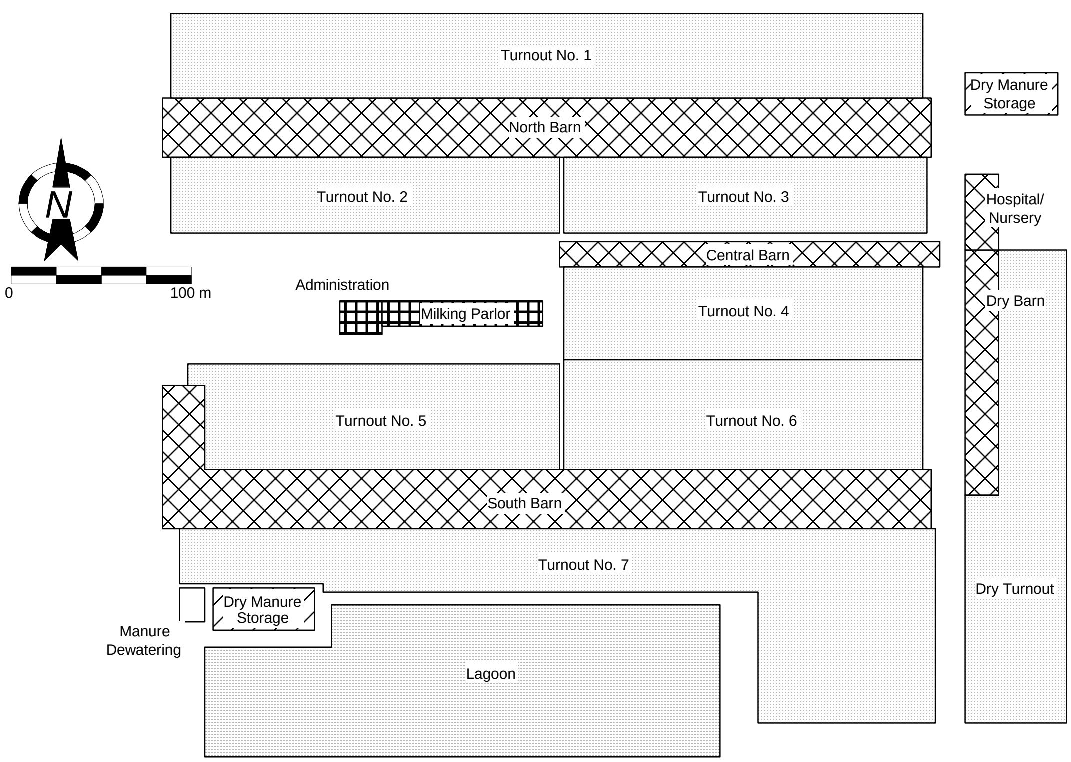


Table 3.1 – Component Surface Areas for Dairy 1 and Dairy 2.

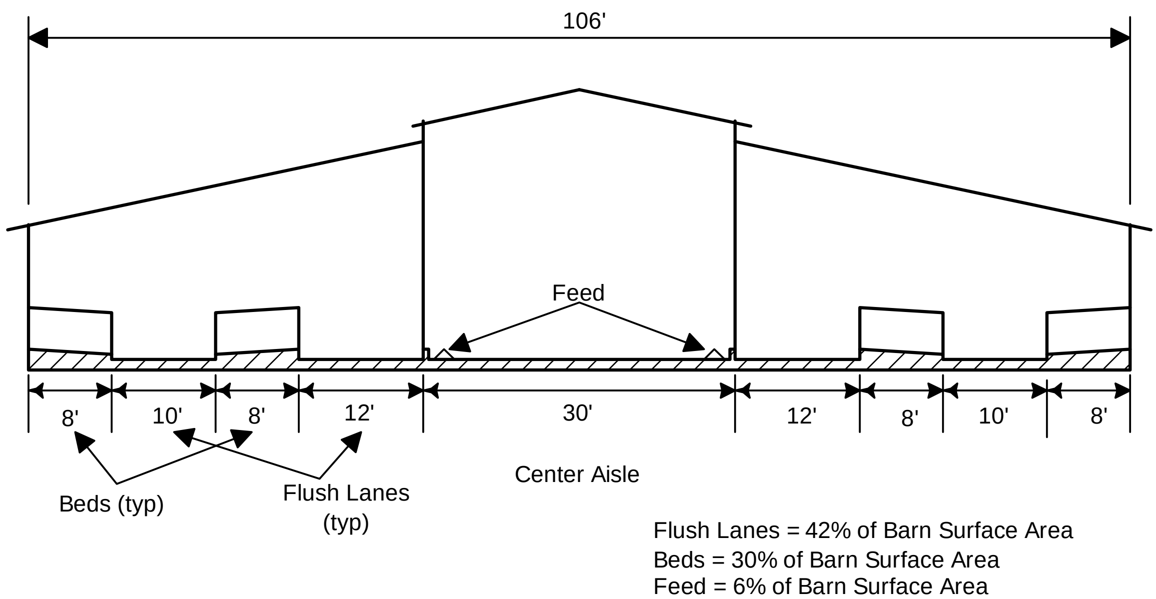
Dairy 1 Process Areas

Component		Area (m2)	
Turnouts			
1		19,558	
2		9,096	
3		8,505	
4		10,271	
5		11,644	
6		12,139	
7		21,527	
	Total	92,739	
Dry Cow Turnout		12,218	
Lagoon		22,478	
Manure Storage			
Fresh		66	
Solids		1,250	
Bedding		1,209	
	Total	2,526	
Active Milker Barns			
North Barn		13,995	
Central Barn		2,964	
South Barn		15,098	
	Total	32,057	
Flush Lane		13,464	
Beds		9,617	
Feed		1,923	
Dry Barn			
Barn total		2,548	
Flush Lane		1,070	
Beds		764	
Feed		153	
Milking Parlor		1,254	
Total Area		165,819	m2
		41.0	acres

Dairy 2 Process Areas

Component		Area (m2)	
Turnouts			
A		7,763	
B		7,763	
C		4,149	
D		5,501	
E		7,825	
F		16,565	
G		5,520	
	Total	55,086	
Wastewater Sources			
SS Pond		750	
SS Lagoon		2,821	
Storage Lagoon		15,495	
Solids Storage		2,000	
Barns			
A		9,417	
B		5,083	
C		9,490	
D		9,490	
	Total	33,480	
Barn Emission Sources			
Flush Lane		14,062	
Beds		10,044	
Food		2,009	
Silage Face		200	
Total Area		102,466	m2
		25.3	acres

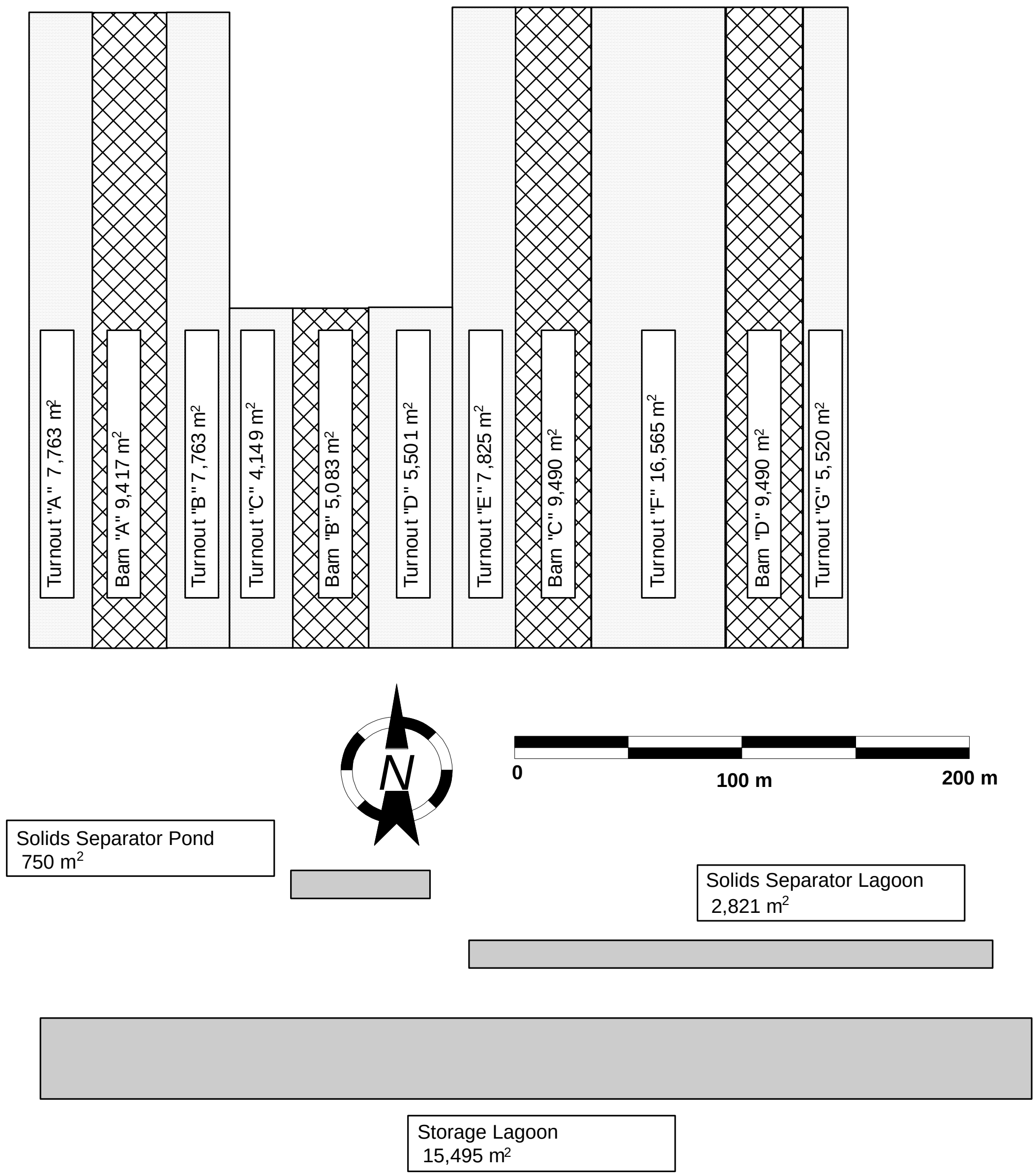
Figure 3.2 – Typical Barn Cross Section for Dairy 1



3.2. Dairy 2

Figure 3.3 shows the arrangement and surface areas for Dairy 2. In addition to these areas, there was a solids storage pile (20 x 100 meters) and an open silage pile face (10 x 20 meters). The barn at Dairy 2 had a slightly different configuration than Dairy 1, but essentially had the same fractional portion of sub areas (bedding, flush lane, and food bunker). Dairy 2 had 4725 cows on site during the testing event.

