October 2006 Research Symposium Dairy Emissions:
Recent, Ongoing, and Future Research in California

Dairy Emission Measurements Using the USEPA Surface Emission Isolation Flux Chamber Technology

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Project Objectives

1) Quantify ROG (total) and species emissions including VFAs, phenols, ammonia/amines, sulfur species, alcohols, other compounds from key dairy sources
2) Use different analytical methods to validate test results and identify the best analytical methods

Project Objectives

3) Validate VFA recovery efficiency from the flux chamber

4) Compute emission factors for ROG, VOCs, VFAs, and amines

5) Develop an empirical emissions model for estimating dairy emissions

Program Components

- VFA verification/validation study
- 2004 Dairy #1 Emissions Test
- 2005 Dairy #1 Emissions Test
- 2005 Dairy #2 Emissions Test
- 2005 Dairy #1 Turnout 24-Hour Test

Dairy Unit Processes Tested in 2005 (sources)

- Flushed lanes: pre-flushed
- Separator solids storage piles
- Lagoon (single lagoon, three part lagoon system)
- Separator solids piles
- Turnouts (corrals)
- Feed in barn bunkers
- Silage piles (working face)

DAIRY #1

- Located in the San Joaquin Valley
- 3,443 cows (annual estimate)
- Flush lane manure management
- Not all cows in production
- Centralized food management system for multiple dairies

DAIRY #2

- Located in the San Joaquin Valley
- About 4,725 cows (annual estimate)
- Flush lane manure management
- Vast majority of cows in production
- Dedicated food management system

RESULTS

#1- Per cow emissions for ROG and NH_3 were calculated for Dairy 1 and Dairy 2, 2005. Insufficient data are available to recommend industry-wide emissions.

#2- ROG emissions are dominated by livestock feed sources as compared to other dairy sources.

#3- NH_3 emissions were affected by seasonal and operational variables.

#4- NH_3 emissions (turnout) are diurnal.

RESULTS

#5- Turnout ROG emissions for D1 are 6 times D2; NH_3 emissions are 10 times.

#6- Bunker feed ROG emissions for D2 are 8 times D1; corn silage emissions for D1 are 2 times D2.

#7- Flushed lane, wastewater, and solids ROG emissions are similar for D1 and D2 and low compared to other sources.

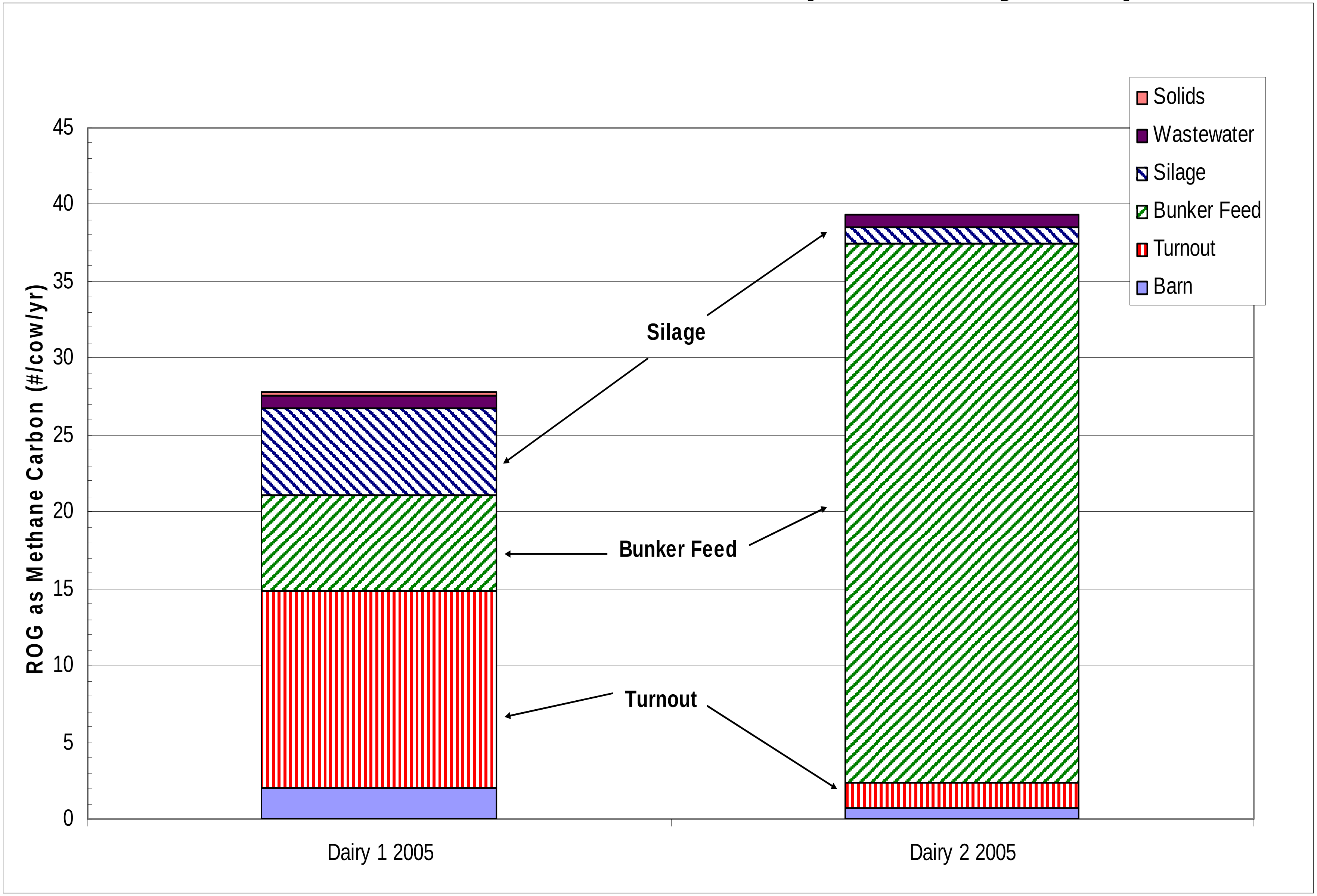
#8- VFA's are significant contributors to ROG emissions.

#9- Aldehydes/ketones, SVOCs/phenols, amines, and organic sulfur compounds are not significant contributors to ROG emissions.

