AFO's and Methanol:
Ethanol/Methanol Field Research at Fresno State

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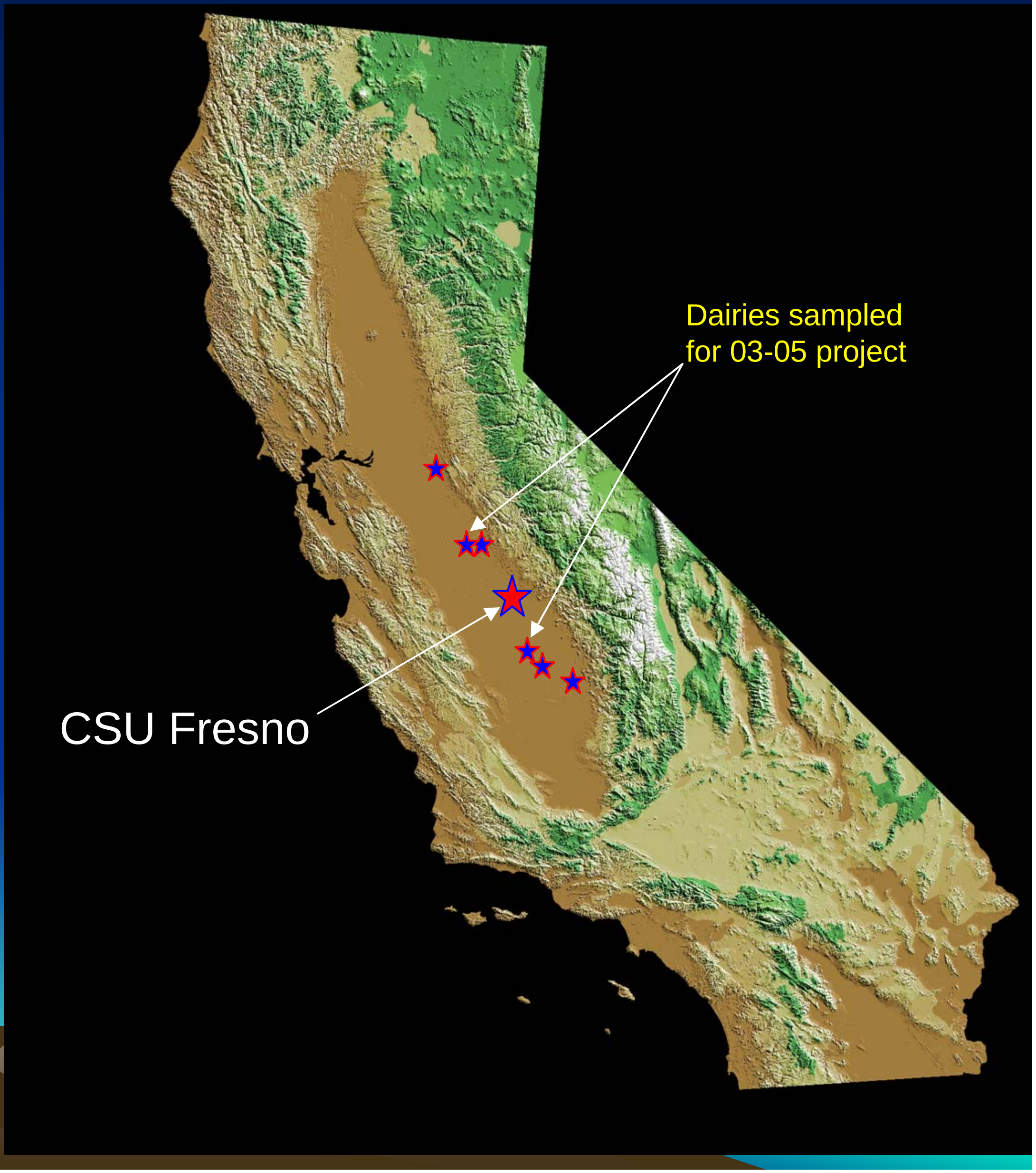
Dairy Operations: An Evaluation and Comparison of Baseline and Potential Mitigation Practices for Emissions Reductions In the San Joaquin Valley

- Funded by the CA Air Resources Board, 4/06 to 12/08
  - Select 6 dairies with different manure handling systems
  - Year-1: Develop a preliminary sampling plan, determine the significant ozone reactive VOC's (ROG) and the appropriate methods to monitor them.
  - Year-2: Develop a monitoring program to be used at each dairy for three sampling periods (fall, winter, early summer)
  - Compare emissions from the various practices at the different dairies to identify those that may reduce emissions of significant ROG's
- Additional funding from CSU-ARI, UNH, and USDA have been added to extend the scope and duration of the study. These additions have augmented the monitoring program to include various N compounds, alcohols, photosynthetic lagoons, GHG's, and land applications

CSU-Fresno Dairy Air Quality Projects in the Central Valley of California

- The initial study was done at two dairies from 2003-05. Upwind and downwind canister samples were collected and used to calculate an emission rate using dispersion modeling.
- The project was amended in 2005 by the ARB to provide for speciation of VOC's from various dairy operations to identify the dominant ROG's from each operation.
- The current study focuses on the relative fluxes from operation at six dairies and the range of those fluxes as they are affected by differences in the operations.



Dairy A. A 2000 cow dairy located near Hanford. The dairy utilizes “free stall” management where the cows are fed on gently sloping concrete that is flushed with a large flow of water several times a day to remove the waste. Solids in the flush water are separated from the liquid which is stored in a series of lagoons for subsequent flushing of the free stalls and eventually is part of the irrigation water for the surrounding cropland.

The dairy is surrounded by sorghum and alfalfa fields that are used to recycle nutrients from the dairy waste and to produce forage for the dairy herd.

Sampling sites at the dairy were: DW1, upwind, DW2-downwind of the lagoon, DW4-downwind of the free stalls and flush lanes, and DW3-300m downwind of DW2 across a field (ammonia sampling only).

