Monitoring and Modeling of ROG at California Dairies

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ABSTRACT
Three dairies in the Central Valley of California were selected to be sampled for Reactive Organic Gasses (ROG) and ammonia flux profiles from the fall of 2002 through the summer of 2004. Sampling was conducted quarterly to evaluate seasonal differences. Sampling locations at each dairy included an upwind site and sites downwind of significant dairy operations such as the animal housing, the lagoon system and surrounding cropland. The ROG samples were collected in canisters over a period of two hours. The analysis was by GCFID for total non-methane hydrocarbons (TNMHC) for the initial samples in 2002 and by GCMS using EPA-TO-15 for better speciation for the later sampling episodes. Wind along with other meteorological data was collected to assist in calculating emission factors for ammonia and ROG. Emission rates were modeled using the dispersion model ISC-STv3 for sampling periods that combined an acceptable level of confidence in the analytical results with wind conditions that allowed modeling. Emission rates modeled from the initial sampling evaluated as TNMHC were somewhat higher than those calculated from the later TO-15 analysis.

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A typical dairy cow in California produces between 80 and 140 pounds of manure each day. Within California's San Joaquin Valley, there are nearly 1.5 million producing dairy cows. For decades, the typical practice for managing this waste has been to flush the manure into storage lagoons. The water in the lagoons is used for subsequent flush water and, along with the recovered solid manure, is eventually applied to crops. Based on current California Air Resources Board estimates, dairies are a significant source of reactive organic gas (ROG) emissions in the San Joaquin Valley. Accurately quantifying dairy emissions is extremely difficult due to the complexity of the source, with its many dispersed biological process, as well as the challenges in sampling, analyzing, and modeling the collected emissions data. Quantification of ROG emissions is important since it is a component in the reaction that forms ground-level ozone, an air quality category for which the valley is designated as "non-attainment".

Air quality research has been conducted at the CSU Fresno Center for Irrigation Technology since 1998. The initial project was a study of ammonia emissions related to commercial fertilizer applications to various crops in California. The study was a cooperative effort funded by the California Air Resources Board to provide data for their ammonia inventory. CSU Fresno was responsible for the collection of field data and Chris Potter of the Ames Research Center – NASA modeled regional emission factors from the field data. Results from that project were presented at this conference in 2002 and the project report was submitted that same year. A second project, supported by the ARB was begun in 2001 to sample ambient ammonia levels related to various crops and natural vegetation to establish variability due to seasonal weather, soil type and other environmental factors. Some results of that study were presented at this conference in 2003. The increased interest related to dairy emissions has driven the priority of this research project toward the development of methods to sample and model ROG from the wide variety of agricultural operations associated with milk production and the disposal of waste from dairies and the related crop production operations. The application of the ammonia sampling methodology developed for the previous projects was easily converted to the sampling of ammonia at dairies. The development of collection and analytical methods for ROG has proven to be much more difficult. The modeling of emission factors from the collected field data was the capability requiring the most development. The process used by NASA-ARC in the previous fertilizer project was not applicable so a new method had to be found and validated. In 2004, our presentation at this conference focused on the selection and validation of methods to sample ROG and model emission factors based on those initial samples. In the past year, several additional data sets have been obtained by sampling and analyzing upwind and downwind canisters at three dairies. Calculating an emission rate for these sampling episodes required appropriate wind conditions and confidence in the analytical results. Wind conditions were consistently good at one of the dairies, acceptable some of the time at another and generally poor at the third. Analytical problems were such that only results from 1 winter sample, 1 spring sample and 3 early summer samples have produced usable emission rates to date. Additional sampling episodes are being evaluated but the five reported here are from the best quality data.