Figure 3.3 – Process Area Plan for Dairy 2



4. Sampling

Sampling details are provided in the sampling protocol document and the Data Validation Technical Memorandum prepared by Dr. Charles Schmidt. However a brief description of the sampling event is provided here. Figure 4.1 shows the sampling locations for Dairy 1 in 2004, Figure 4.2 shows the sampling locations for Dairy 1 2005, and Figure 4.3 shows the sampling locations for Dairy 2 in 2005.

Figure 4.1 – Sampling Locations for Dairy 1 in 2004.

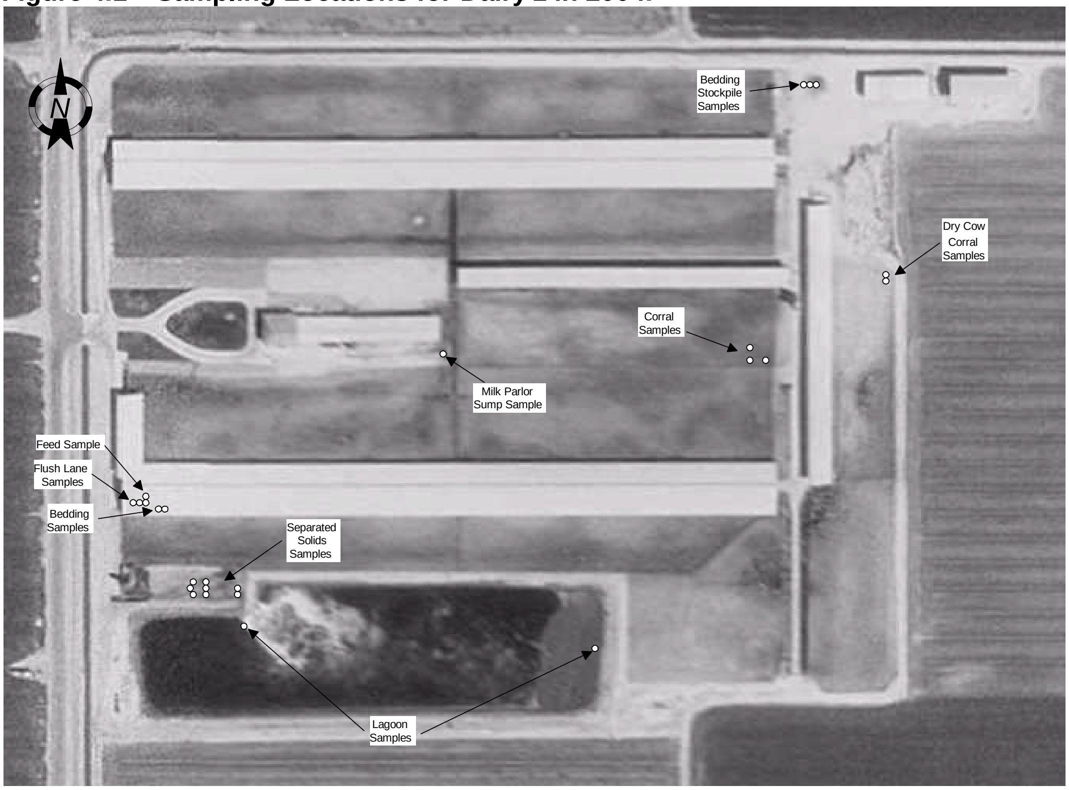


Figure 4.2 – Sampling Locations for Dairy 1 in 2005.

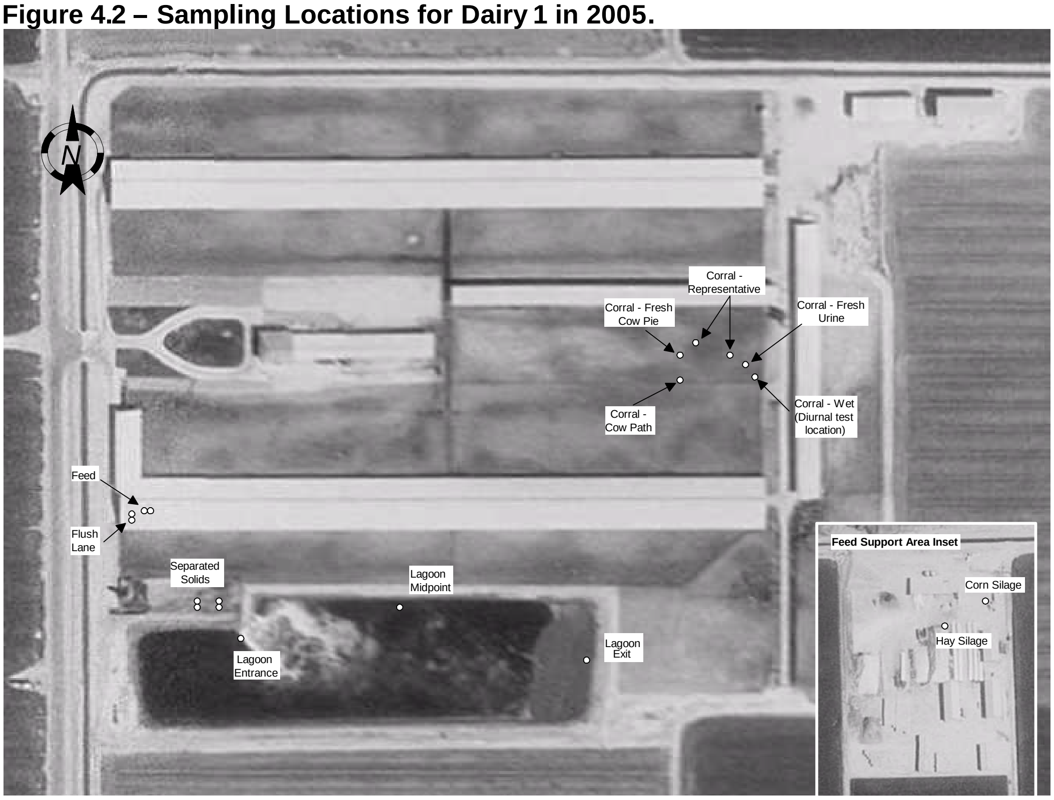
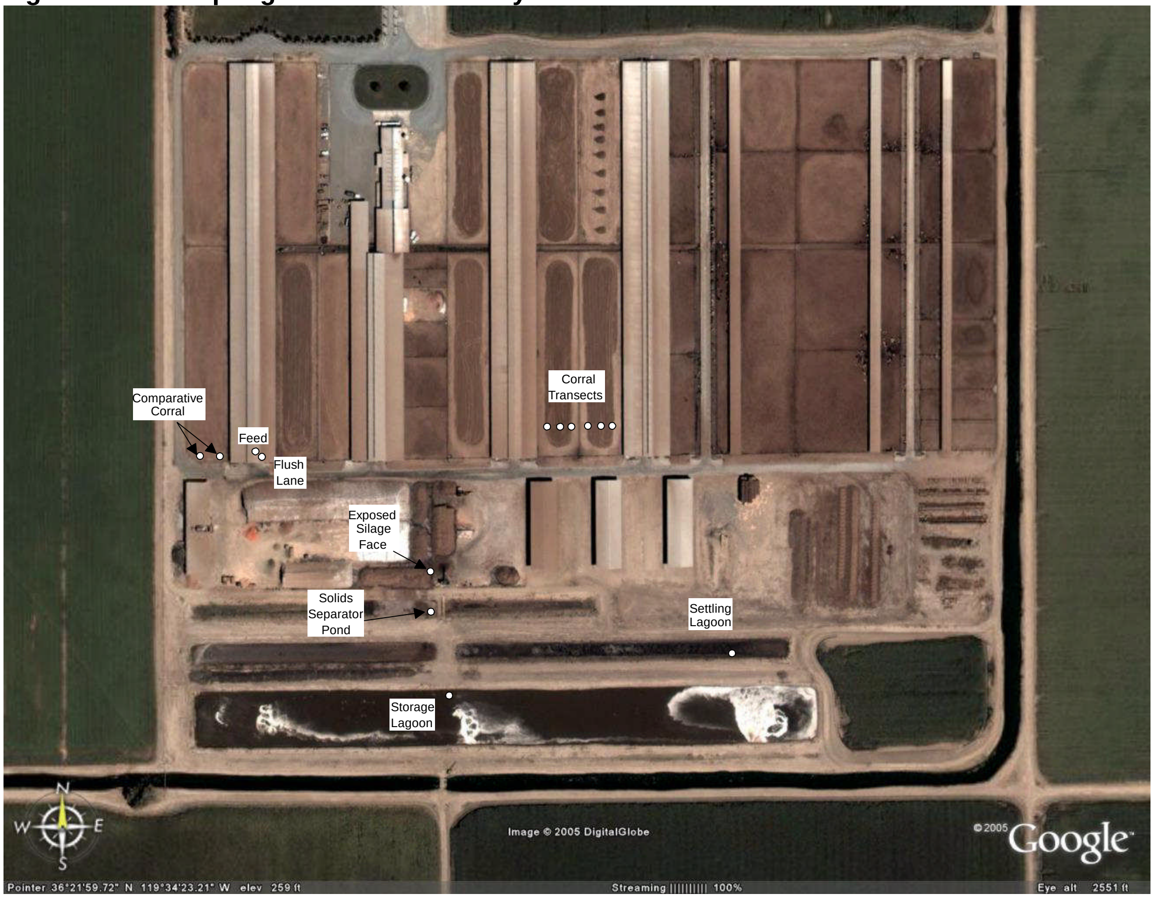


Figure 4.3 – Sampling Locations for Dairy 2 in 2005.