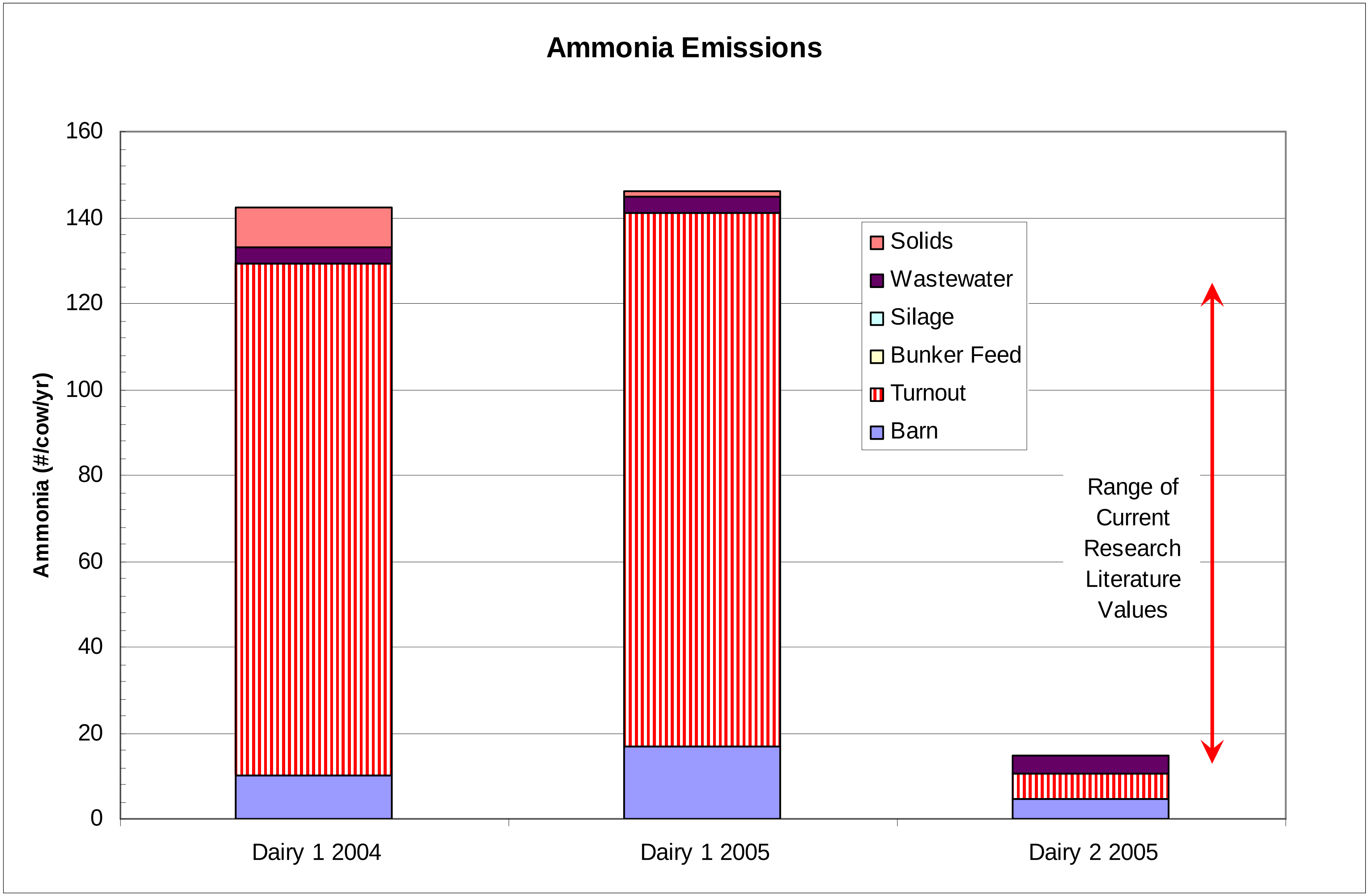
RESULT #1

- **Per cow emissions for ROG and NH3 were calculated for Dairy 1 and Dairy 2, 2005.**
- Insufficient data are available to recommend industry-wide emissions.
- 2004 Dairy 1 ROG emissions are not comparable to 2006 Dairy 1 and Dairy 2 SCAQMD 25.3 ROG emissions

Total ROG Emissions (#/cow/year)



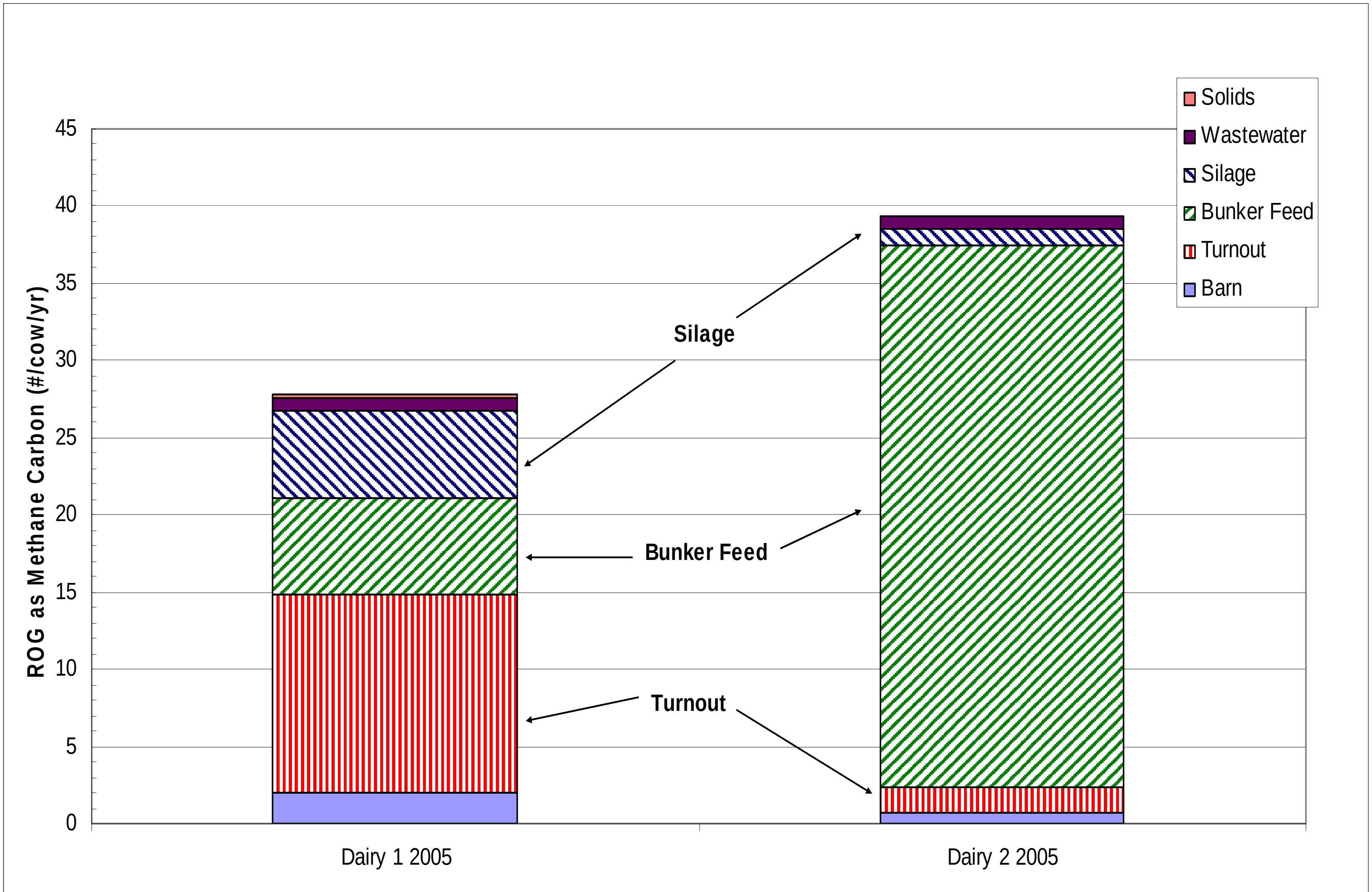
Total NH3 Emissions (#/cow/yr)



RESULT #2

- **ROG emissions are dominated by livestock feed sources as compared to other dairy sources.**
- Dairy 1 had higher bunker feed ROG emissions and Dairy 2 had higher silage ROG emissions.
- Dairy 1 ROG turnout emissions were higher than Dairy 2 ROG turnout emissions.

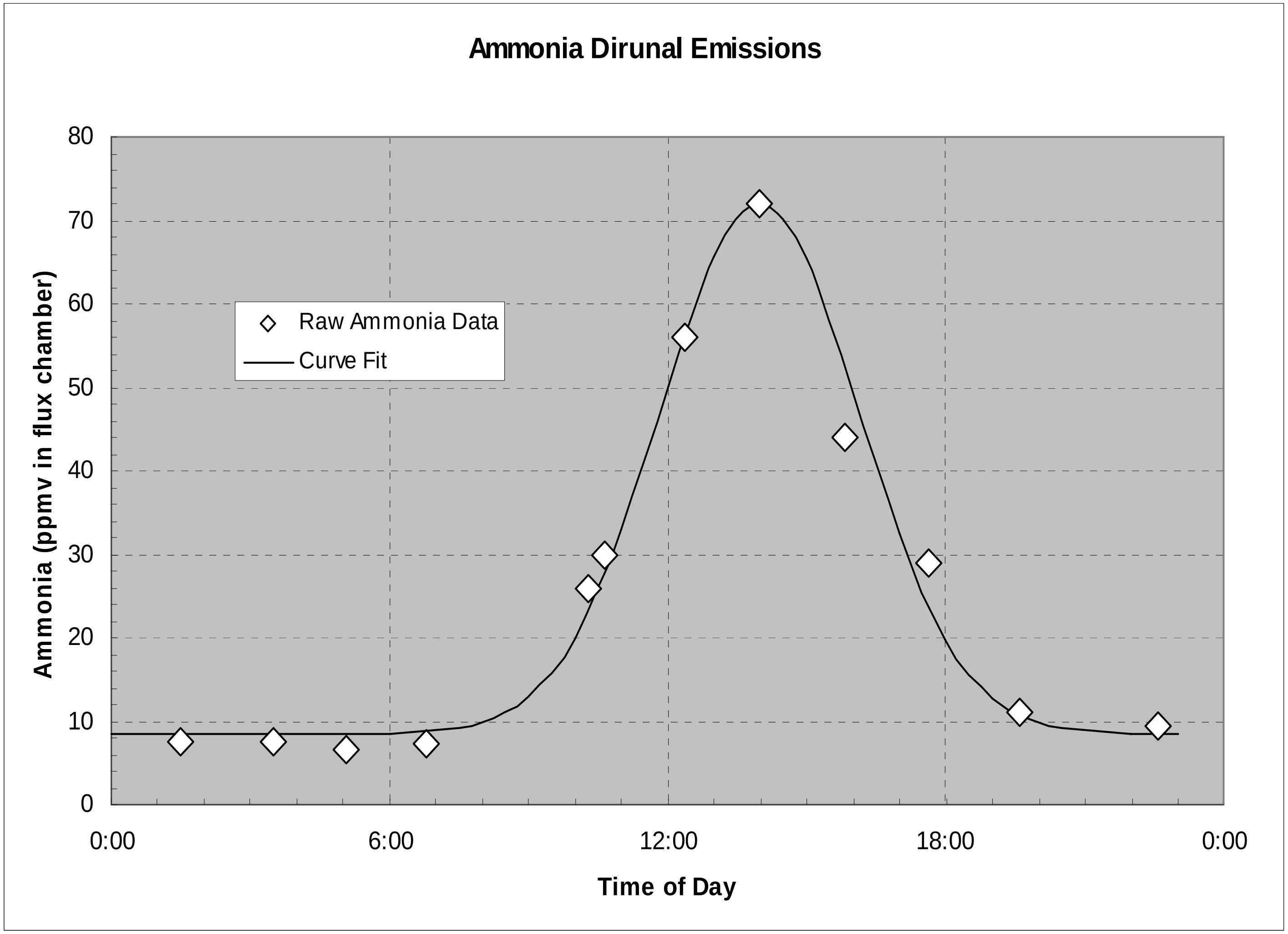
Summary of ROG Emissions for Year 2005 Events