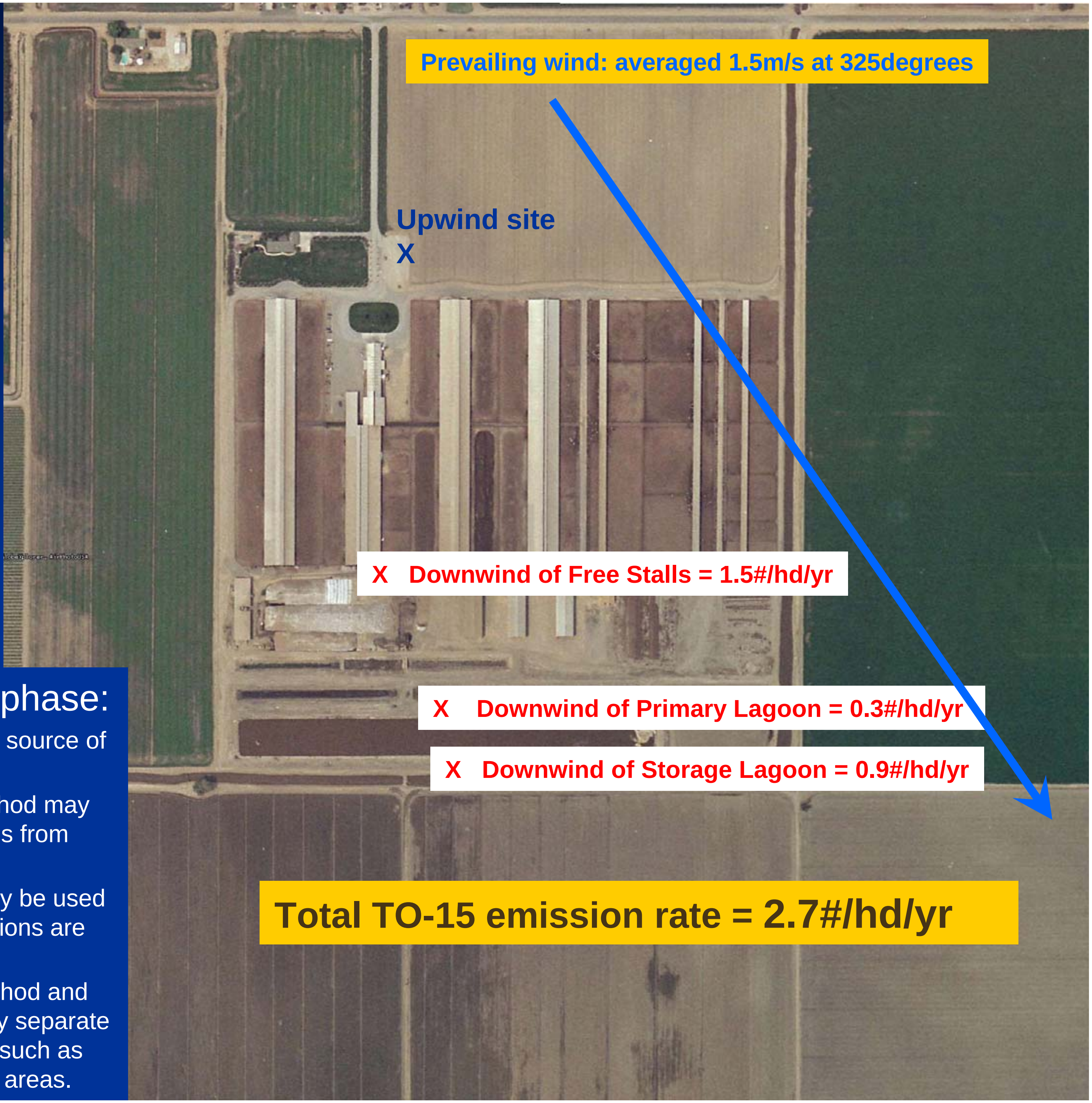
Up Wind Fenceline site (DW1).
Looking SE, downwind.

Dairy A

July 22, 2004

1330 to 1600

Summer wind direction (325) and speed (1.5m/s) were typical for this location. Wind speed in the early afternoon was less than at other locations but the direction was sufficiently consistent for modeling.