4.1. Dairy 1 2004

The processes tested during this event included flush lanes, bunker feed (feed distributed to cows for eating), corrals (turnouts), wastewater solids, lagoons, stall bedding, and milk parlor wastewater. Dry cow areas were tested separately from production cow areas. Samples were analyzed for ammonia and speciated organics out of a canister. A limited amount of sorbent sampling for aldehydes/ketones/organic acids was also completed.

4.2. Dairy 1 2005

The processes tested during this event included flush lanes, bunker feed (feed distributed to cows for eating), silage stockpiles (working face), corrals (turnouts), wastewater solids, and lagoons. Only production cow areas were sampled. Samples were analyzed for ammonia and TNMNEOG (total carbon minus carbon dioxide, methane, and ethane). In addition extensive speciation was completed.

4.3. Dairy 2 2005

The processes tested during this event included flush lanes, bunker feed (feed distributed to cows for eating), silage stockpile (working face), corrals (turnouts), and lagoons,. Only production cow areas were sampled. Samples were analyzed for ammonia and

TNMNEOG (total carbon minus carbon dioxide, methane, and ethane). In addition extensive speciation was completed.

5. Emission Estimate Development

Emission estimates were developed for the tested dairy components on a surface area basis and on a per cow basis. These emissions only represent the estimated emissions for the components tested at the specific dairies tested during the specific time they were tested. Emission estimates were developed using the following steps:

1. Using the sampling program results, representative unit area emissions (emissions/m^2) were developed for each process. The exact technique used for each process is described below.
2. The per day unit area emission estimates were then multiplied by the component surface area.
3. For livestock unit emissions (i.e., emissions/cow/yr) the component surface emissions were summed, then multiplied by 365 days, and then divided by the active cow count.

Note that the turnouts (corrals) are only used for six months per year (they are not used during the winter wet season) and the annual emissions are sample day emissions multiplied by 365 days. Therefore, these annual emissions could be off by much as a factor of two if the winter time emissions levels are substantially lower. This has the most impact on ammonia emissions.

In addition, it is technically possible to use other parameters rather than area or number of cows to compute emission estimates. For example, silage emission could be related to the volume of silage piles or the area of the exposed face. These alternative methods are not explored in this study, however the measured emissions data here could be scaled to other metrics in the future as they are available.

5.1. Organic Gas Reporting Background

Organic gas emissions are complicated because of the many methods available to quantify them and report them. We will focus on two types of analysis and one method of reporting.

5.1.1. Reactive Organic Gas (ROG)

It is our recommendation that the SCAQMD Method 25.3 results be used for the representative total organic gas measurement. This method is designed to capture all carbon and then subtract out carbon dioxide, methane, and ethane. In addition, this project subtracted out non-photoreactive compounds as well, to provide an estimate of photo-reactive organic emissions, also know as reactive organic gas (ROG) by the California Air Resources Board. The non-photoreactive compounds consist of 17 compounds (e.g. acetone). This non-photoreactive compound subtraction has an insignificant impact on the results and was only completed to comply with previously established protocols.

For this project all organic gas reporting, unless specifically noted otherwise, is provided as carbon as methane. This means that the total count of molecular carbon from qualifying organic species is added up and then multiplied by 16 g/gmole to get total mass. This is referred to in this report as methane carbon. The official Method 25.3 reporting instructions specify a molecular weight of 14.36 g/gmole and a method bias factor of 1.086. Using these values, an end value (mass basis) that is 3% lower than the values reported here would be produced. This project did not complete these last adjustments because they are specific to the SCAQMD jurisdiction and not necessarily representative of other jurisdictions that may be regulating the dairy industry.

In addition, many industries report emissions using different reference values and different methods, so, it is usually inappropriate to directly compare carbon as methane or other values between industries unless corrections have been made to normalize them for a representative comparison.

5.1.2. Species Reactive Organic Gas (ROG)

In order to compare provide comprehensive data sets, the data are also presented as a species ROG value. This is the sum of all identified USEPA Method TO-15 species that are photo-reactive plus relevant non-canister results. The non-canister results were usually organic acids or USEPA Method TO-13 compounds (phenols/SVOC). These values have a built in low bias compared with SCAQMD Method 25.3 because they only addresses compounds that can be identified.

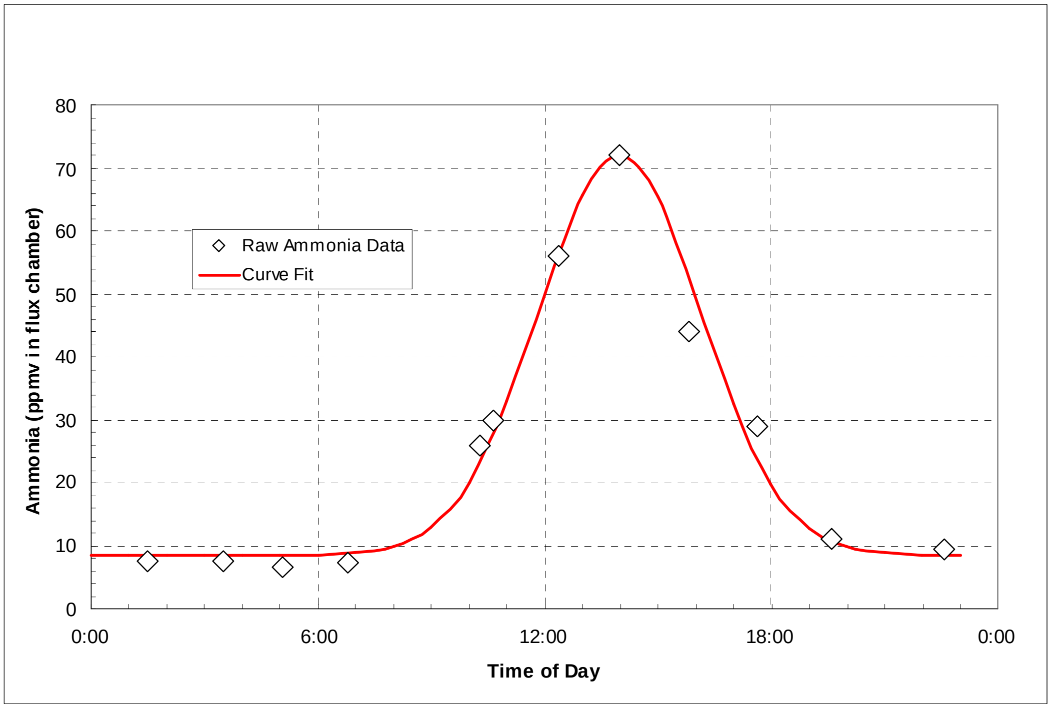
5.2. Time of Day Variability

Based on previous work it was known that ammonia emissions could be a strong function of time of day. The dominant source of ammonia emissions were the turnouts. Therefore a diurnal emissions sampling event was completed under this study. Only ammonia was found to have a significant diurnal profile. The ammonia results for the 24 hours study are shown in Figure 5.1. The data set was fit to the curve represented by the following equation.

$$NH_3(ppmv) = (NH_{3(MAX)} - NH_{3(AvgMIN)}) * \exp\left(\frac{-(t - T_{Peak})^2}{2\sigma^2}\right) + NH_{3(AvgMIN)}$$

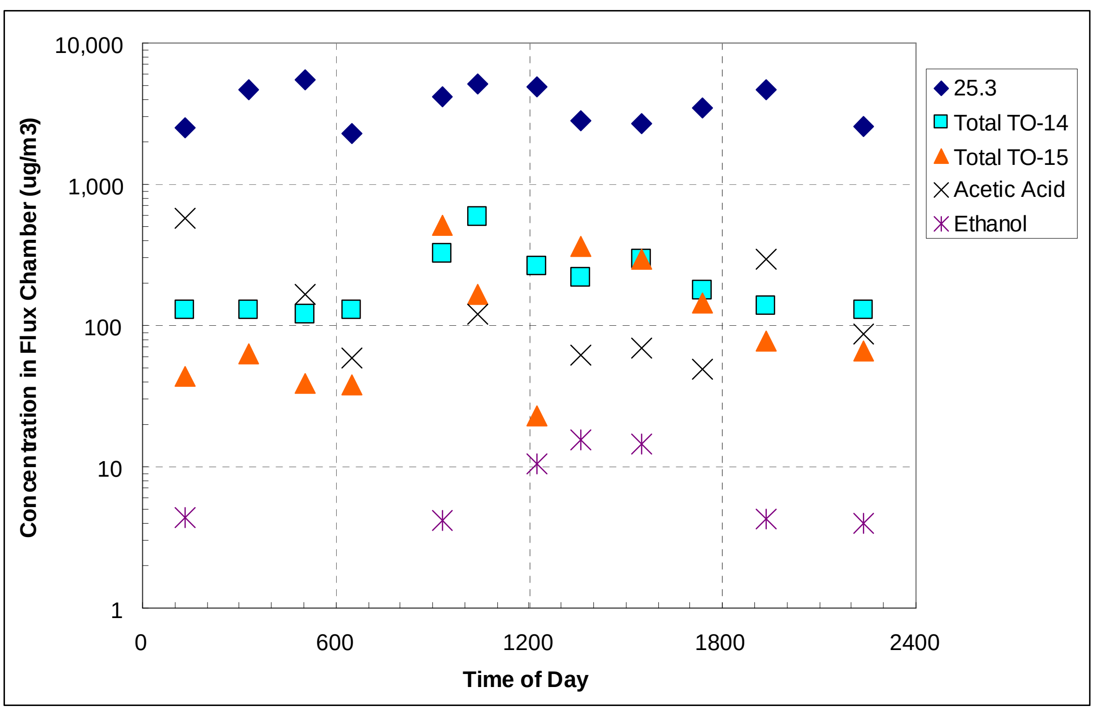
Where NH_{3MAX} = 72, $NH_{3AvgMIN}$ = 8.5, σ = 0.09, T_{peak} = 0.5826, and t = fraction of day (minutes/1440). All ammonia sampling data for the turnouts in 2005 were normalized against this curve. This had a significant impact on ammonia emissions for Dairy 1, but insignificant for Dairy 2. In addition, annual emissions were not corrected for the fact that the turnouts are only used in the summer. They are normally not used during the winter rainy season. This could affect ammonia emissions by up to a factor of two.