RESULTS #3 and #4

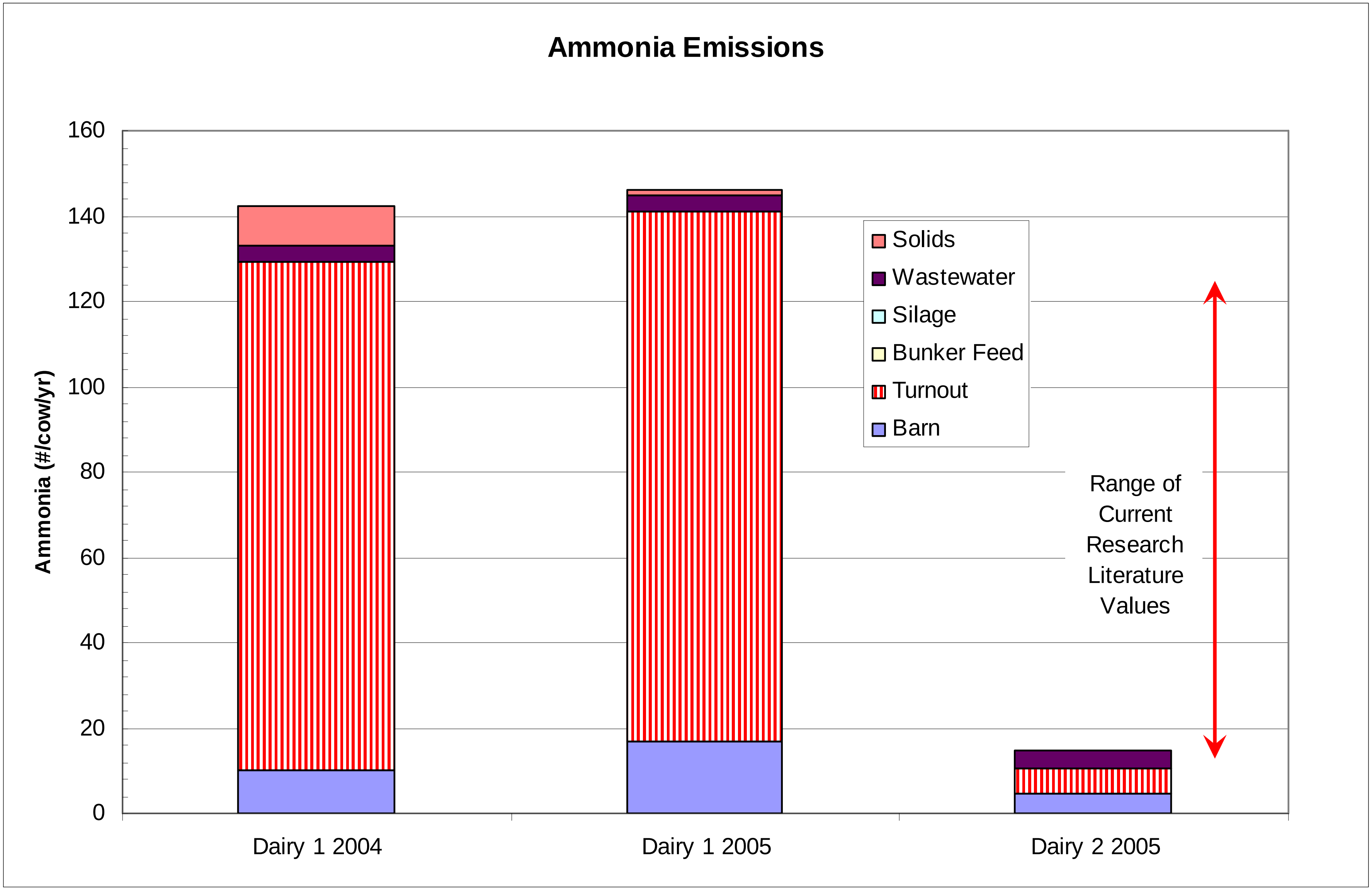
- **NH3 emissions were affected by seasonal and operational variables.**
- **NH3 emissions are diurnal.**
- 2004 Dairy 1 turnout testing was done just after the annual cleanout.
- 2005 Dairy 1 turnout testing was three days after the first fall rain.
- Dairy 2 routinely scrapes and harrows turnouts.

Ammonia Diurnal Emissions



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

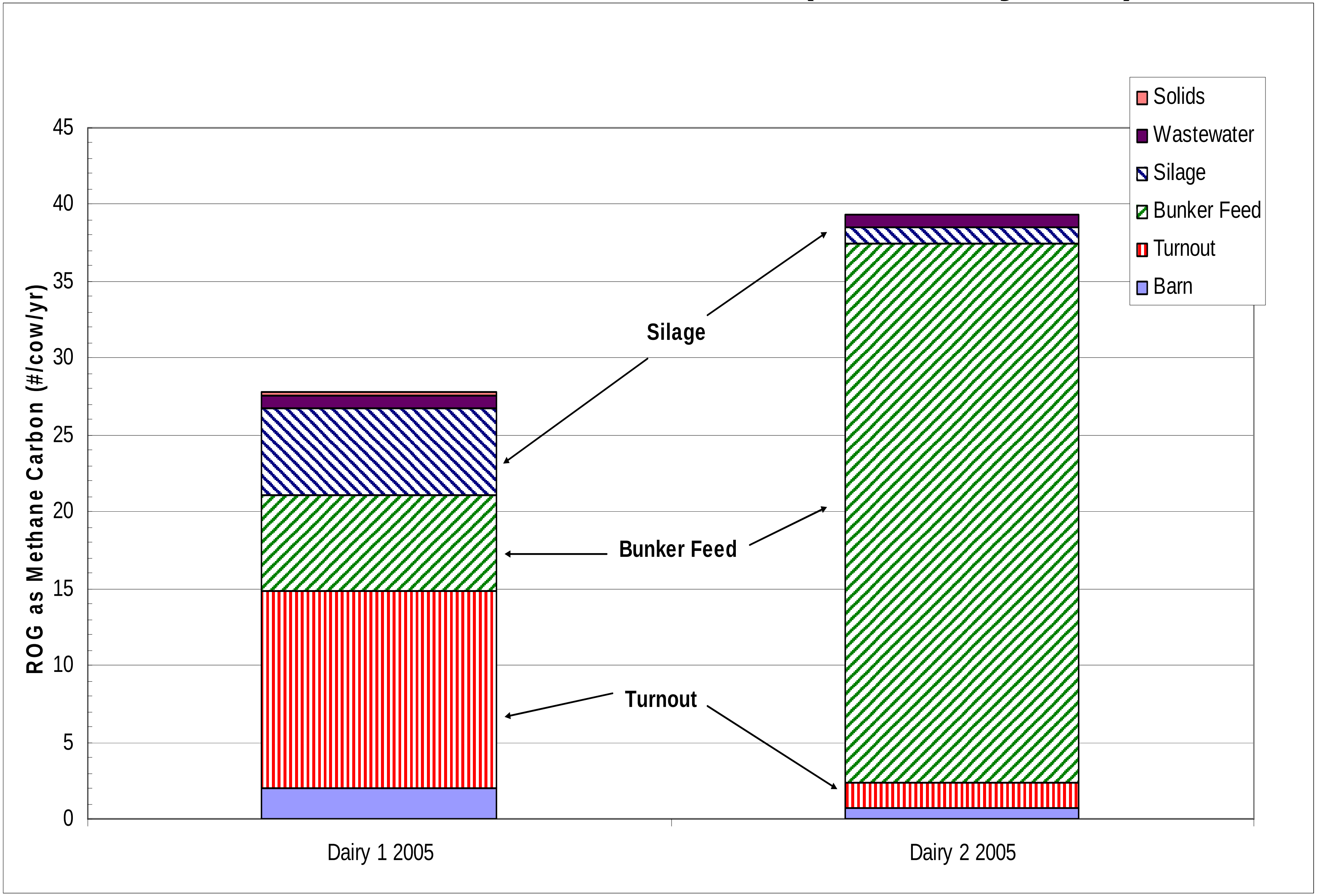
Summary of Ammonia Emissions, Dairy #1 2004/2005 and Dairy #2 2005