The ROG sampling was done in 6 liter summa canisters according to published methods (EPA-TO-15, 1999). The method is described in more detail in the papers presented at the '02 and '03 conferences (Krauter, 2002 and Krauter, 2003). The analysis of the first samples collected in October, 2002, discussed in last year's paper, were done at the Oregon Graduate Research Institute by Dr. R. Rasmussen. Subsequent samples were analyzed

at CSU Fresno by gas chromatography (Varian Saturn CP3800) with a cryogenic concentration unit and a mass spectrometer (Varian 2100T) according to published methods (EPA-TO-15, 1999).

The model selected for this project was the Industrial Source Complex Short Term version 3 (ISC-STv3). It is a steady state Gaussian plume model that can be used to predict downwind concentration from area sources (EPA, 1999). ISC-STv3 is used to calculate 1-hour average concentrations at receptor locations placed anywhere around the source. The inputs for the model include the relative placement of sources and receptor locations, as well as recorded meteorological conditions and emission fluxes. The output from the model is the predicted concentration at the selected receptor locations. In order to predict concentrations from area sources, the source is broken into multiple finite-length line sources. The finite-length line source equation results from the integration of the point source equation in the crosswind direction as shown in equation 1.

Equation (1) $$C = \frac{Q_A}{2u\pi}\int_x \frac{V}{\sigma_y \sigma_z}\left(\int_y \exp\left[-0.5\left(\frac{y}{\sigma_y}\right)^2\right]dy\right)dx$$

where

C = concentration of pollutant (µg/m3)
Q_A = pollutant emission rate (µg/s-m^2)
V = vertical term used to describe vertical distribution of the plume
σ_y, σ_z = Pasquill-Gifford plume spread parameters based on stability class
u = average wind speed
X = upwind direction
Y = cross wind direction

The integration of this equation results in equation 2.

Equation (2) $$C = \frac{2q}{\sqrt{(2\pi)}\sigma_z u}\left\{\exp\left[-\frac{-(z-H)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{-(z+H)^2}{2\sigma_z^2}\right]\right\}(G_2 - G_1)$$

where

C = concentration of pollutant (µg/m^3)
q = emission rate (µg/m/s)
σ_z = Pasquill-Gifford plume spread parameter based on stability class (m)
u = average wind speed at pollutant release height (m/s)
H = emission height (m)
Z = Receptor height (m)
G_2, G_1 = Gaussian distribution function to account for edge effects

The correction for edge effects is a function of the crosswind distance from the end of each line source to the receptor (Y) and the horizontal plume spread parameter (σ_y). Since the horizontal plume shape is represented by a normal distribution, equation 3 can be used to determine the fractional portion of the area under a normal curve. This value is used as a scalar to decrease the predicted concentration.