Figure 5.1 – Summary of Ammonia Emissions Over a 24 Hour Period.



This regular variability did not extend to other compounds. Figure 5.2 shows the diurnal variability of some other representative compounds and compound groups.

Figure 5.2 – Variability of Representative Organic Compound Emissions Over a 24 Hour Period.

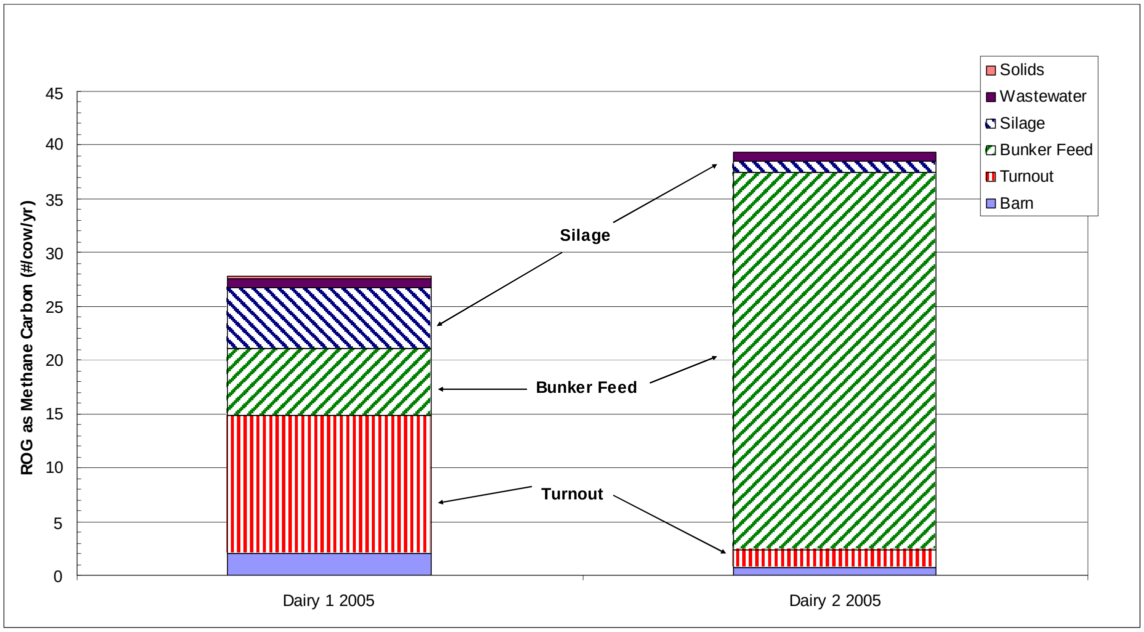


5.3. Summary of Emissions Tests

5.3.1. Organic Compound Results

Figure 5.3 shows a summary of hydrocarbon results for the year 2005 test events. The results are grouped into wastewater solids stockpiles, wastewater (lagoons), bunker food (food trough in barn), silage (operating face of pile), turnout (corrals), and barn (flush lanes and bedding). These results show turnouts dominate at Dairy 1 and food emissions dominate at Dairy 2. All other sources were insignificant. Organic compounds considered non-photochemically reactive (CARB listed) have been removed from the Method 25.3 data used in this figure.

Figure 5.3 – Summary of ROG Emissions for Year 2005 Events.



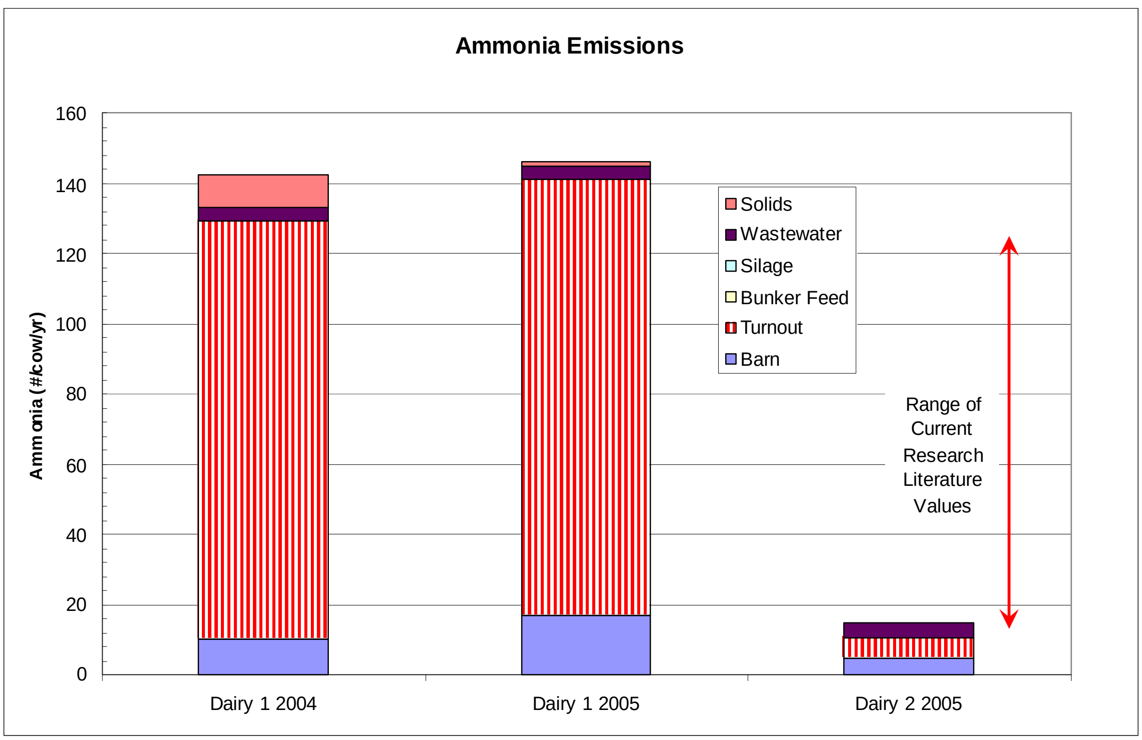
Dairy 1 was sampled in 2004 as part of a previous project where a different sampling and analytical method was used to estimate organic gas emissions (speciated ROG). The results using this previous method showed that Dairy 1 had speciated ROG emissions that were about 10 times higher in 2005 as in 2004.

5.3.2. Ammonia Results

Figure 5.4 presents a summary of ammonia results for all three facilities. At this time, the results for 2004 are not normalized against the diurnal curve. The results for Dairy 1 are quite high. The double headed arrow shows the current range of research literature values for this parameter. The primary source of ammonia emissions were the turnouts.

Dairy 2 had exceptionally low ammonia emissions. The primary difference between Dairy 1 and Dairy 2, as tested in 2005, was that the turnouts were constantly managed in Dairy 2 and were only cleaned out once per year at Dairy 1. The sampling at Dairy 1 happened the day prior to the annual clean out, so it could be conceivable that Dairy 1 was sampled at the peak annual ammonia emissions condition and the annual average was much lower. In addition, there was a non-seasonal light rainfall event two days prior to sampling at Dairy 1 in 2005. Water will react with solid phase urea in the turnout material to form ammonia.

Figure 5.4 – Summary of Ammonia Emissions.



5.4. Summary of Unit Emission Estimates

This section presents the unit emission estimates for ROG (per SCAQMD Method 25.3 reported as methane carbon with exempt compounds subtracted) and ammonia.

5.4.1. Dairy 1

The Dairy 1 unit emission factors are reported in Table 5.1 (main testing event) and 5.2 (24 hour study). In general, the full component emission estimates were developed by averaging the individual test location emission estimates. However, for the turnouts, a weighted average was developed based on visual observation of the turnout condition and manure loading during the test.

Table 5.1 – Summary of Dairy 1 (2005) Unit Emission Estimates (ROG per SCAQMD Method 25.3 as Methane Carbon minus exempt compounds) reported in micrograms per square meter per minute ($\mu g/m^2/min$).

Emissions Source	Fraction Allocation	ROG ($\mu g/m^2/min$)	Ammonia ($\mu g/m^2/min$)
Flush Lane			
Sample 1		167	NS
Sample 2		143	963
Average		155	963
Bunker Feed			
Sample 1		9,496	ND
Sample 2		8,143	ND
Average		8,820	ND
Corn Silage		49,329	ND
Hay Silage		17,656	ND
Lagoon			
Out		76	847
Mid		79	266
Inlet		169	266
Average		108	459
Turnout			
Wet	0.01	341	10,679
Urine	0.02	133	66,331
Representative 4" Thick	0.35	497	1,156
Representative 6" Thick	0.35	NS	3,894
Fresh Cowpie	0.02	378	211
Representative 1" Thick	0.25	183	1,098
Average		359	3,480
Wastewater Solids			
Sample 1		113	ND
Sample 2		117	ND
Average		115	ND

Notes:
1. NS means no valid sample.
2. ROG Turnout Average Emissions = (0.01*341+0.02*133+0.35*497+0.02*378+0.25*183)/(0.01+0.02+0.35+0.02+0.25)

Table 5.2 – Summary of Dairy 1 (2005) Unit Emission Estimates for the 24 hour study (ROG per SCAQMD Method 25.3 as Methane Carbon minus exempt compounds) reported in micrograms per square meter per minute (μg/m²/min).

Emissions Source	ROG (μg/m²/min)	Ammonia (μg/m²/min)
Turnouts	150	598

5.4.2. Dairy 2

The Dairy 2 unit emission estimates are reported in Table 5.3. The most complicated component to estimate was the turnout. For this case, it was assumed that 20% of the turnout was represented by the scraped condition, 40% by the harrowed condition, and 40% by the unscraped condition.