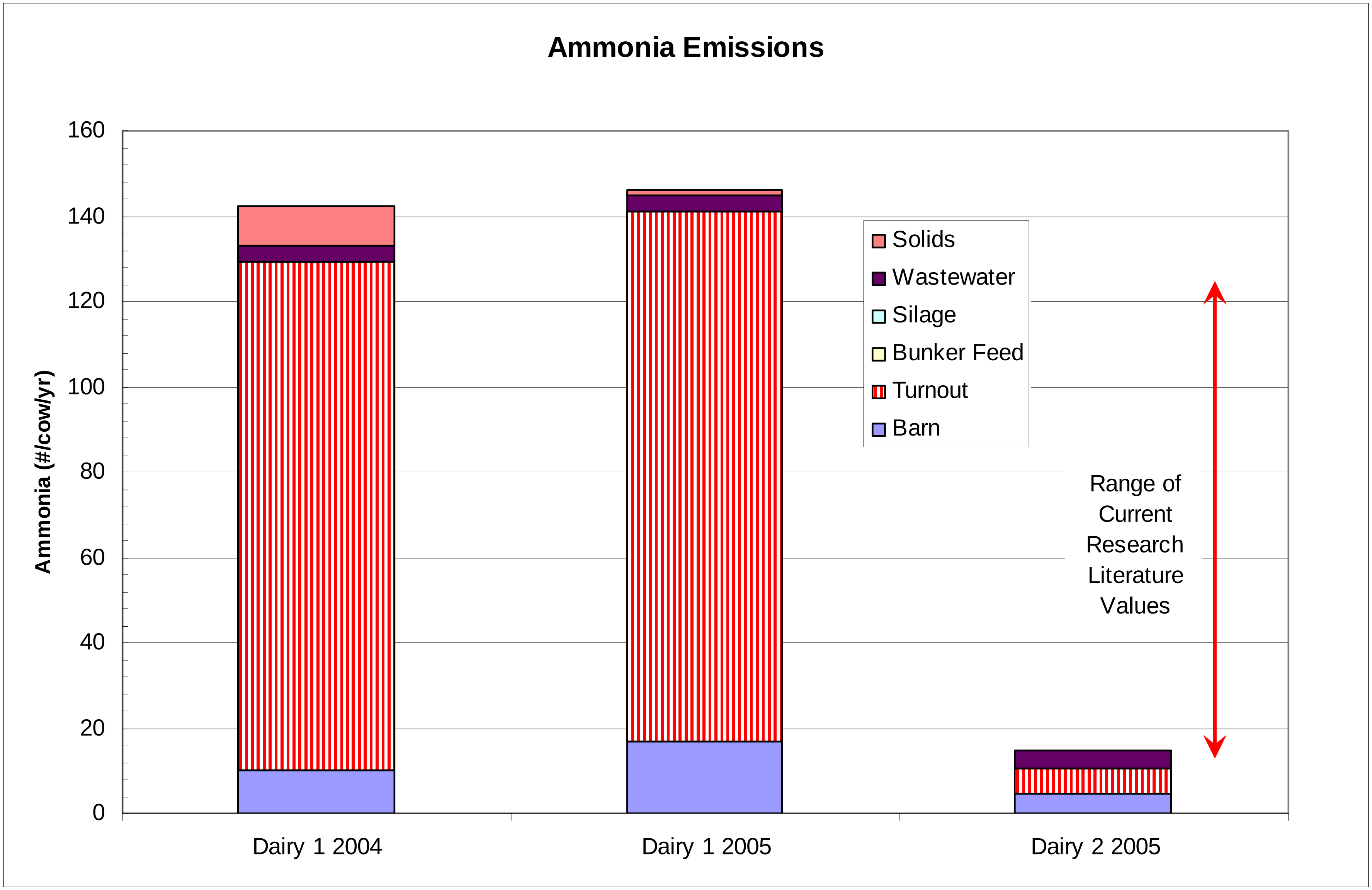
RESULT #5

- **Turnout ROG emissions for D1 are 6 times D2 and NH_3 emissions are 10 times D2.**
- D1 was tested about three days after the first fall rain event.
- D1 scrapes the turnouts annually and D2 scrapes and harrows weekly.
- D1 had high acetic acid emissions compared to D2.

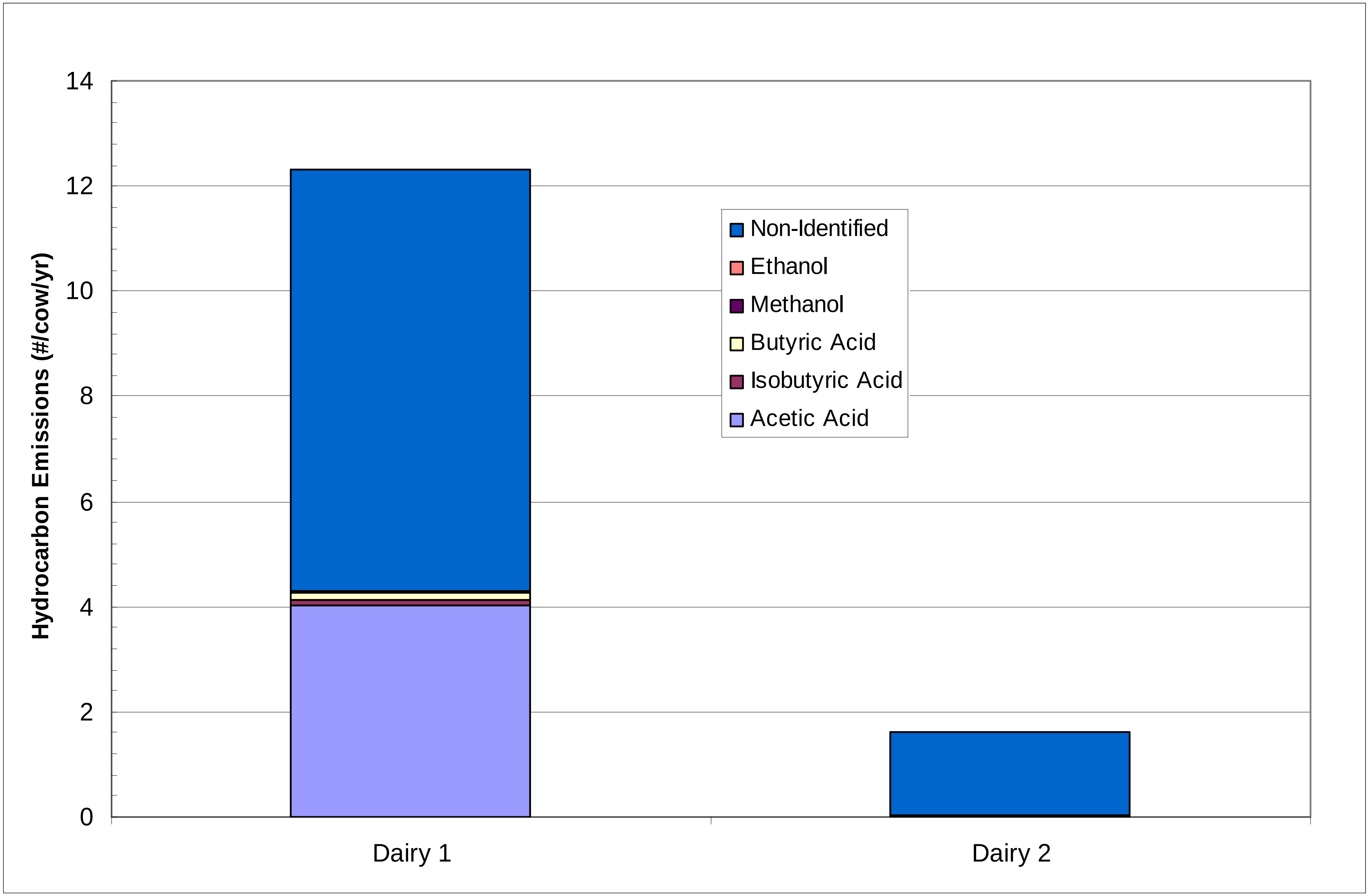
Total ROG Emissions (#/cow/year)