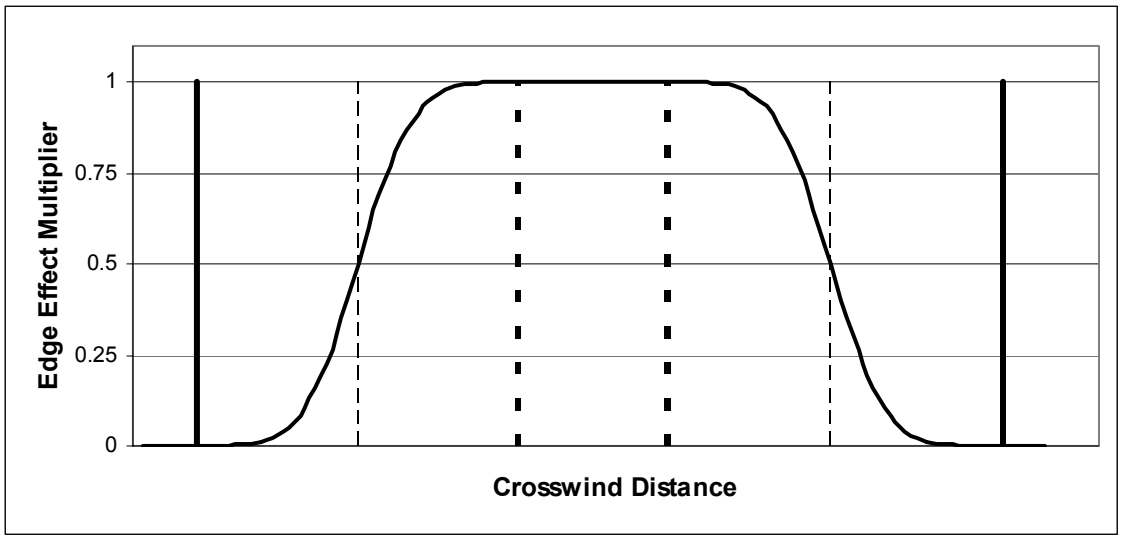
Equation (3) $$G = \frac{Y}{\sigma_y}$$

where:

G = number of standard deviations
Y = crosswind distance between receptor and edge of line source
σ_y = horizontal plume spread standard deviation

The edge effect phenomenon is due to the horizontal dispersion of the pollutant. When the receptor is more than 3.8 σ_y from the edge of a line source, the edge effects are accounted for in ISC-STv3. The result of edge effects produces the plume shape shown in figure 1.

Figure 1. The magnitude of edge effects in the crosswind direction is shown here. The dashed lines represent a position directly downwind of the end of the line source. The peak concentration is reached at a distance of 3.8 σ_y towards the center of the field. There is no contribution to the concentration when the receptor is placed greater than a distance of 3.8 σ_y outside the edge of the field.



This process of dividing the area source into multiple line sources is similar to the algorithm used in the Point Area and Line Sources 2.0 model (PAL) (EPA, 1995). The summation of the predicted concentration from each line source is the resulting concentration at the receptor location. In order to determine the modeled concentration at any receptor location, the number of line sources used is increased until the predicted concentration with N line sources converges with that predicted with N-1 line sources. The difference between ISC-STv3 and PAL is the method used for evaluation of the integral as well as the specific limits used to determine convergence. These changes were made in order to optimize the computing time used to determine the concentration (EPA, 1995) but yield the same results. ISC-STv3 can also handle more variations in the configuration of area sources while PAL was limited to strictly North-South East-West orientations (EPA, 1987). The method used by ISC-STv3 also allows for the placement of receptors at any location in or around area sources. The only limitation on placement of receptors is the upwind distance to the nearest line source. The limitation is due to the calculation of the σ_z parameter. When the upwind distance from source to receptor approaches zero, this value approaches zero, yielding inconsistent results. Therefore, ISC-STv3 limits the minimum downwind distance, from source to receptor, to 1 meter.

The Gaussian model is typically used to determine a concentration at a given location due to a known emission flux. In this case, the concept is used in reverse, to determine an emission flux, from a known concentration. Due to the fact that equation 1 cannot be solved directly for flux, it is necessary to use a multi-step process. This is done using the proportional nature of flux, Q_A, to the predicted concentration. The goal is to determine a flux that will predict the measured net concentration when used in ISC-STv3 with the actual meteorological conditions present during sampling.

The process can be most simply described for a single area source. First, the source receptor orientation is modeled using an emission flux unit (EFU) of 1 $\mu g/m^2/s$. Then the ratio of the modeled concentration to the

measured net concentration is used to scale the EFU. If 1 $\mu g/m^2/s$ is chosen as the initial EFU, the required flux to match the measured concentration will be equal to the ratio of measured to predicted concentration. The units of the resulting flux can then be adjusted to those required for the given operation. In the case of multiple area sources with different emission fluxes it is necessary to have a receptor for each area source emitting at a different rate. Each receptor is then used to determine an emission flux for an individual area source. The dairy used as an example here has two identified sources with different fluxes (see figure 2). There were three sampling locations setup to handle this configuration. Location DW1 was setup as a background receptor, upwind from the dairy to determine ambient concentrations of the target pollutants. The DW4 sampling site was directly downwind of the free stall and exercise pens. The DW2 site was downwind of the large lagoon. The first step in determining the two different emission fluxes was to calculate the flux from the free stall areas as described above. In this case the free stalls and exercise pens were assumed to have uniform fluxes. Once the flux from the free stall/exercise pens was determined, it could be used to calculate its contribution to the receptor at the edge of the lagoon. The net concentration at the edge of the lagoon was determined by subtracting the upwind concentration and the free stall/exercise pen concentration from the measured concentration at the lagoon site. The same process could then be used to determine the flux from the lagoon.