Table 5.3 – Summary of Dairy 2 (2005) Unit Emission Estimates (ROG per SCAQMD Method 25.3 as Methane Carbon minus exempt compounds) reported in micrograms per square meter per minute (μg/m²/min).

Emissions Source	Fraction Allocation	ROG (μg/m²/min)	Ammonia (μg/m²/min)
Flush Lane		102	963
Bunker Feed		71,302	39
Corn Silage		21,021	ND
Lagoons			
Separation Vault		229	578
Settling Lagoon		265	847
Storage Lagoon		149	847
Turnouts			
Scraped, 1"		149	178
Scraped, 1"		100	38
Scraped, 1"		84	132
Average	0.20	111	116
Harrowed, 2"		115	336
Harrowed, 3"		167	304
Harrowed, 2"		138	236
Average	0.40	140	292
Unscraped #1		96	526
Unscraped #2		144	1,053
Average	0.40	120	790
Turnout Weighted Average		126	456

5.5. Discussion of Unit Emission Estimates

5.5.1. Turnouts

Dairy 1 had about six times the ROG unit emission rate and almost ten times the ammonia unit emission rate as Dairy 2. Dairy 2 had much more intensive turnout manure management, which may or may not relate to the differences in emissions. Dairy 1 scraped and removed manure from turnouts once per year. Dairy 2 scraped and harrowed turnouts frequently, between once every few days to once per two weeks.

The 24 hour emissions study on Dairy 1, performed about a month after the initial testing, showed about a 50% reduction in the measured ROG emissions (at the same sampling location), and a reduction in the ammonia measurements by a factor of seven. This suggests that the main sampling event on Dairy 1 could be more representative of peak emissions rather than average typical emissions.

5.5.2. Flush Lanes

The flush lanes had essentially identical organic gas measurements for each dairy. This suggests that further evaluation of flush lane emissions could be de-emphasized if resources are limited. Both dairies flushed the lanes between two and four times per day.

5.5.3. Food

The unit level bunker food ROG emissions placed in the feed lanes for the cows to eat were a factor of eight higher for Dairy 2 than Dairy 1. ROG emissions from corn silage maintained in storage piles were a factor of two higher at Dairy 1 than Dairy 2. Ammonia emissions from food were trivial The bunker food at Dairy 2 was fresh and the bunker food at Dairy 1 was four to eight hours old.

5.5.4. Wastewater

Lagoon emissions were fairly similar and relatively low for both dairies. All measured values were within a +50% differential.

5.5.5. Wastewater Solids

Wastewater solids emissions of ROG are quite low at Dairy 1 for both 2004 and 2005. They were not measured at Dairy 2 (2005).

6. Special Issues

6.1. Food Components

Since food was such a dominant factor in hydrocarbon emissions, the known data on the food ration is presented here. The ingredient identification came from the Dairy Operations staff and it is likely that more definition will be required for further analysis.

Table 6.1 presents a summary of the food ration for Dairy 1 and Table 6.2 presents a summary of the ration for Dairy 2. Note that the ROG emissions for Dairy 2 were many times higher than Dairy 1. Also, the Dairy 1 feed emission measurements for 2004 were far lower than the 2005 measurements. The feed profiles indicate somewhat similar rations, so the feed emissions variability may be more complicated than just ingredient type, and also be affected by the age of the feed, weathering, exposure to the atmosphere, or other factors.

Table 6.1 – Food Ration for Dairy 1 (percent of total as dry weight).

	2004 Ration	2005 Ration		
Ingredient		Min	Cow Weighted Average	Max
Alfalfa Hay	19.9%	0.0%	0.4%	6.1%
Alfalfa Chop		9.9%	12.7%	17.3%
Alfalfa Silage	14.9%	6.3%	11.3%	11.8%
Corn Silage		0.0%	35.8%	50.2%
BMR Corn Silage	27.3%	0.0%	2.2%	34.1%
Distillers Grain	2.6%	1.7%	2.3%	2.5%
Cottonseed	5.7%	5.1%	6.6%	7.2%
Corn/Barley	11.4%	8.7%	11.4%	12.4%
Bakery	4.6%	2.8%	3.6%	3.9%
Beet Pulp		2.8%	3.6%	3.9%
Orange Pulp	3.6%			
Canola	5.7%	4.5%	5.9%	6.4%
Vitiamins/Minerals	1.2%	1.0%	1.2%	1.3%
Liquid Supplement	3.1%	2.4%	3.1%	3.4%
Buf/Min/Vit/Rum		0.0%	0.1%	1.2%

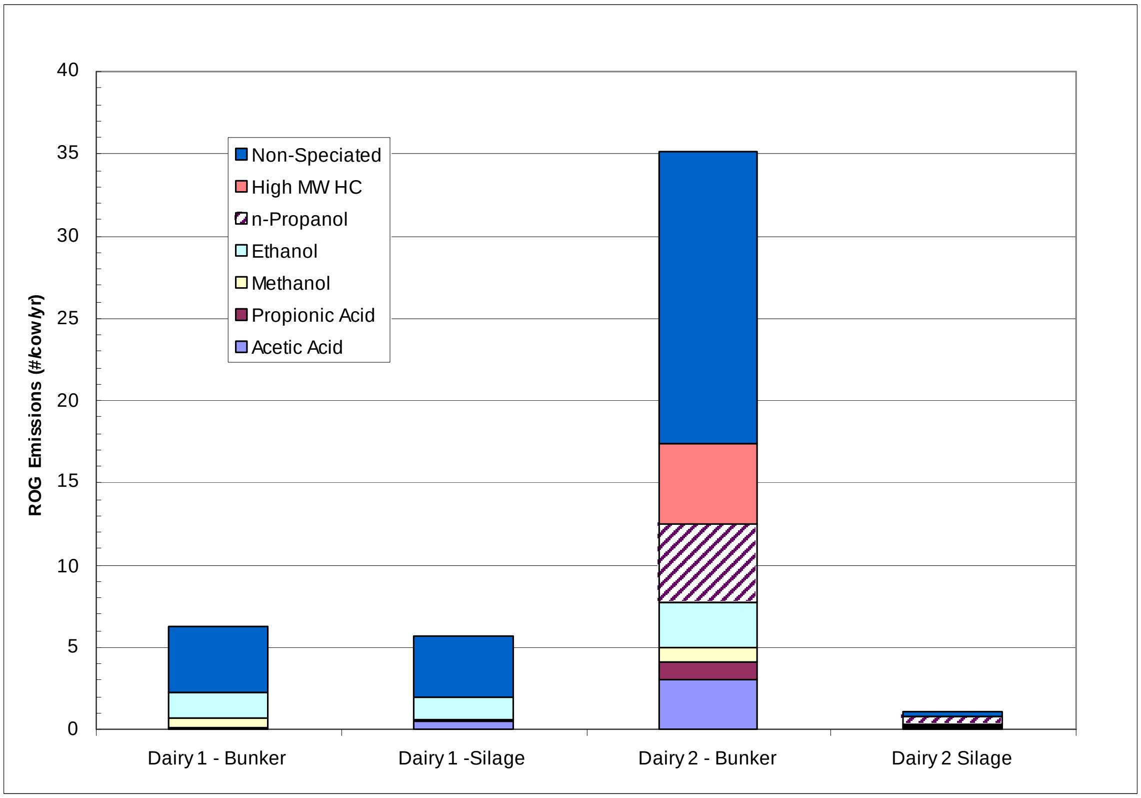
Table 6.2 – Food Ration for Dairy 2 (percent of total as wet weight).

Ingedient	Pounds	Percentage
Canola	8.79	7.6%
Rolled Corn	8.17	7.1%
Beet Pulp	6.01	5.2%
Distillers Grain	5.5	4.8%
Whole Cotton Seed	3.5	3.0%
Ground Pims Cotton Seed	3.25	2.8%
Almond Hulls	2.5	2.2%
Mineral Package	1.5	1.3%
Corn	30.1	26.1%
Wheat	16	13.9%
Green Chop Alfalfa	15	13.0%
Pressed Orange Pulp	8	6.9%
Alfalfa Hay	6	5.2%
Energy 2 Mix	0.8	0.7%
Total	115.12	

Figure 6.1 shows the major chemical species that contribute to the total food emissions from Dairy 1 and Dairy 2. Ethanol and methanol are the only similarly emitting compounds. Dairy 2 had substantial higher amounts of acetic acid, n-propanol, and a inconclusively identified hydrocarbon with a molecular weight of about 135 g/gmole.

The data shown in Figure 6.1 are a composite of results from several analytical methods used in the project.

Figure 6.1 – Chemical Speciation of Food Emissions



6.2. Organic Gas Emissions Methods

Figures 6.2 and 6.3 present a summary organic gas emissions data as measured by the various hydrocarbon emissions methods used for this project. These graphs quantify estimation methods based on canisters (Method 25.3, TO-14 and TO-15), non-canister methods (sorbents), as well as quantifying the amount of non-photoreactive compounds.

The following data are displayed in the graphs (note that all data are normalized to be reported as methane):

- 25.3 ROG: A summary of the total organic gas measured using the SCAQMD Method 25.3, with exempt compounds (measured by TO-15) subtracted out.
- TO-14 TNMHC (Integrated Detector): Total hydrocarbon non-methane carbon measured using a flame ionization detector (FID), which includes all carbon compounds.
- TO-15 Summed Species: Specifically identified hydrocarbons measured using TO-15. Compounds not explicitly identified by the method are not included in the mass.

- Non-canister Photo-reactive: The sum of all the compounds not measured in the canisters. This includes all impinger and sorbent methods for alcohols, VFA's, SVOC, etc.
- ARB Exempt Species Sum: Total of measured species listed as exempt compounds because they are defined as being non-photochemically reactive (e.g. acetone).

These figures demonstrate the following results:

1. As expected Method 25.3 produces the highest hydrocarbon values and the entire data set suggests that Method 25.3 is comprehensively measuring all hydrocarbons.
2. Dairy 1 turnouts have significant hydrocarbon emissions that are not picked up by canister methods using chemical speciation. Based on analysis of the available data, it was determined that the compound not measured in the canister is acetic acid.
3. Dairy 2 hydrocarbon emissions are completely food dominated.
4. Several non-photoreactive compounds were identified through the various test methods, but the measured mass is trivial.
5. About 40% of the ROG was able to be speciated for Dairy 1 and Dairy 2. Most industries that have a diverse hydrocarbon component (petroleum refining) can speciate between 5% and 20% of the total hydrocarbons.