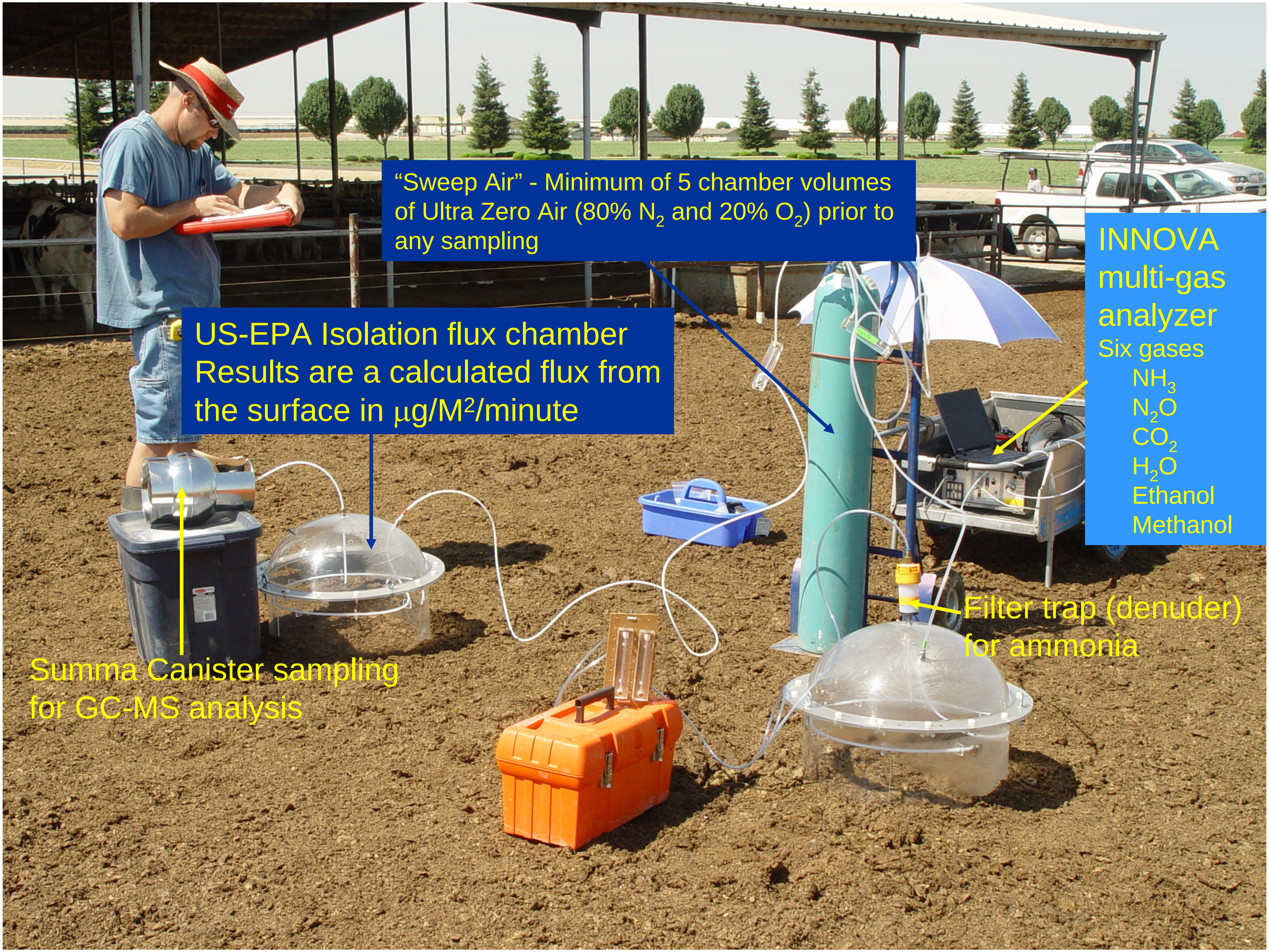


Conclusions from this phase:

1. Lagoons are not the primary source of ROG's
2. The sampling/analytical method may not be accurate for emissions from dairy operations.
3. Dispersion modeling can only be used when the proper wind conditions are obtained.
4. This sampling/analytical method and dispersion modeling can only separate large scale dairy operations such as lagoons and animal housing areas.

DAIRY		E
TYPE		Flux
location		Solids
location I	solids pile fresh loc 1	
can #		2214
directory		cows0606
Injection volume cm3		300
Type		Flux
date		23-Jun-06
time		8:26
Methane (ppmv)	ppmv	2
CO (PPBV)	ppbv	238
Ethanol (B)	pptv	18,700
Methanol (B)	pptv	5,979
Acetone (MS)	pptv	364,878
D-Limonene (B)	pptv	2,396
DMS (MS)	pptv	791
alpha Pinene (MS)	pptv	3,692
n-Hexane (B/E/MS)	pptv	2,247
Ethane (E)	pptv	1,514
OCS (MS)	pptv	49,561
2-Methylpentane (B)	pptv	115
3-Methylpentane (B)	pptv	73
Ethene (E)	pptv	165
Propane (B/E)	pptv	716
Propene (B/E)	pptv	114
CH3Cl (MS)	pptv	9,826
Isoprene (MS)	pptv	1,027
beta Pinene (MS)	pptv	447
HCFC-22 (MS)	pptv	21,415
CFC-12 (C/D/MS) (PPTV)	pptv	540
Ethylbenzene (MS)	pptv	15,319
CH2Cl2 (MS)	pptv	5,030
1,2,4-Trimethylbenzene (MS)	pptv	12,827
Ethyne (E)	pptv	263
i-Pentane (E)	pptv	284
CFC-11 (C/D/MS)	pptv	255
n-Butane (B/E)	pptv	128
i-Butane (B/E)	pptv	103
MeONO2 (C/D)	pptv	6
n-Pentane (E)	pptv	94
EtONO2 (C/D)	pptv	4
m-Ethyltoluene (MS)	pptv	6,523
Toluene (B/MS)	pptv	123
i-PrONO2 (C/D)	pptv	10
p-Xylene (MS)	pptv	4,586
m-Xylene (MS)	pptv	4,585
HFC-134a (MS)	pptv	5,651
CHCl3 (MS)	pptv	16
CCl4 (C/MS)	pptv	4,434
o-Ethyltoluene (MS)	pptv	5,553
CS2 (MS)	pptv	1,522
Benzene (MS)	pptv	72
2-BuONO2 (C/D)	pptv	6
CFC-113 (MS)	pptv	75
C2Cl4 (C/D/MS)	pptv	324
o-Xylene (MS)	pptv	1,968
HCFC-141b (MS)	pptv	2,001
HCFC-142b (MS)	pptv	1,659
1,3,5-Trimethylbenzene (MS)	pptv	1,113
CH3 Br (MS)	pptv	14