Summary of Ammonia Emissions, Dairy #1 2004/2005 and Dairy #2 2005



Turnout Organic Compound Emissions Comparisons



RESULT #6

- **Bunker feed ROG emissions for D2 are 8 times D1; corn silage emissions for D1 are 2 times D2.**
- D1 and D2 rations are similar.
- D2 bunker feed was fresh; D1 bunker feed was 4-to-8 hrs old.
- Methanol/ethanol emissions similar but D2 had higher acetic acid and n-propanol emissions.
- Feed has insignificant NH3 emissions.

Food Components

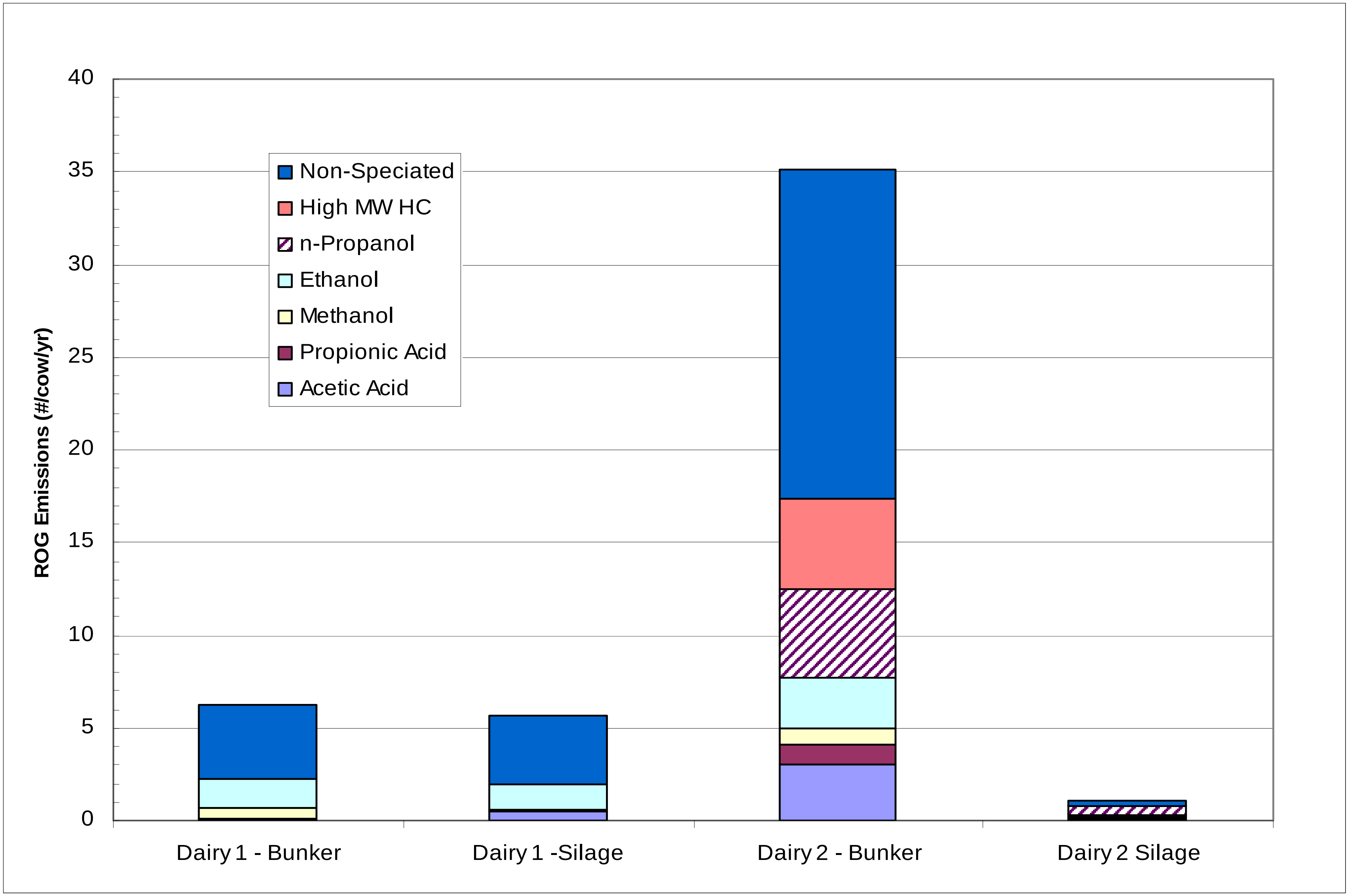
Dairy #1

	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%

Dairy #2

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	

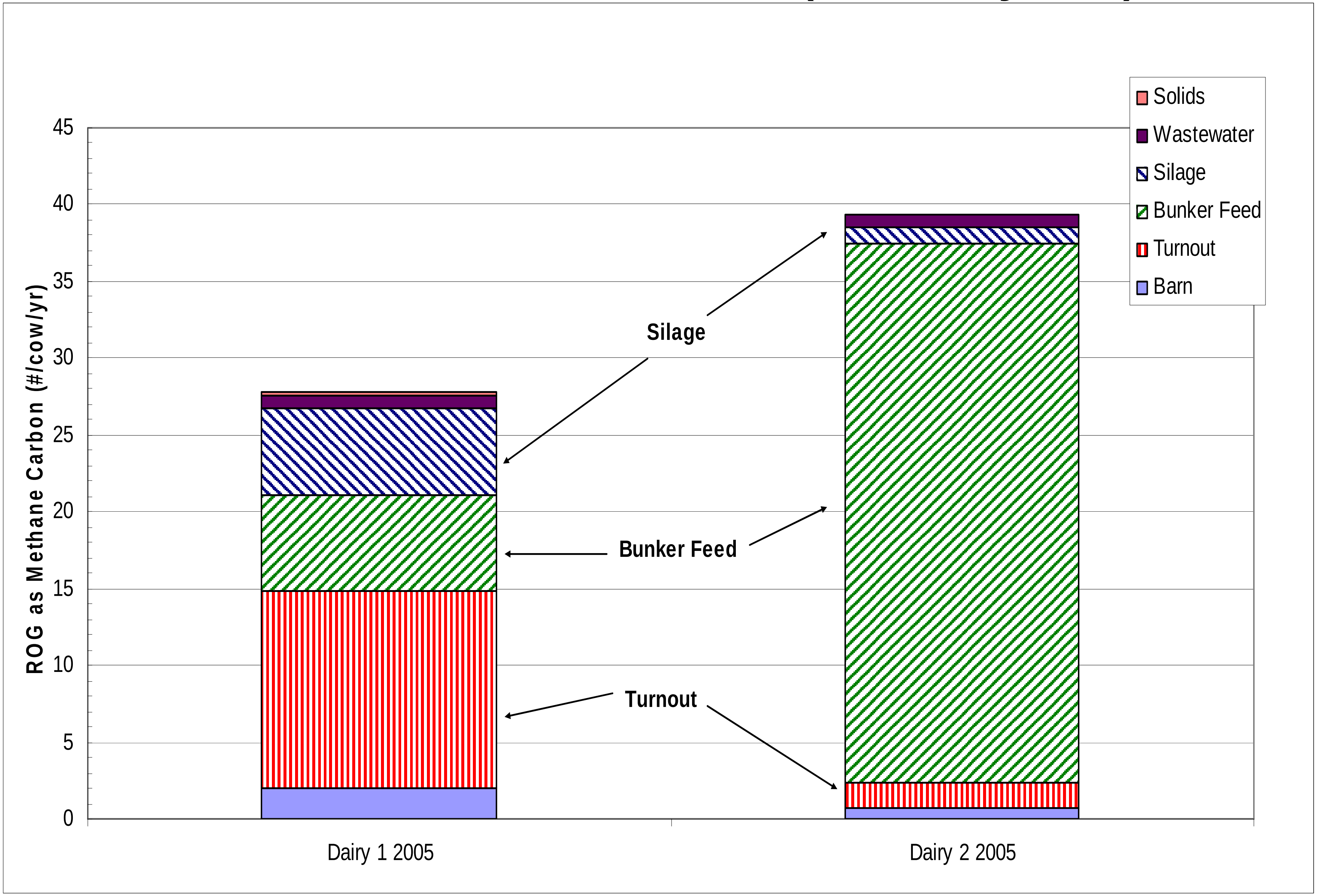
Chemical Speciation of Food Emissions



RESULT #7