Figure 6.2 – Dairy 1 Organic Gas Emissions Comparisons.

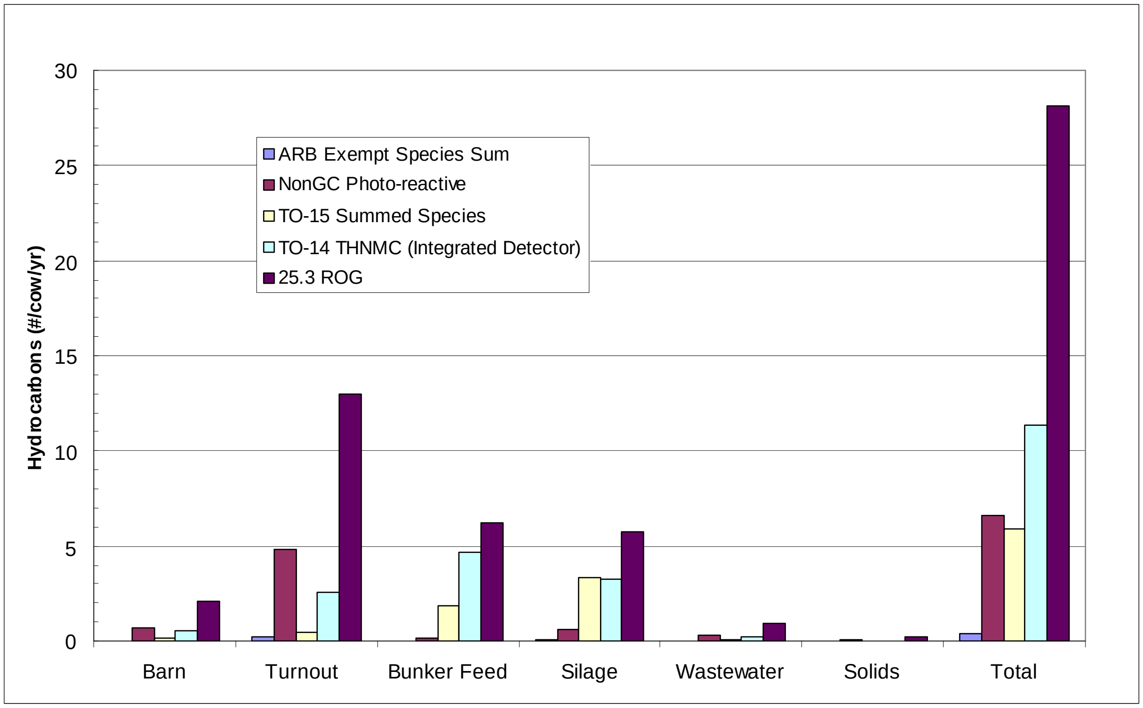


Figure 6.3 – Dairy 2 Organic Gas Emissions Comparisons.

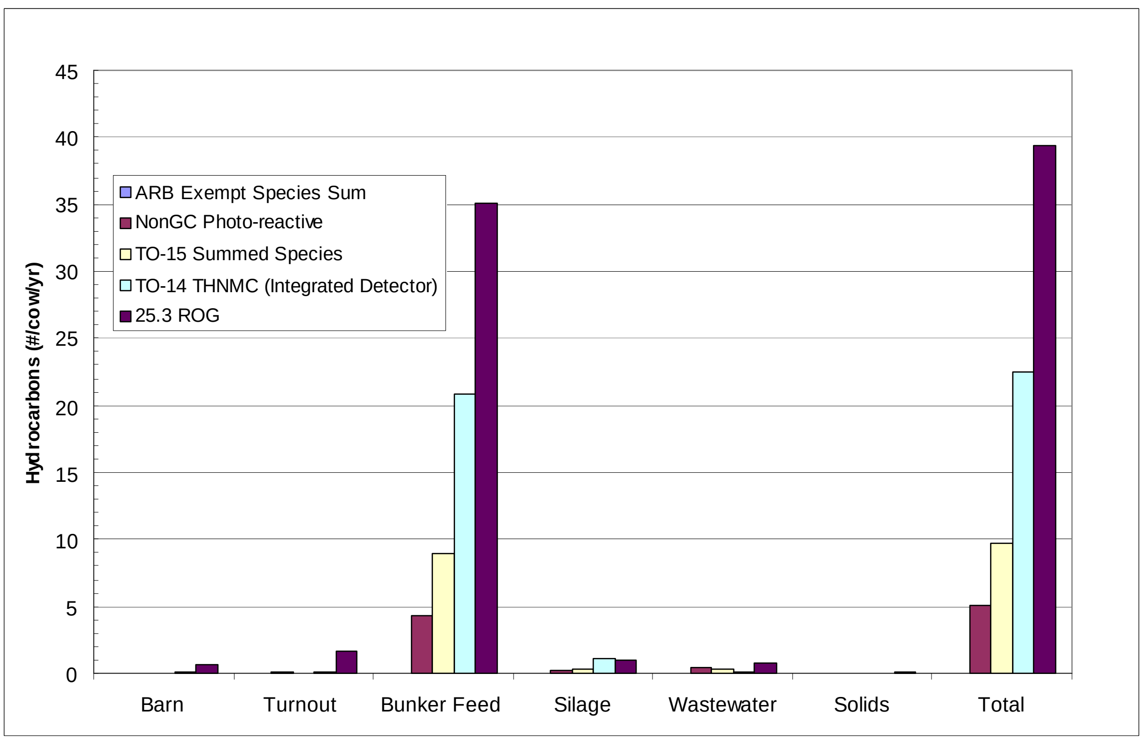
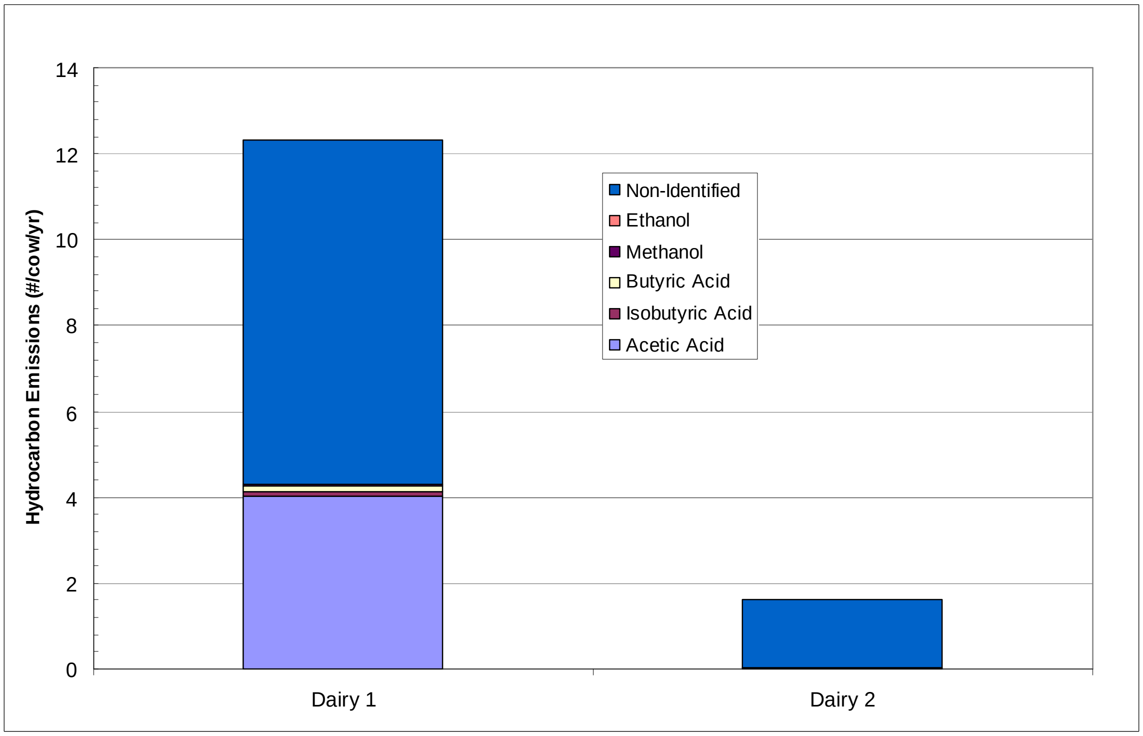


Figure 6.4 shows the details about the differences in turnout (corral) emissions from Dairy 1 and Dairy 2. The measured values of acetic acid for the turnout at Dairy 1 are substantial, but there is no clear explanation for this. The displayed data are based on a composite of TO-17, TO-15, and other data sources, normalized to carbon as methane and corrected for known exempt species.

Figure 6.4 – Turnout Organic Compound Emissions Comparisons.