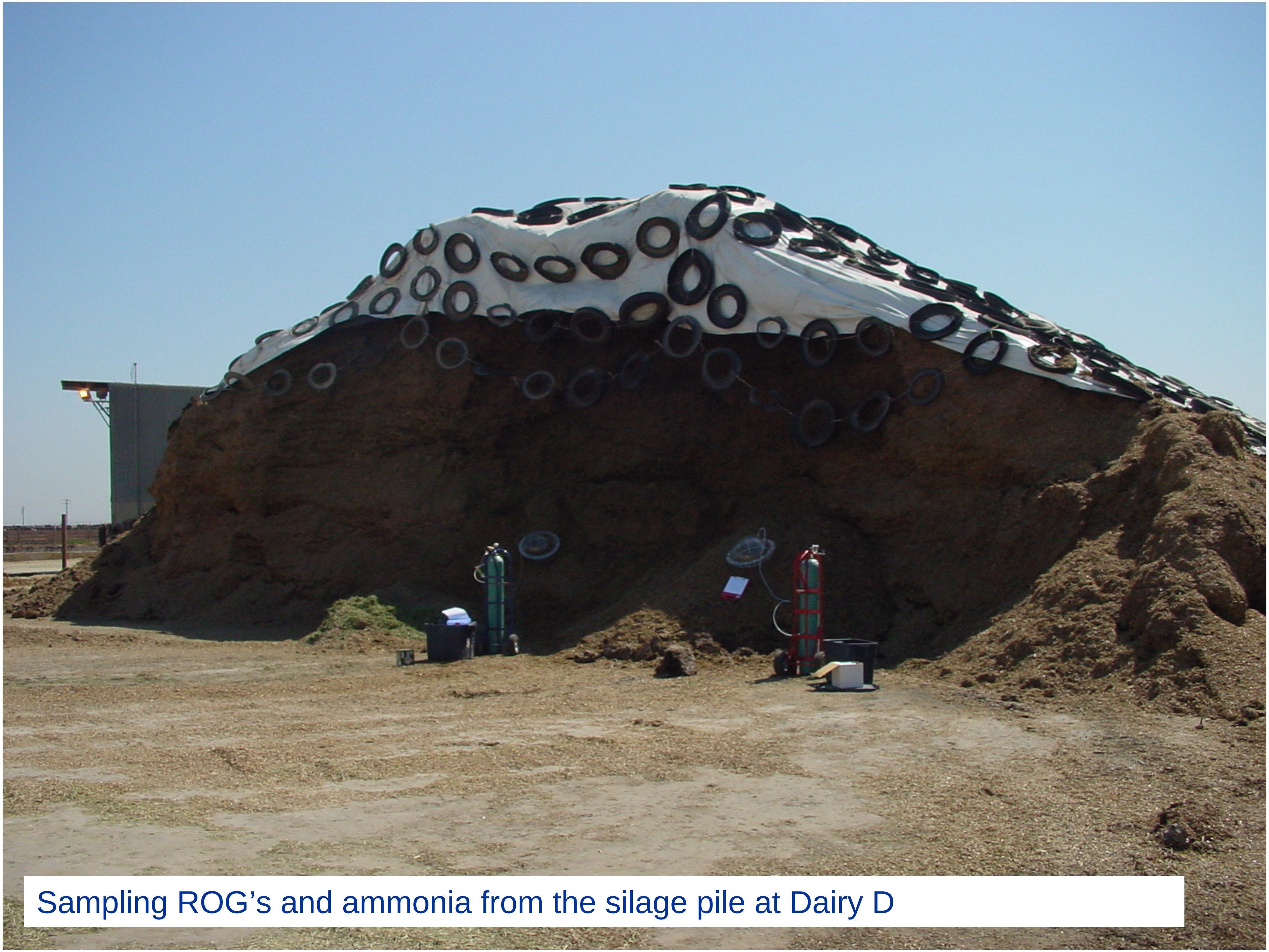
Speciation sampling of separated solids at Dairy E in June, 06. Canister and GC-MS analysis by Dr. Donald Blake at UC Irvine.


"Sweep Air" - Minimum of 5 chamber volumes of Ultra Zero Air (80% N_2 and 20% O_2) prior to any sampling
US-EPA Isolation flux chamber Results are a calculated flux from the surface in μg/M²/minute
INNOVA multi-gas analyzer
Six gases
NH_3
N_2O
CO_2
H_2O
Ethanol
Methanol
Filter trap (denuder) for ammonia
Summa Canister sampling for GC-MS analysis

Progress related to alcohol emissions

- Both ambient (upwind/downwind) and flux chambers were used in Year-1. Flux chambers proved to be better and will be used for Year-2
- Initial monitoring was by sampling with canisters for GC-MS analysis by Donald Blake at UC Irvine
- Initial results indicated the dominant VOC's were alcohols. This confirmed results from a contemporary study by Frank Mitloehner at UC Davis
- A real-time gas analyzer (INNOVA 1412) was purchased and configured for ethanol, methanol, CO_2, NH_3, and N_2O.
- Alcohol concentrations monitored by the INNOVA were higher than the corresponding canister/GC-MS data but the relative values were very consistent.
- Silage piles produced the highest alcohol fluxes with feed (TMR) second, followed by bedding and corrals.

Flux Chamber monitoring of flush lane at Dairy B



Sampling ROG's and ammonia from the silage pile at Dairy D

Sampling ethanol, methanol, ammonia, N_2O and ROG's from Total Mixed Ration (TMR) using flux chambers at Dairy A.

Silage		
Flux Rate ($\mu g/M^2$/min)		
	5 INNOVA samples with 8 UCI canisters	
Summary and Comparison of UCI Canisters with INNOVA data		
	INNOVA Ethanol $\mu g/M^2$/min.	40,849
	INNOVA Methanol $\mu g/M^2$/min.	8,690
	UCI Ethanol $\mu g/M^2$/min.	10,042
	UCI Methanol $\mu g/M^2$/min.	469
	Total VOC's (UCI) $\mu g/M^2$/min.	10,990
	Total ROG (UCI) $\mu g/M^2$/min.*	10,640
	Ethanol %	94.4%
	Methanol %	4.4%
	Total Alcohol %	98.8%
	*Total ROG's = UCI total VOC - (methane+CO+Acetone)	

TMR		
Flux Rate ($\mu g/M^2$/min)		
	12 INNOVA samples with 18 UCI canisters	
Summary and Comparison of UCI Canisters with INNOVA data		
	INNOVA Ethanol $\mu g/M^2$/min.	15,974
	INNOVA Methanol $\mu g/M^2$/min.	1,970
	UCI Ethanol $\mu g/M^2$/min.	3,501
	UCI Methanol $\mu g/M^2$/min.	515
	Total VOC's (UCI) $\mu g/M^2$/min.	4,497
	Total ROG (UCI) $\mu g/M^2$/min.*	4,187
	Ethanol %	83.6%
	Methanol %	12.3%
	Total Alcohol %	99.0%
	*Total ROG's = UCI total VOC - (methane+CO+Acetone)	

Flush Lane (Pre Flush)		
Flux Rate ($\mu g/M^2$/min)		
	8 UCI canisters	
Summary Comparison of UCI Canisters		
	Total VOC's (UCI) $\mu g/M^2$/min.	365
	Total ROG (UCI) $\mu g/M^2$/min.*	213
	Ethanol %	76.5%
	Methanol %	15.5%
	Total Alcohol %	92.1%
	Methane % of VOC	41.4%
	*Total ROG's = UCI total VOC - (methane+CO+Acetone)	