- **Flushed lane, wastewater, and wastewater solid ROG emissions are similar for D1 and D2 and low compared to other sources.**
- A more extensive study of dairy ‘source’ emissions was conducted in 2004 which supported this result.
- Livestock feed dominates ROG emissions and turnouts dominate NH_3 emissions.

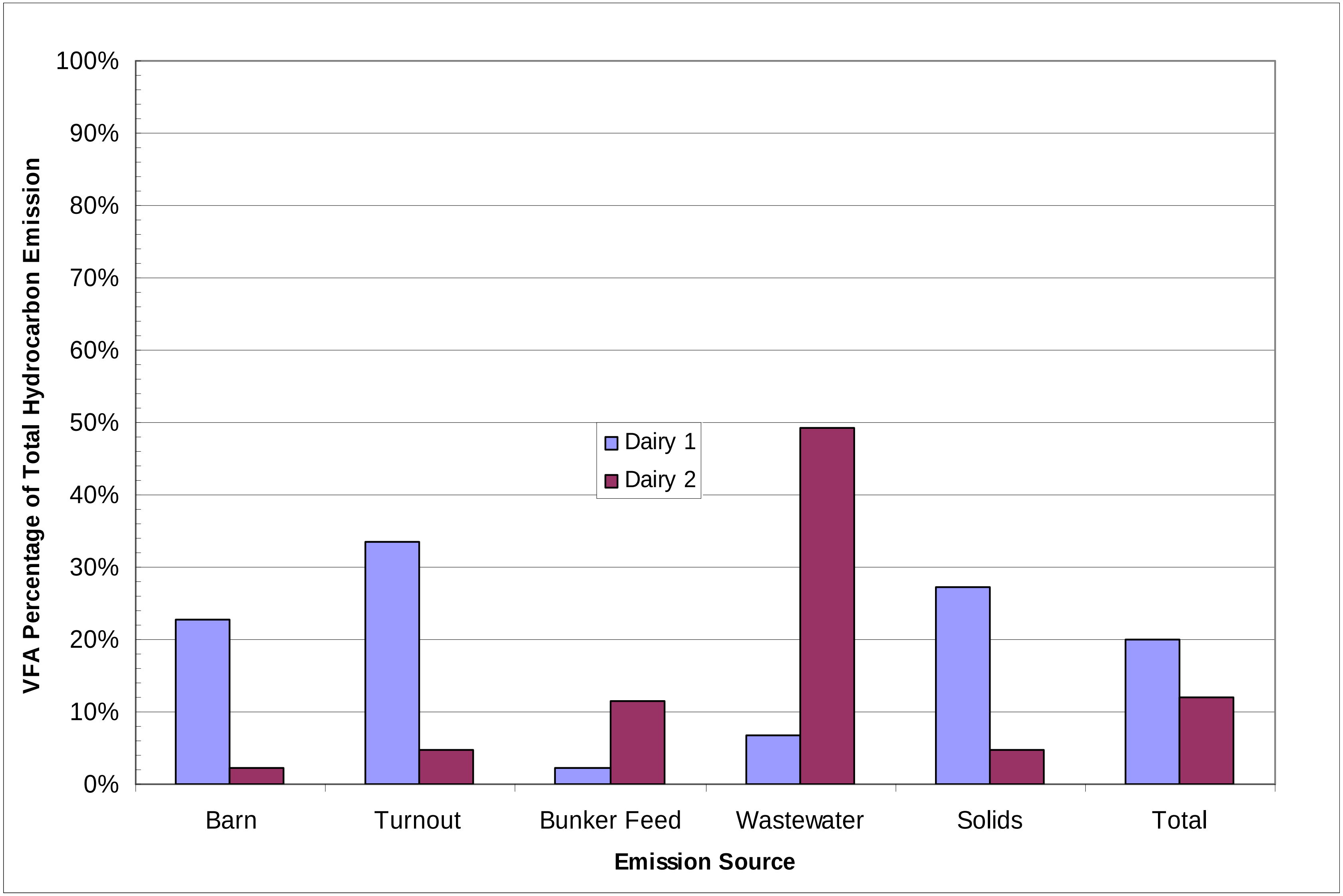
Total ROG Emissions (#/cow/year)



RESULT #8

- **VFA's are significant contributors to ROG emissions.**
- VFA's are captured quantitatively by the flux chamber and SCAQMD 25.3 (trap compound) and speciated by TO-17 (carbotrap/GC/MS).
- A validation study was conducted demonstrating VFA recovery from the USEPA flux chamber.

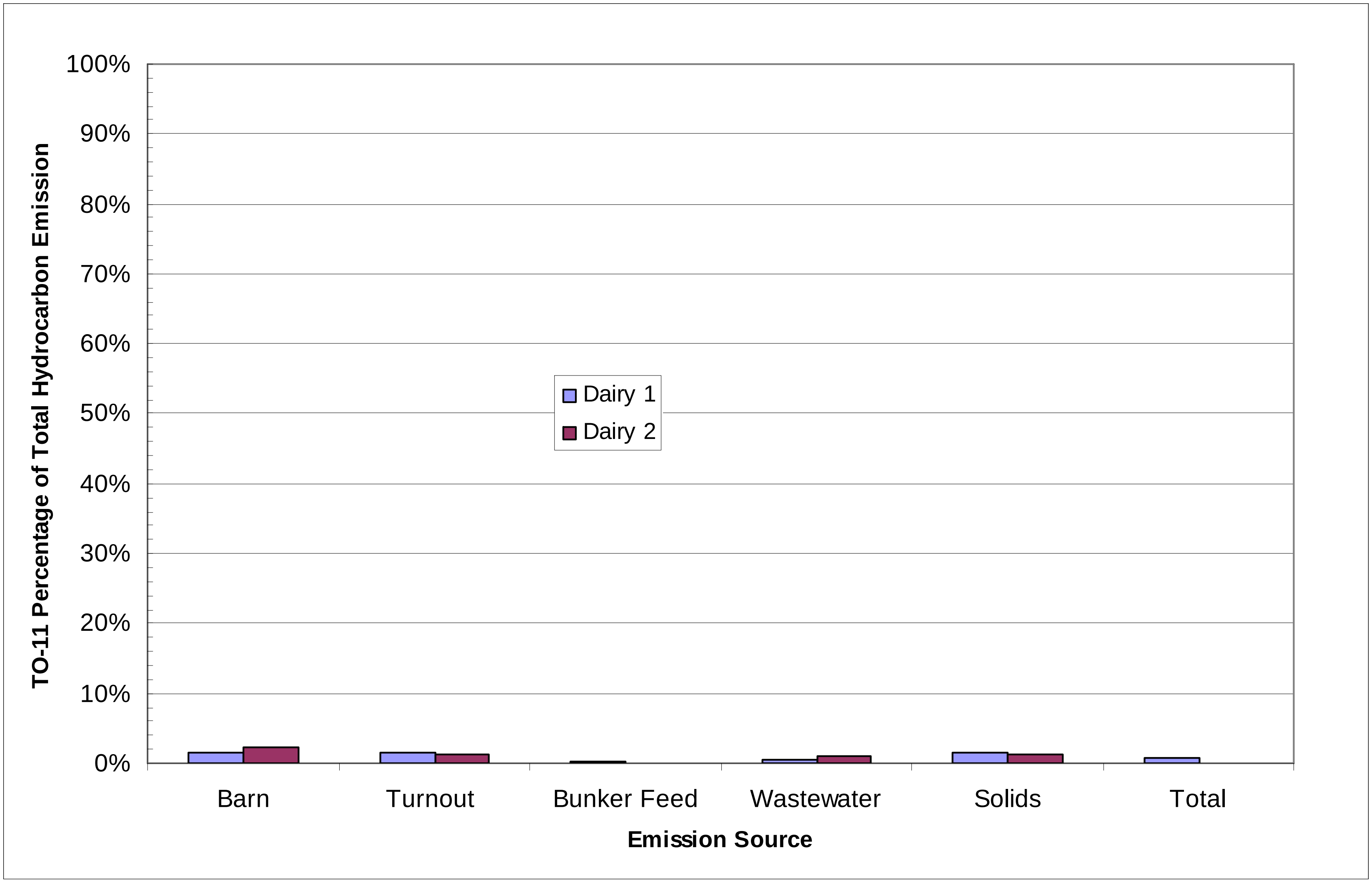
Contribution of VFAs to Total Site Emissions