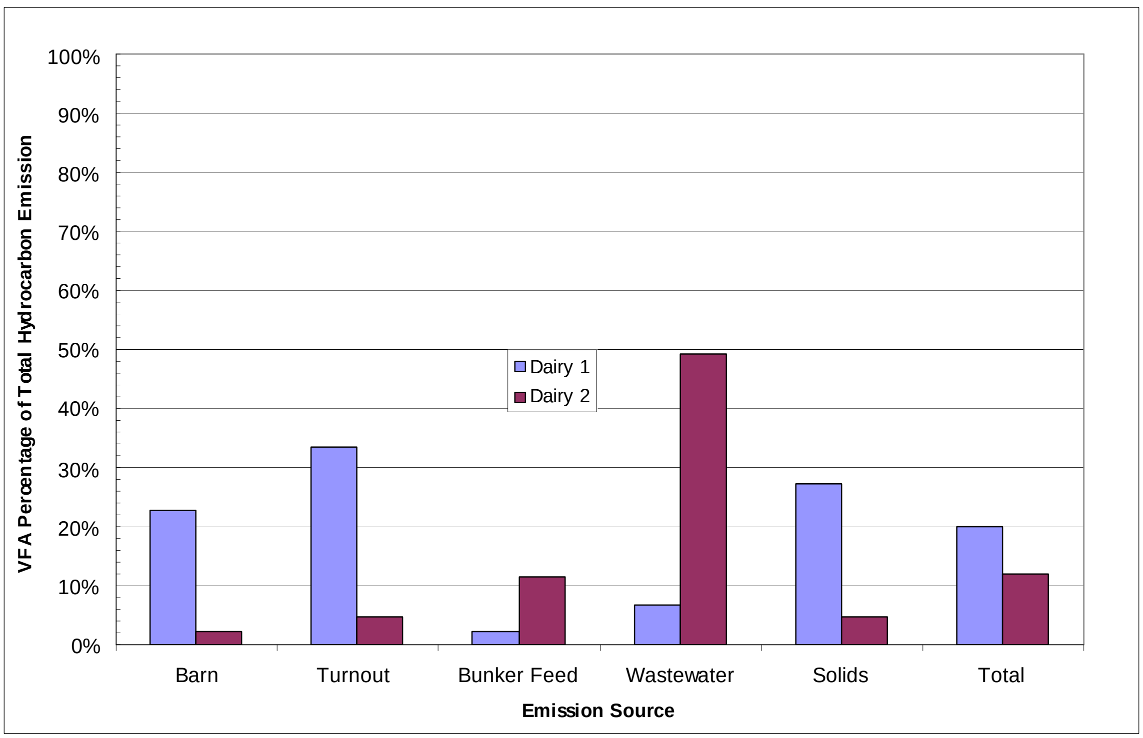
6.3. *Chemical Species*

This project completed a comprehensive assessment of chemical species. This section provides a summary of the results of that work. Graphs for the individual species are shows, which are followed by a summary table of the data used in the graphs.

6.3.1. Volatile Fatty Acids (VFAs)

Figure 6.5 shows the contribution of VFA's to the sum of the emissions for all of the tested processes. These compounds are significant contributors to the total measured organic gas emissions. The graph was generated using the ratio of the TO-17 VFA measurements divided by the total 25.3 organic compound mass (corrected for exempt compounds. Because of the significance of the measured VFA mass, total hydrocarbon methods that include these compounds, such as SCAQMD Method 25.3, should be used for future quantification efforts trying to estimate the complete organic compound mass.

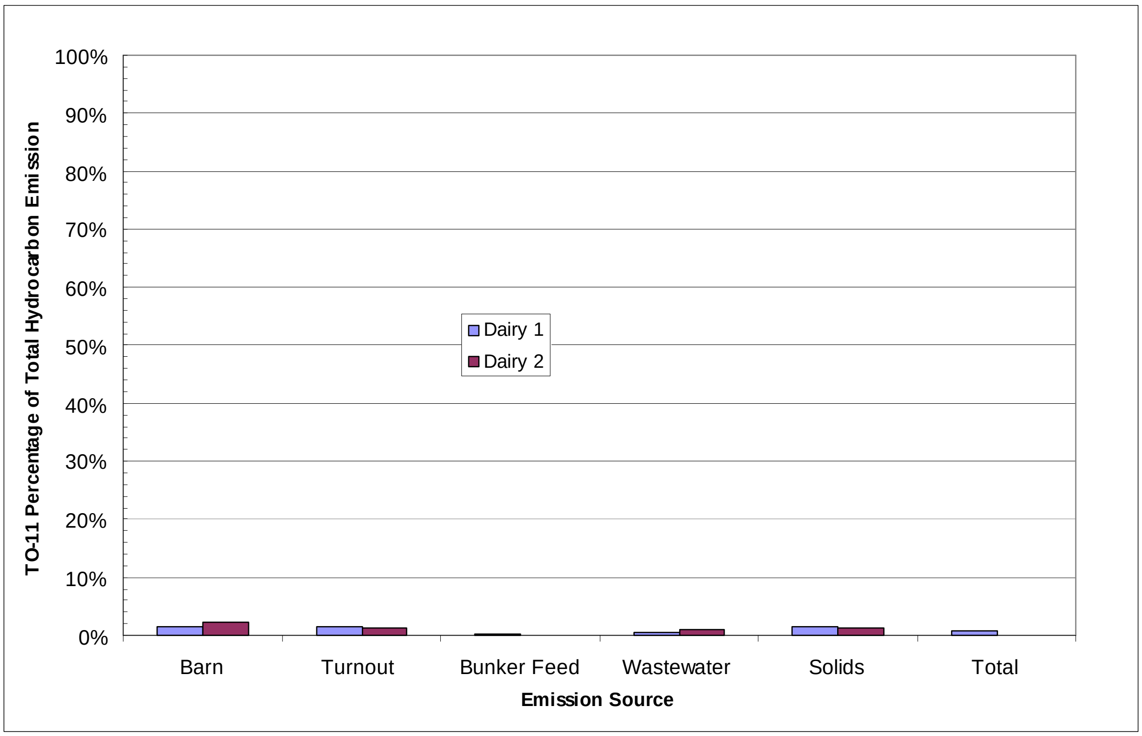
Figure 6.5 – Contribution of VFAs to Total Site Emissions.



6.3.2. TO-11 (Aldehydes/Ketones)

Figure 6.6 shows the percentage of TO-11 (Aldehyde/Ketone) compounds compared to the total organic compounds measured using Method 25.3. Based on the values collected during this test, the measured emissions of aldehydes and ketones for the locations tested are extremely low.

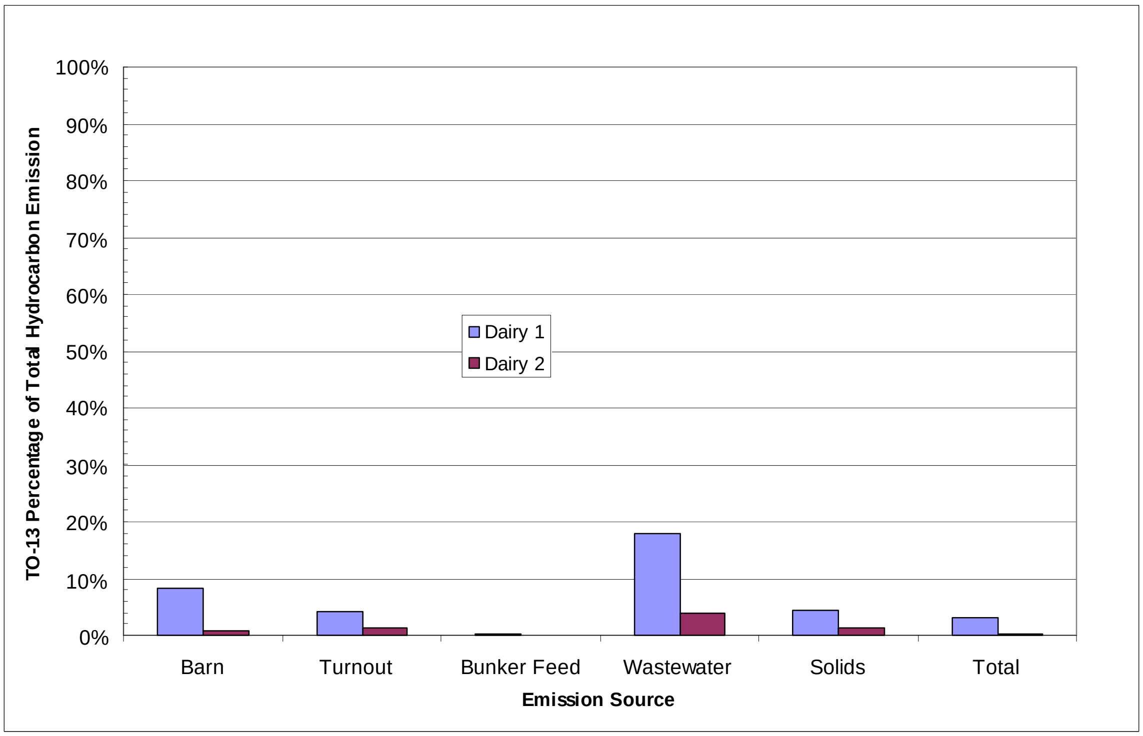
Figure 6.6 – Contribution of TO-11 (Aldehydes/Ketones) Compounds to Total Site Emissions.



6.3.3. TO-13 (SVOC/Phenols)

Figure 6.7 shows the percent contribution of TO-13 (SVOC/Phenol) compounds compared to the total organic emissions measured using Method 25.3 The magnitude of the SVOC/Phenols is very low in comparison to the other types of organic gas emissions measured during the project. SVOC/Phenols were measured at at Dairy 1, but they were near the detection threshold, which makes the reported results very uncertain.

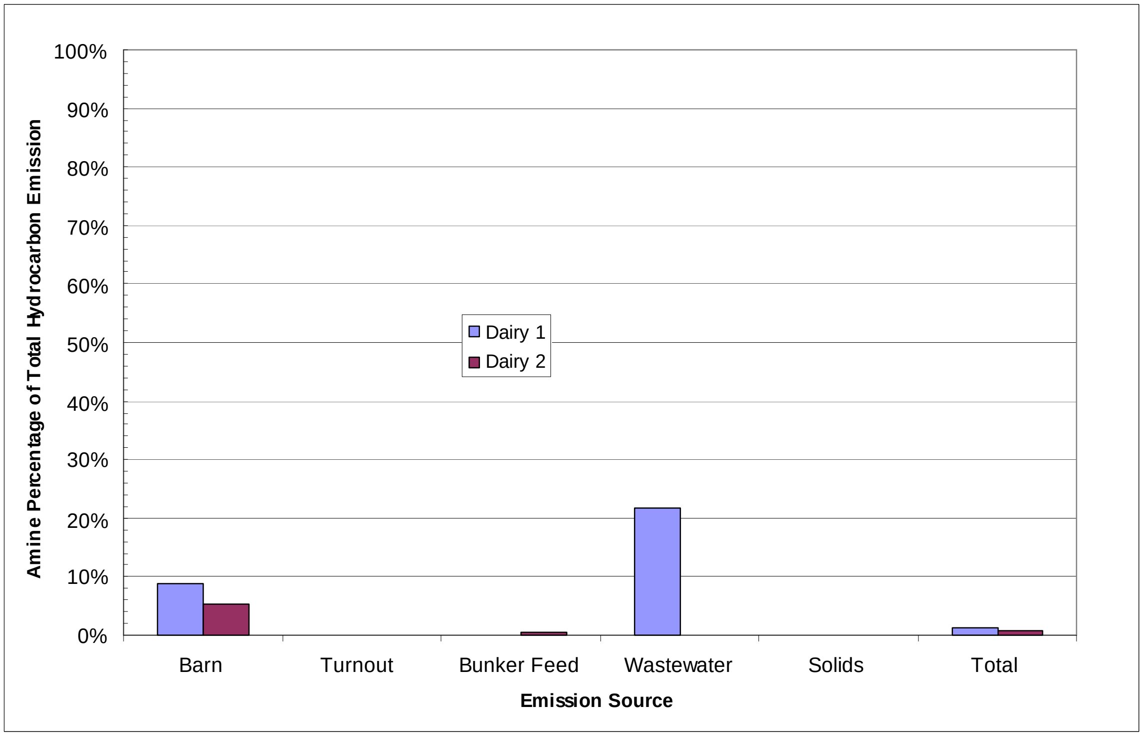
Figure 6.7 – Contribution of TO-13 (SVOC/Phenol) Compounds to Total Site Emissions.