Corrals		
Flux Rate ($\mu g/M^2$/min)		
	3 INNOVA samples with 3 UCI canisters	
Summary and Comparison of UCI Canisters with INNOVA data		
	INNOVA Ethanol $\mu g/M^2$/min.	918.3
	INNOVA Methanol $\mu g/M^2$/min.	
	UCI Ethanol $\mu g/M^2$/min.	8.3
	UCI Methanol $\mu g/M^2$/min.	9.2
	Total VOC's (UCI) $\mu g/M^2$/min.	205.6
	Total ROG (UCI) $\mu g/M^2$/min.*	19.6
	Ethanol %	42.6%
	Methanol %	47.0%
	Total Alcohol %	89.6%
	*Total ROG's = UCI total VOC - (methane+CO+Acetone)	

Summary of Year-1 data for alcohol fluxes. Sampling occurred from June,06 through February, 07. All samples were collected during the day. Values are fluxes in $\mu g/M^2$/minute; calculated according to the USEPA Isolation Flux Chamber method found on the EPA website.

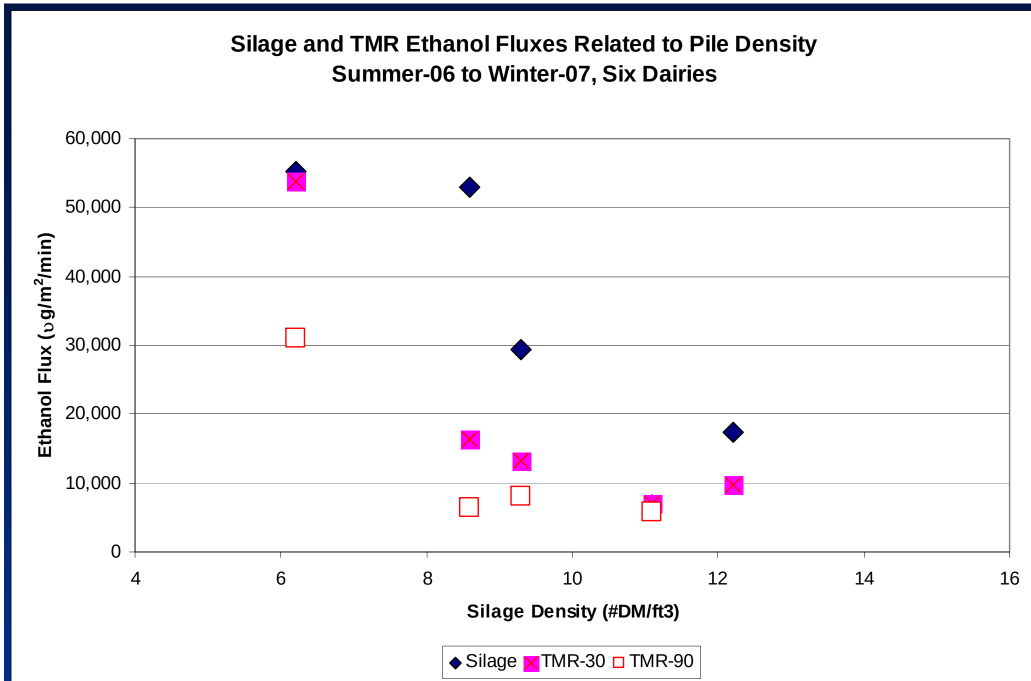
These initial results can be used to speculate about the relative emissions from a typical, large dairy.

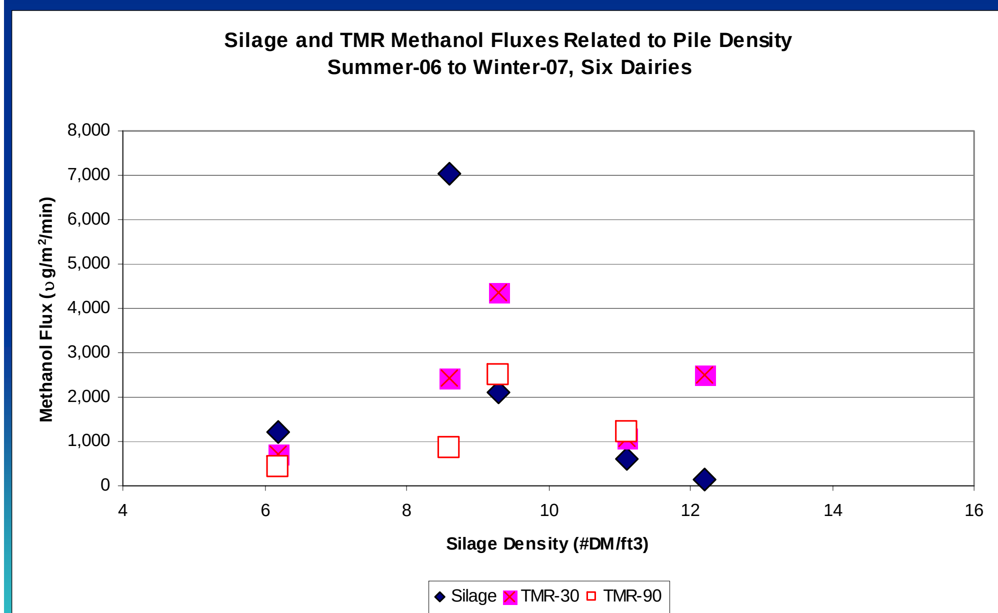
(these calculations are an example of a hypothetical dairy and are not intended as a conclusion)

Estimated ROG Emissions from a hypothetical, flushlane dairy of 2000 cows

	ROG	Time	Area	ROG	ROG	% of	ROG
	μg/M²/min.	Factor	M^2	g/min.	lb./day	Total	lb./hd/yr
Silage	10,639	100%	175	1.86	5.91	39%	1.1
TMR	4,187	25%	1,200	1.26	3.98	26%	0.7
Fresh Manure	214	50%	7,200	0.77	2.44	16%	0.4
Exercise Corral	20	100%	48,000	0.94	2.98	19%	0.5

The silage, though the smallest area on the dairy, is the highest ROG emission source (39%) due to its high flux rate. The TMR is the second highest source (26%) by these calculations but the decrease in flux with time has not been completely characterized and may decrease after additional monitoring has been done. The low flux rate from the open lots/exercise corrals offsets the large area.