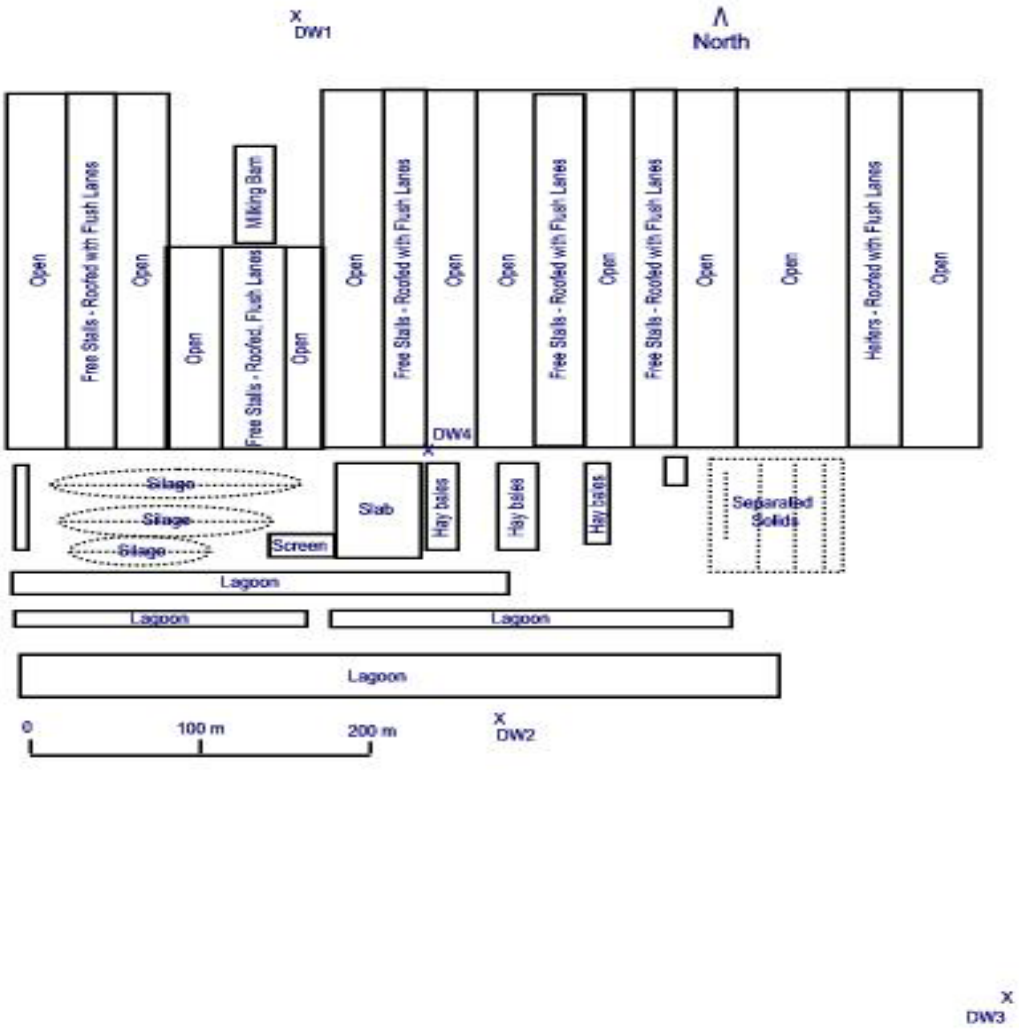
Dairy Sampling

Three dairies were selected for a series of ammonia and ROG sampling periods that began in October of 2002. The criteria for dairy selection included: medium-large sized of about 2000 head, built or renovated at least 3 years but no more than 10 years ago and equipped with the common free stall management system. Free stall dairies have feeding lanes and bedding stalls that the animals move into by choice. In addition to the free stalls which are usually covered for shade in summer and warmth in winter, the animals have a larger, open exercise corral that is usually bare soil. The free stall and corral unit are designated as the "animal holding area" for purposes of modeling emission rates in this study. The free stalls are arranged on long, sloping concrete lanes that can be flushed several times each day to remove waste. The waste is flushed into a pit to allow sand and soil to settle. The light solids are then separated from the liquid, usually by a screen system. The separated solids, primarily undigested fibers from the animal feed, are dried and used as either bedding in free stalls or soil amendments on surrounding cropland. The liquid from the separation process still contains a considerable load of fine solids. It usually goes to another settling basin or directly to a large storage lagoon. Water from the lagoon is used for subsequent flushing cycles and will eventually become irrigation water on adjacent cropland to recycle the nutrients. The three selected dairies included the first one near Hanford in Kings County (Fig.2). and two others in Fresno and Merced counties. They were each to be sampled every three months beginning in the summer of 2003. The objective was to determine seasonal variability for emission rates of ammonia and ROG for average sized dairies with the most common waste management systems.

The field sampling was done as scheduled but problems with the analytical system did not allow emission rates from the field sampling to be calculated until the winter of 2003 and spring/summer of 2004. The required minimum detection level for the various species of ROG was 0.1 $\mu g/m^3$. Achieving that capability with our GCMS system required the addition of a cryogenic sample concentrator and several months of system development to obtain consistent results at that level of accuracy. The need for an elaborate sample canister cleaning system and application of the QA/QC requirements from the TO-15 procedure also delayed the availability of results. Once the field sampling and analytical procedures were in place, data