6.3.4. Amines

Figure 6.8 shows the percent contribution of amine compounds to the total organic gas emissions as computed using Method 25.3 Emissions of amines measured during this project and at the sites tested were very low when compared with the magnitude of other organic compounds. .

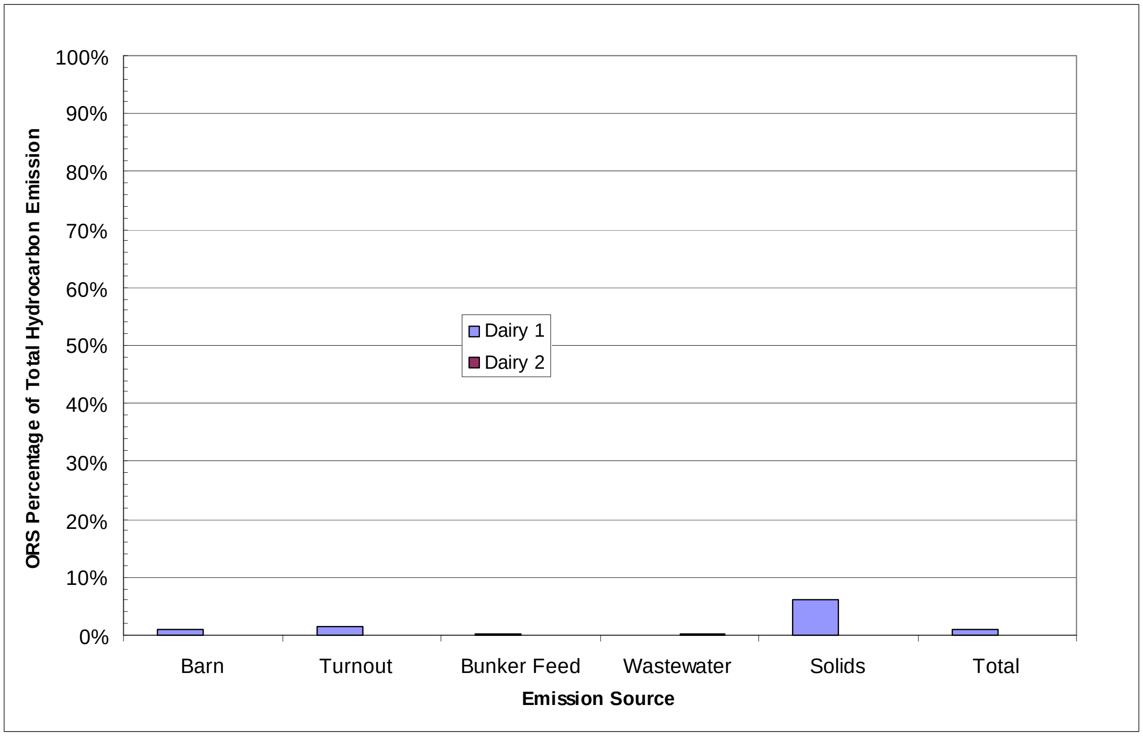
Figure 6.8 – Contribution of Amine Compounds to Total Site Emissions.



6.3.5. Organic Reduced Sulfur

Figure 6.9 shows the percent contribution of organic reduced sulfur compounds to the total organic gas emissions as determined using Method 25.3, corrected for exempt species. The magnitude of the reduced sulfur emissions measured during the project are very low, less than 5% of the measured total organic gas.

Figure 6.9 – Contribution of Organic Reduced Sulfur Compounds to Total Site Emissions.



6.3.6. Summary of Chemical Species Data

Tables 6.3 and 6.4 present a summary of the chemical species information collected at Dairy 1 and Dairy 2 in 2005.

Table 6.3 – Summary of Chemical Species Components for Dairy 1 in 2005.

	Measured Emissions (#/day)								
Component	Barn	Turnout	Bunker Feed	Silage	Waste water	Solids	Total	Total/ Hd	Tot/Hd/ yr
Field Instruments									
Ammonia	187	1,648	0.02		9	19	1,864	0.55	199
PID Response	56	474	3	17	55	9	612	0.18	66
FID Response	27	194	20	8	323	1,781	2,353	0.69	252
Laboratory									
SCAQMD 25.3	19	122	58	54	8	1.9	263	0.08	28
TO-14 (Integrated Detector)	5	24	43	31	2.2	0.3	106	0.03	11
TO-15 (Summed Species)	1	5	17	32	0.4	0.1	55	0.02	5.9
Ammonia	159	1,160			35	13	1,367	0.40	146
Amines	1.7	0.1			1.77	0.0	4	0.00	0.4
Organic Acids	4	40	1.3	5	0.54	0.5	52	0.02	5.5
Aldehydes/Ketones	0.2	1.3	0.1	0.03	0.04	0.0	1.7	0.00	0.2
SVOC	1.6	4.9	0.2		1.46	0.1	8	0.00	0.9
Phenols/Creosols				0.6		0.3	0.9	0.00	0.1
Total Organic Reduced Sulfur	0.2	2.0	0.1	0.3		0.1	3	0.00	0.3
ARB Non-Photoreactive Exempt Sum	0.4	2.2	0.1	0.4	0.3	0.0	3.3	0.00	0.4

Note:
1. Blank spaces indicate no value was above the method detection limit.

Table 6.4 – Summary of Chemical Species Components for Dairy 2 in 2005.

	Measured Emissions (#/day)								
Component	Barn	Turnout	Bunker Feed	Silage	Waste water	Solids	Total	Total/ Hd	Tot/Hd/ yr
Field Instruments									
Ammonia	66	71			31	3	170	0.04	13
PID Response	149	748	7,685	1	74	27	8,685	1.84	671
FID Response	9	14	131	9	6,824	1	6,988	1.48	540
Laboratory									
SCAQMD 25.3	9	22	455	13	10	0.8	510	0.11	39
TO-14 (Integrated Detector)	2	2	270	15	1.8	0.1	291	0.06	22
TO-15 (Summed Species)	1	0.3	116	4	4.9	0.0	126	0.03	9.7
Ammonia	58	80	0.2		51	3	191	0.04	15
Amines	0.5		3	0.0			3	0.00	0.3
Organic Acids	0.2	1.0	52.8	2	5.03	0.0	61	0.01	4.7
Aldehydes/Ketones	0.2	0.3	0.0	0.01	0.09	0.0	0.6	0.00	0.05
SVOC	0.1	0.3	0.9	0.0	0.40	0.0	0.8	0.00	0.06
Phenols/Creosols				0.3			0.3	0.00	0.02
Total Organic Reduced Sulfur				0.2	0.02		0.3	0.00	0.02
ARB Non-Photoreactive Exempt Sum	0.1	0.2	0.00	0.00	0.2	0.0	0.5	0.00	0.04

Note:
1. Blank spaces indicate no value was above the method detection limit.

7. Conclusions and Recommendations

This data set suggests the following conclusions and recommendations:

1. SCAQMD Method 25.3 was effectively used to develop an estimate of total organic gases emitted from specific dairy process sites. It is recommended that this method be used for future dairy emissions quantification work when the total mass of hydrocarbons is needed.
2. It is possible that for future comparative studies between dairies or dairy processes, detailed hydrocarbon speciation may not be needed except in the cases where knowledge about the chemical mechanisms for the emissions or reactivity of the emissions are desired.
3. Speciated canister (TO-15) and TO-17 (organic acids) accounted for about 90% of the speciated compound mass. Semi-volatile organic compounds (SVOCs by USEPA Method TO-13) were the only other compound group with any significance as to total mass of emissions.
4. Feed and feed handling emissions (storage, transport, bunker feed) appear to be a major source of organic gas emissions from the sources tested. Because of very high variability and limited sampling of feed storage and handling compared to sampling of other dairy emission sources to date, additional research will be necessary to better quantify feed-related emissions. Identification of higher emitting components of feed and feed handling will be important for understanding how to reduce these emissions. Additional research in this area is recommended to both better quantify these emissions on an industry scale and to support improve understanding of reduction strategies.
5. This study focused on only two dairies. It is recommended that additional emissions work be performed at other dairies using a variety of survey methods such as SCAQMD 25.3 or real-time methods that can characterize the variability between dairies and emission sources, but without performing the exhaustive chemical analysis performed in this study.
6. There are significant knowledge gaps in the variability of ammonia emissions related to seasonal effects and management practices. The results of this report may be representing annual ammonia emissions as too high by as much as a factor of two as related to seasonal variability.
7. The important variability parameters for ammonia include season-to-season and livestock turnout management. Future ammonia sampling data is needed mid-winter, in the spring (just prior to turnout use), mid-summer, and immediately prior to end-of-turnout-season. In addition, ammonia emissions from turnout management (scraping and harrowing) need to be quantified.