Dairy	Date	Avg. DM Denstiy
CSUF	3/24/2006	18.7
CSUF	4/7/2006	11.2
A	4/10/2006	17.9
A	4/13/2006	15.1
A	4/24/2006	16.9
A	9/26/2006	11.1 X
B	7/10/2006	14.1
B	9/6/2006	9.3 X
C	1/11/2007	11.3
C	8/8/2006	6.2 X
D	6/1/2006	14.1
D	11/14/2006	12.2 X
E	6/23/2006	9.9
F	7/24/2006	8.6 X

Guidelines for silage production suggest compaction to a density of 10 #/ft^3 or more to reduce diffusion of air into the pile so that yeast fermentation will be inhibited. This fermentation may occur in low compaction piles, resulting in the production and emission of ethanol and, perhaps, other alcohols.

A limited number of silage samples in Year-1 were correlated with silage densities and, as expected, the lower density piles had significantly higher ethanol fluxes. The fluxes of methanol were also related to density but not as clearly as the ethanol. Further data will be collected in the Year-2 program to confirm or modify these results.

Recent Data from Summer-07

- The Year-2 sampling program will not be implemented until Fall-07 but most of the sampling and analysis procedures were used at each of the six dairies in a monitoring period from May to July of this year.
- The results were similar to those of the previous sampling periods but were more complete and systematic.
- In addition to the flux chamber monitoring, samples of the manure, silage, feed, flush water and soil were collected. Ambient and chamber conditions were recorded as well. Correlation of these fluxes with the substrate samples have not been completed for this sampling period.

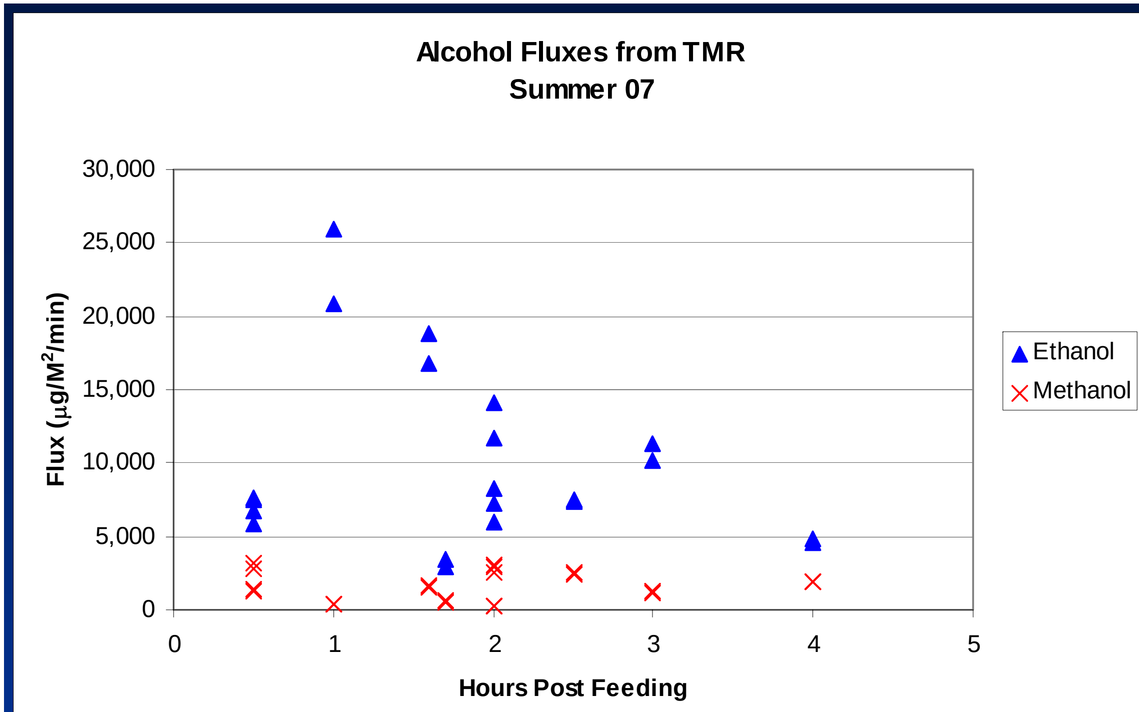
Summary of INNOVA Data for Spring/Summer-07