from the sampling of the dairies was used in the dispersion model to estimate emission rates for ROG's for each sampling episode. The modeling process required a consistent wind direction and speed for the 2 hour period required to fill the sample canisters. Those wind conditions were relatively common from late spring through early fall, especially at the Merced County dairy. During the winter, these reliable, thermal winds were replaced by variable winds from passing weather systems alternating with calm conditions due to winter inversions. A few short sampling

periods (5 minutes) were attempted with limited success to collect samples during these less favorable modeling conditions.

Figure 2. A diagram of the dairy near Hanford, CA where ROG and ammonia samples were taken for modeling of emission fluxes.



The initial sampling of this dairy was done in October of 2002 as a trial of the sampling systems. At the time it was selected, no model had been chosen. This monitoring of ammonia and ROG differs from later work in that the sampling equipment was rented and the analysis was done at Oregon Graduate Research Institute Lab. Since no model had been selected at that time, the location of sampling sites for this first attempt was changed for each of the three days of sample collection to anticipate the needs of a variety of possible models. There were four sampling periods of two hours on each of the three days. Each period included an upwind sample (DW1) and a sample at the downwind edge of the dairy where the lagoon was located (DW2). A third sample was taken but its location was different for each day. On the first date, October 18, the third sample was co-located with DW2 but at 10m instead of the usual 2m height. On the second sampling date, October 21, the third sample was located in the center of the dairy downwind of the free stall area but upwind from the lagoon (DW4). That proved to be the proper location for the ISC-STv3 modeling program. The ISC-STv3 model requires an upwind and downwind sample difference to calculate a net concentration. On the 21st, the free stall sampling site, DW4 on Figure 2, was ideally located as an upwind lagoon value. Ammonia samples were taken at the same time and location as the ROG canister samples. Data from the ROG samples with the results of the

modeling are shown in Table 1. Analysis for ROG at OGRI was done as total non-methane hydrocarbons (TNMHC). Characterization of ROG as TNMHC may be done as long as it is recognized that the values are an over estimation since not all volatile organic compounds (VOC) are reactive as ozone precursors (ROG).