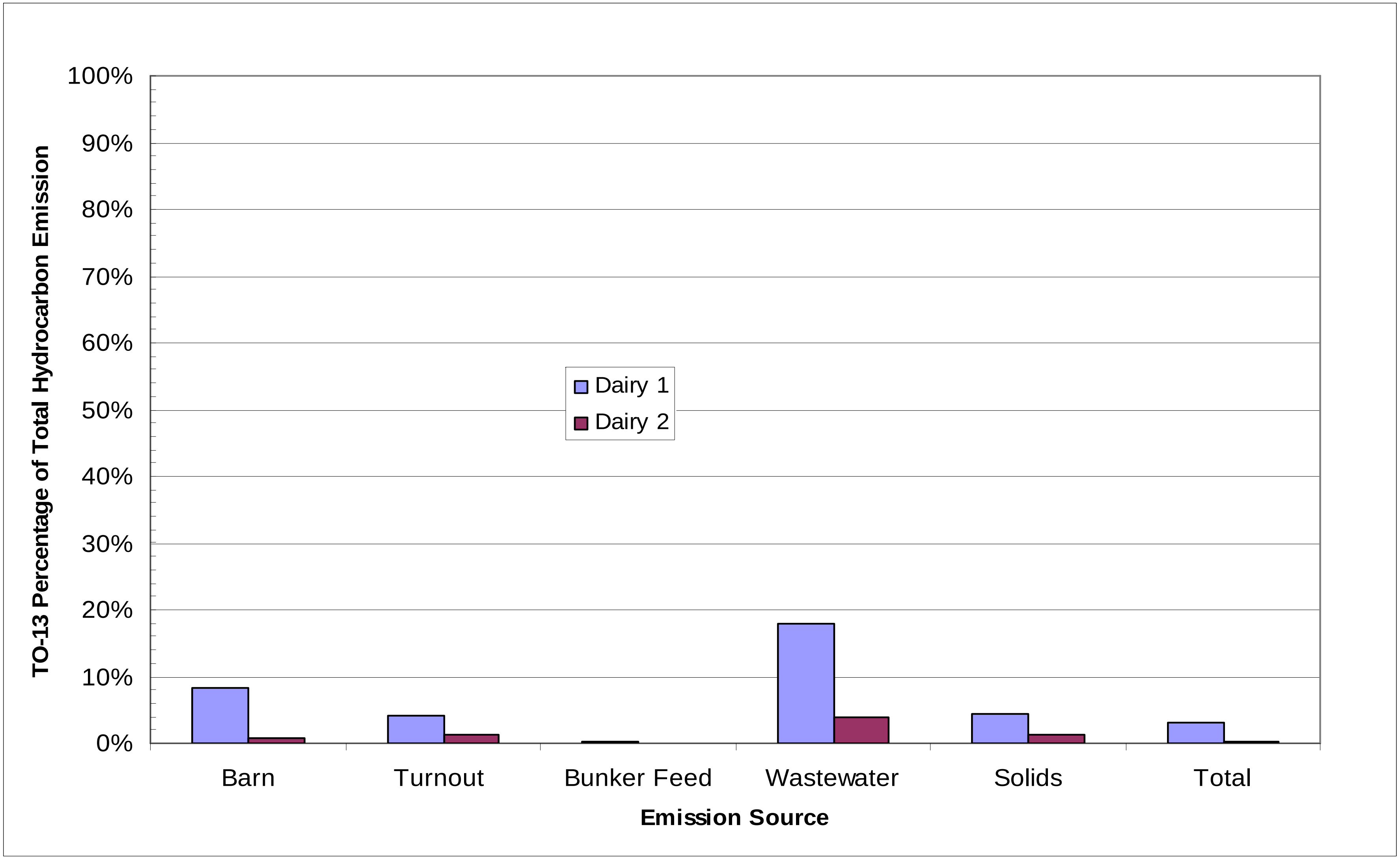
RESULT #9

- **Aldehydes/ketones, SVOCs/phenols, amines, and organic sulfur are not significant contributors to ROG emissions.**
- These compounds are included in SCAQMD 25.3 (tank or trap) if they have carbon.
- Speciation for these compounds in future studies is optional.

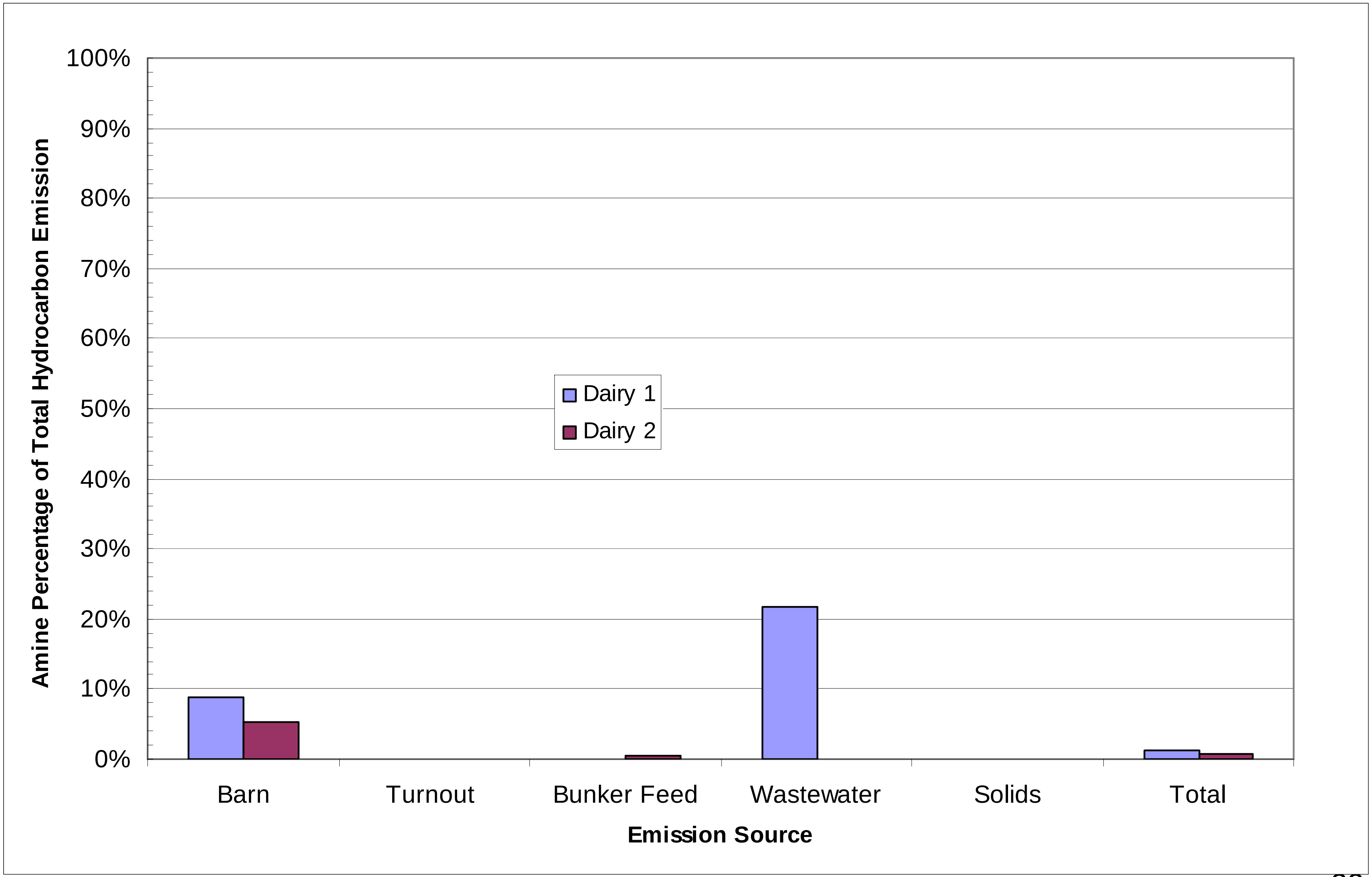
Contribution of Aldehydes/Ketones to Total ROG Emissions