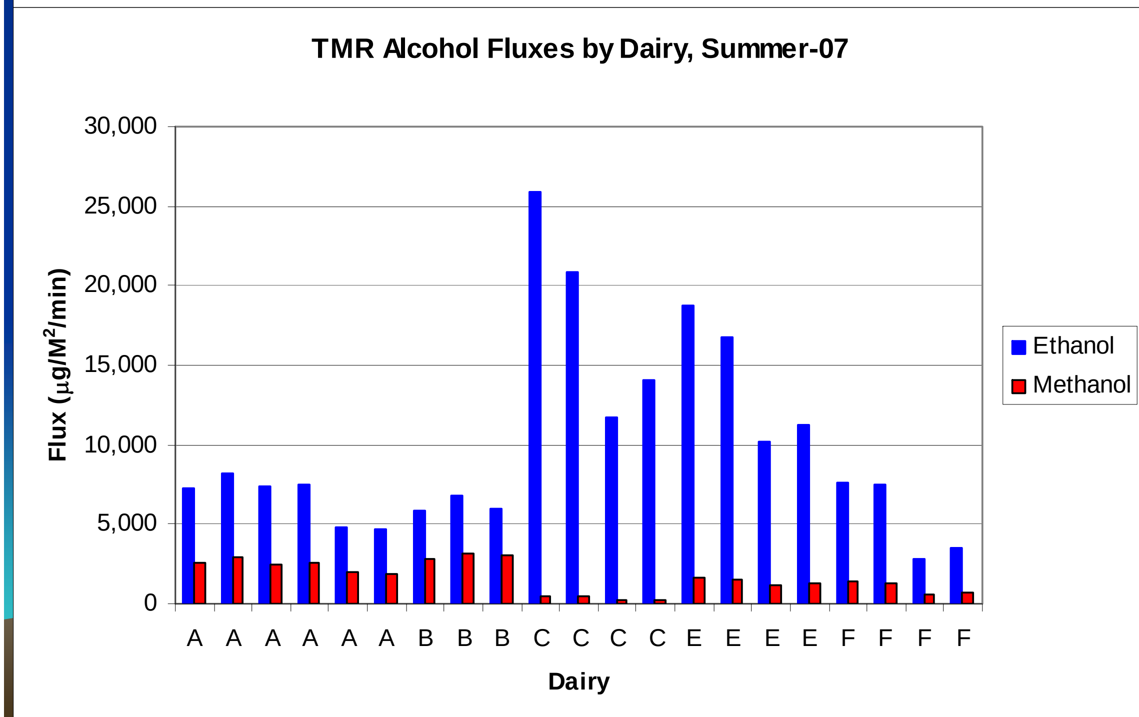
FLUXES in µg/M^2/minute

AVERAGES

Count	Source	NH_3-N	Ethanol	Methanol	CO_2	N_2O-N
12	Bedding	4,322	4,837	667	23,969	6
10	Fl Ln post	278	2	9	11,674	1
12	Fl Ln pre	747	52	12	17,837	0
10	OL deep	370	5	20	37,565	22
12	OL shallow	226	5	18	23,664	6
10	Silage corn	1,075	25,189	2,935	27,236	17
2	Silage winter	290	63,235	909	43,433	16
22	TMR	336	9,974	1,637	46,034	6

Each value is an average of all samples taken by the INNOVA unit from each of two flux chambers at each of the six dairies.





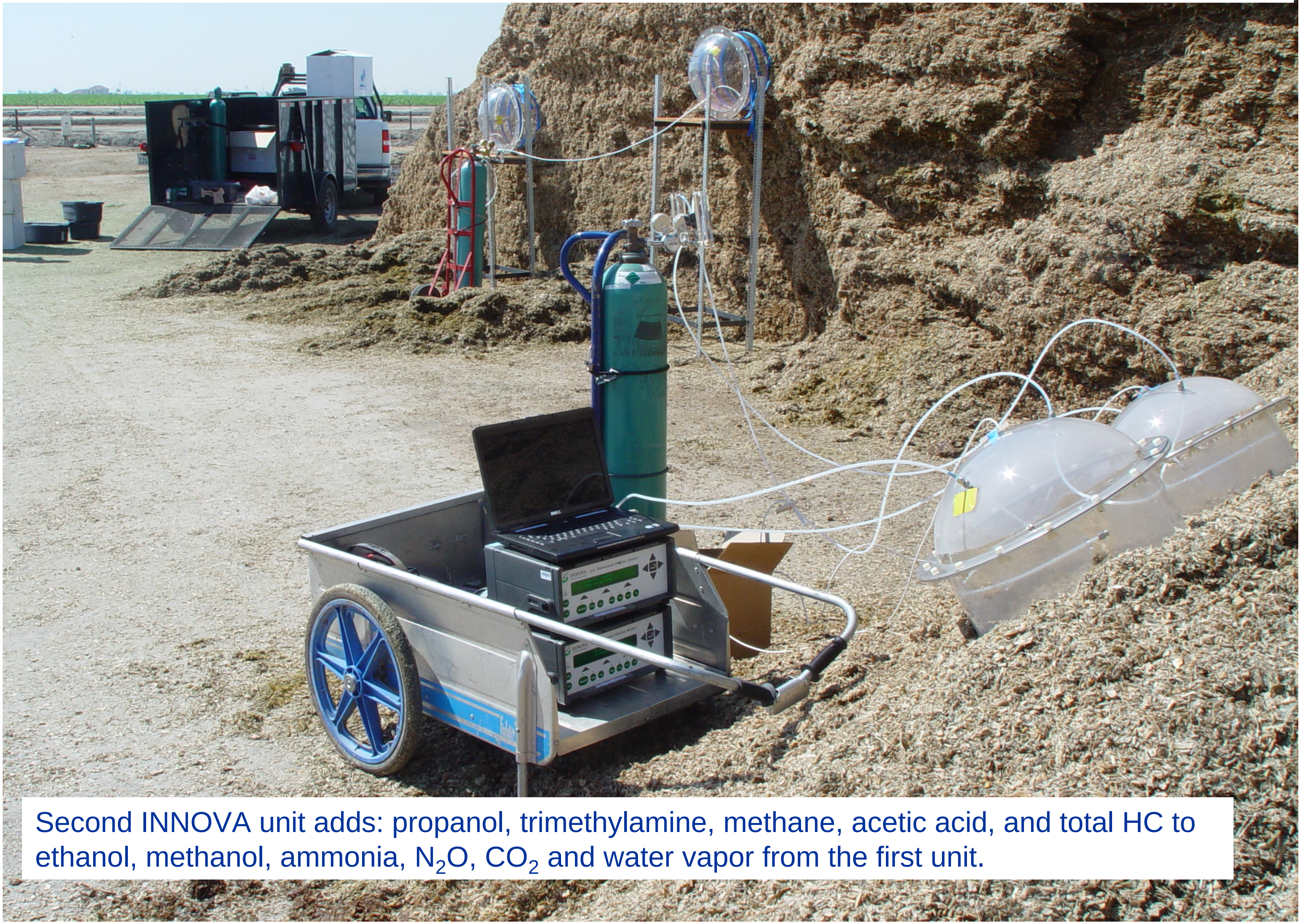
The Year-1 results indicated the probability that alcohol fluxes from the TMR decreased from the time the feed was delivered by the feed truck. Ethanol flux declined significantly with time after feeding but methanol did not appear to do so.