Table 1. Initial sampling of methane and ROG at the Kings County Dairy, October, 2002. Analysis done at the Oregon Graduate Research Institute.

Sampling Conditions, Kings Dairy

Sampling Periods			Up-wind Conditions					
Date	Start	End	CH4 $\mu g/m^3$	TNMHC $\mu g/m^3$	Wind Speed (m/s)	WD degrees	Stablility Class	Air Temp. Degree F
21-Oct-02	1248	1440	1560	44.5	1.26	343.5	2	74.5
21-Oct-02	1522	1722	1428	51.4	2.20	320.0	4	75.5
21-Oct-02	1737	1940	3443	139.7	0.95	312.1	6	67.4
21-Oct-02	2005	2155	1830	75.7	0.23	318.4	6	62.1
Average			2066	77.8	1.2	323.5		69.9

Modeled Emissions from Animal Housing Area (Freestall/corral)

Sampling Periods			Methane	Methane	ROG TNMHC	ROG TNMHC
Date	Start	End	kg/hd/yr	lb./hd/yr	kg/hd/yr	lb./hd/yr
21-Oct-02	1248	1440	53.9	118.6	7.8	17.3
21-Oct-02	1522	1722	118.9	261.6	8.8	19.3
21-Oct-02	1737	1940	94.5	207.9	2.9	6.4
21-Oct-02	2005	2155	85.5	188.1	1.7	3.7
Average			88.2	194.0	5.3	11.7

Modeled Emissions from Lagoon System

Sampling Periods			Methane	Methane	ROG TNMHC	ROG TNMHC
Date	Start	End	kg/hd/yr	lb./hd/yr	kg/hd/yr	lb./hd/yr
21-Oct-02	1248	1440	6.7	14.7	0.5	2.3
21-Oct-02	1522	1722	5.9	13.0	1.0	2.3
21-Oct-02	1737	1940	N/A	N/A	N/A	N/A
21-Oct-02	2005	2135	4.0	8.7	0.9	2.1
Average			5.5	12.1	0.8	2.2

Modeled Emissions Estimated for Total Dairy

Sampling Periods			Methane	Methane	ROG TNMHC	ROG TNMHC
Date	Start	End	kg/hd/yr	lb./hd/yr	kg/hd/yr	lb./hd/yr
21-Oct-02	1248	1440	60.6	133.3	8.4	19.6
21-Oct-02	1522	1722	124.8	274.5	9.8	21.6
21-Oct-02	1737	1940	N/A	N/A	N/A	N/A
21-Oct-02	2005	2135	89.5	196.8	2.6	5.8
Average			93.7	206.2	6.1	13.9

These results should be considered as examples of emissions from one dairy for a single sampling event rather than representing dairy emissions in general. They are presented here only to show the initial results of the