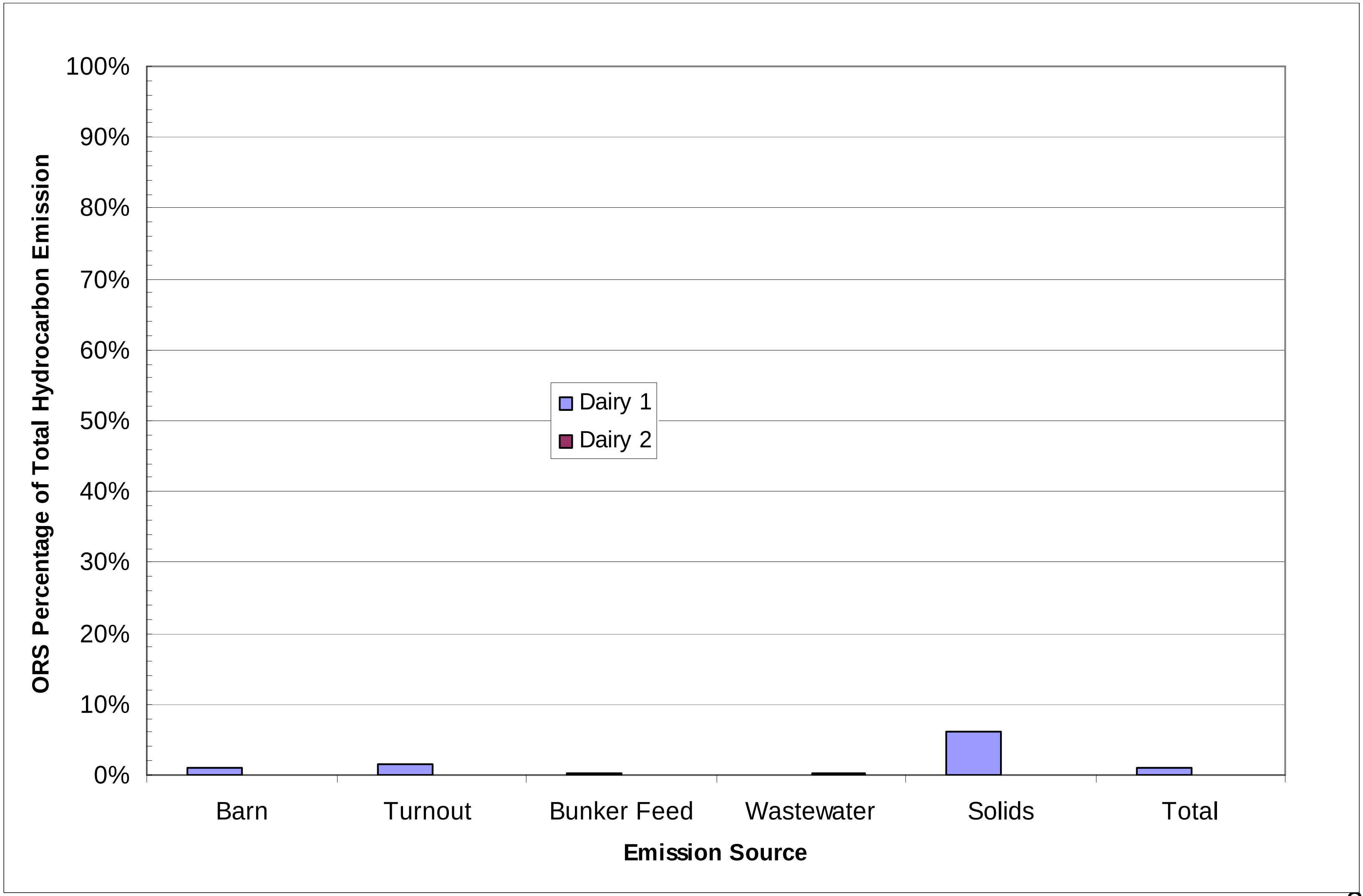
Contribution of SVOCs/Phenols to Total ROG Emissions



Contribution of Amines to Total ROG Emissions



Contribution of Reduced Organic Sulfur Compounds to Total ROG Emissions



Conclusions and Recommendations

- **SCAQMD Method 25.3** was effectively used to develop an estimate of total organic gases emitted from specific dairy process sites.

- It is possible that for future comparative studies detailed hydrocarbon speciation may **not** be **needed**.

- 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.

- **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.

Conclusions and Recommendations

- 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 and to support our understanding of reduction strategies.

- It is recommended that additional emissions work (USEPA Flux Chamber and SCAQMD 25.3 ROG and NH3) be performed at other dairies to characterize the **variability between dairies and emission sources**. Exhaustive chemical analysis will not be needed for this study.

- 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.

- 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) needs to be quantified.

Support Information

Summary of 2004/2005 Dairy Testing (continued)

Dairy Unit Process Tested	Dairy #1 2004 ROG NH3	Dairy #1 2004 Other Species	Dairy #1 2005 ROG NH3	Dairy #1 2005 Other Species	Dairy #2 2004 ROG NH3	Dairy #2 2004 Other Species
Turnout or Corral	1 2	1	6*	2*	7	3
Open Feed Storage	2	1	2	1	1	1
Silage Store Pile (open face)	None	None	2	2	1	1
Milk Parlor	2	None	None	None	None	None
Field Blank	2	2	2	2	1	1
Field Replicate	2	2	2	2	1	1
ROG Spike Recovery	None	None	1	1	1	1
TOTAL	38	13	24	15	16	11

Summary of 2004/2005 Dairy Testing

Dairy Unit Process Tested	Dairy #1 2004 ROG NH3	Dairy #1 2004 Other Species	Dairy #1 2005 ROG NH3	Dairy #1 2005 Other Species	Dairy #2 2005 ROG NH3	Dairy #2 2005 Other Species
Flushed Lane Pre-Flush	4	2	2	1	1	1
Flushed Lane Post Flush	4	None	None	None	None	None
Solid Storage Piles	4	1	4	2	None	None
Lagoon or Vault and Ponds	4	2	3	2	3	2
Solids from Separator	4	2	None	None	None	None
Bedding in Pile Freestall Area	2	1	None	None	None	None
Freestall Area	2	1	None	None	None	None
Heifer Pens	3	1	None	None	None	None

Summary of Dairy #1 Turnout 24-Hour Test

- Conducted flux chamber testing on one unit processes, one location using 5 analytical methods every 2 hours for 24-hours (ROG, VOCs, VFAs, and amines)
- Turnout (corral) location- 1
- QC- replicate and blank samples

Analytical Menu
(all locations)

- SCAQMD 25.3, ROG as methane (1-2 ppmvC)
- SCAQMD 207.1, ammonia/amines (0.5 ppmv)
- USEPA TO-15 (GC/MS), VOCs (0.1 ppbv)
- USEPA TO-14 (GC/FID), VOCs (0.7 ppbv)
- USEPA TO-11, aldehydes/ketones (0.7 ppbv)
- USEPA TO-17, volatile fatty acids (7 ppbv)

Analytical Menu

(some locations)

- EAS Method (HPLC/UV), volatile fatty acids (60 ppbv)
- USEPA TO-13, SVOCs (0.1 ppbv)
- USEPA TO-8, phenols (100 ppbv)
- BAAQMD 29, methanol/ethanol (10 ppmv)

Summary of Dairy 1 (2005) Unit Emission Estimates ROG per SCAQMD Method 25.3 as Methane Carbon minus exempt compounds (ug/m2/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

VFA Flux Chamber Recovery

TARGET RUN	CHAMBER RECOVERY	8' LINE RECOVERY
50 ppbv	104% a,b	94% a
150 ppbv	171% c	92% c
300 ppbv	98% c	82% c

Note- average of sample pairs, two runs

a- based on TO-17 inlet data

b- blank corrected

c- based on HPLC inlet data