Alcohol fluxes from feed varied considerably between dairies. This was not unexpected since each dairy used a different ration. Dairy C was the only operation still feeding winter silage rather than corn silage during this sampling period. Correlations between alcohol fluxes and TMR factors will be done in Year-2

Year-2 monitoring program

- Silage sampling will include both disturbed and the undisturbed pile face.
- TMR monitoring will include 4-6 hour post-feeding samples of both feed and the lane surface.
- A second INNOVA unit will be used to add propanol, tri-methyl-amine, methane, acetic acid and total HC data.
- VOA sampling and analysis by a commercial lab will be added to each flux chamber sample.
- The canister and GC-MS analysis by UC Irvine will continue from one of the pair of flux chambers sampled at each operation of each dairy.
- All ambient and flux chamber atmospheric conditions will be monitored.
- A special sampling period following the fall, winter and spring/summer monitoring periods will be conducted at two of the six dairies. Those special samplings will include:
  - Fluxes from land application of solids and lagoon effluent.
  - A more complete time series of the fluxes from feeding operations
  - Fluxes from feed components in addition to silage
  - Ambient upwind/downwind canister samples when wind conditions are appropriate for dispersion modeling of the results.

Fluxes from the silage pile face compared to disturbed silage at Dairy A (September, 07)



Second INNOVA unit adds: propanol, trimethylamine, methane, acetic acid, and total HC to ethanol, methanol, ammonia, N_2O, CO_2 and water vapor from the first unit.

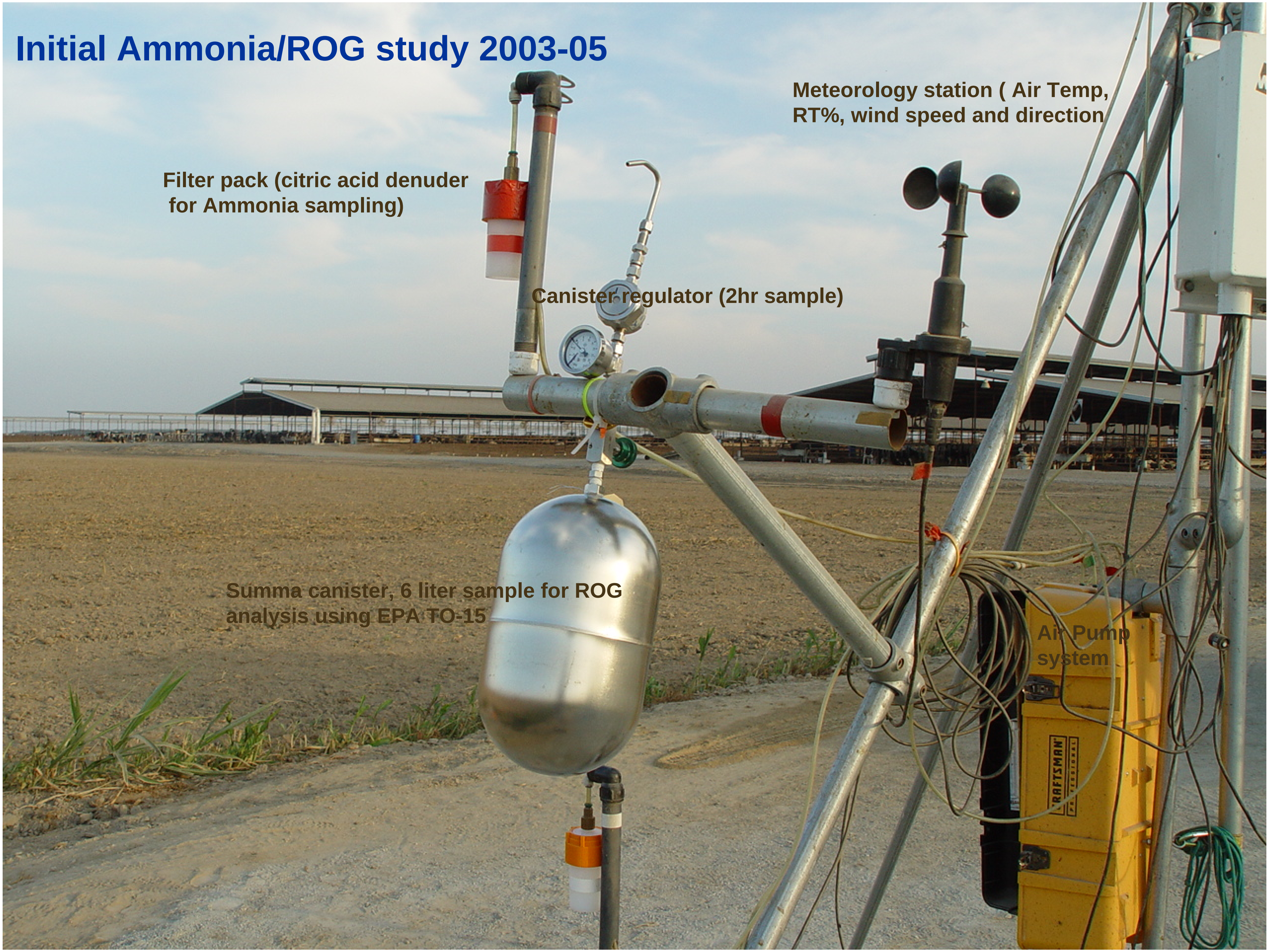
Fluxes from lightly loaded, photosynthetic lagoons for the CDC

Land Application of Lagoon Effluent at Dairy D (June, 2006)


QUESTIONS?

Fluxes from the silage pile face compared to disturbed silage at Dairy A


Flux Chamber monitoring of exercise corral at Dairy B


Initial Ammonia/ROG study 2003-05
Meteorology station (Air Temp, RT%, wind speed and direction
Filter pack (citric acid denuder for Ammonia sampling)
Canister regulator (2hr sample)
Summa canister, 6 liter sample for ROG analysis using EPA TO-15
Air Pump system

Land Application of Lagoon Effluent at Dairy D (June, 2006)