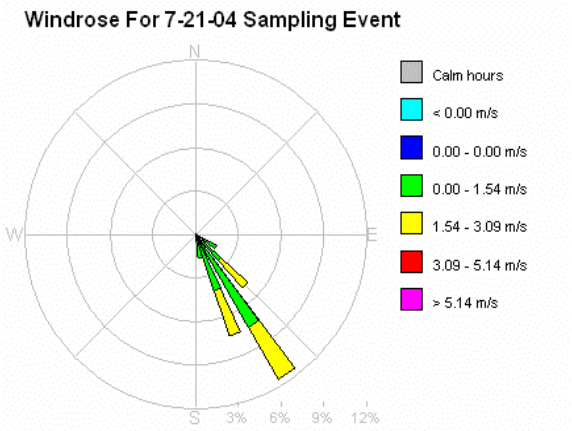
model. It is possible to draw some conclusions from these results of the model for this initial sampling period so long as it is understood that the conditions may be different for other sites and other times of the year and the TNMHC values are an overestimation of ROG. The methane emissions for the free stall areas shown in Table 1 are somewhat higher than the current estimate for dairy cow methane emissions in California but are still reasonably close. The emissions from the lagoon shown in Table 1 are quite low and cast some doubt on the idea that a covered lagoon and digester would harvest most of the methane and ROG from dairy operations. An emission rate for the dairy as a whole for this date can be estimated by adding the averages for the animal housing areas to those from the lagoon since the Kings County dairy was configured with these two separate areas in line along the direction of the prevailing wind. The ROG emissions from the model are interesting and reasonably close to current estimates but should not be construed as anything other than examples. Emissions from the free stalls are near the 5.8 kg./head/year (12.8 lb./head/year) that is currently used by the California ARB as the total ROG emission from a dairy cow. The higher values during the day may correlate with feeding and exercise when animals are more likely to ruminate and excrete waste from which ROG can volatilize. Temperature or other environmental conditions may also be part of the apparent diurnal variability. The same pattern of higher values during the day was commonly seen in particulate emissions from both dairies and feedlots in Texas. Further sampling and modeling at this and the other dairies produced somewhat similar results for ROG emissions from the various components of the dairy operation. These later samples were accomplished with different methods, field equipment and analytical systems that were developed by the CSU Fresno research group for the remainder of this project.

As discussed above, the sampling and analysis of the original samples taken in October, 2002 were primarily to develop a preliminary estimate of emission rates and to provide data for the process of selecting the dispersion model. Once the in-house capabilities for field sampling, analytical and modeling procedures had been selected and tested, further sampling episodes were conduced at each of the three dairies. As described above, the wind conditions that permitted the model to be used and the successful analysis of all the field samples coincided for only five out of the approximately fifteen sampling episodes at two of the three dairies since spring of 2003. Table 2 shows mid-day emission rates for the Kings dairy for July 21, 2004.

Table 2. Kings County dairy emission rates for July 21, 2004. Sampling and analysis by EPA-TO-15 methods. Wind data is collected continuously from the upwind sampling location and is reported in 5 minute averages.

7/21/2004 1300 to 1530

Kings Dairy	Measured TO-15 Concentration	Net TO-15 Concentration	Emission Rate
	µg/m^3	µg/m^3	#/hd/yr
Freestall	72.7	21.5	1.3
Trt Lgn	55.9	27.7	0.2
Storage Lgn	52.4	10.3	0.4



The Kings dairy has the animal housing areas and the lagoon complex arranged along the path of the prevailing wind (Figure 1) so that the sampling point in the middle of the dairy, DW4, can serve as both the down-wind sample for the animal housing area as well as the up-wind sampling point for the lagoon complex. An added sampling point between the tertiary treatment lagoon and the large storage lagoon to the south allowed the separation of emission rates for these two locations. This configuration also allows the addition of the emission

rates for each component operation to get an estimate of the emission rate from the whole dairy operation. The sum of the emission rates in Table 2 equals 1.9 lb./head/year, a value much lower than current estimates. The wind conditions as shown in the wind rose were very well suited to the modeling requirements so these emission rates are presented with considerable confidence. The following day samples were taken both at noon and later in the afternoon at the same dairy and the results are shown in Tables 3 and 4.

Table 3. Kings County dairy emission rates for July 22, 2004. Sampling and analysis by EPA-TO-15 methods. Wind data is collected continuously from the upwind sampling location and is reported in 5 minute averages.

7-22-04 test 1 1100 to 1330

Kings Dairy	Measured TO-15 Concentration	Net TO-15 Concentration	Emission Rate
	µg/m^3	µg/m^3	#/hd/yr
Freestall	64.3	12.4	0.9
Trt Lgn	219.3	161.5	1.7
Storage Lgn	69.7	19.3	1.1

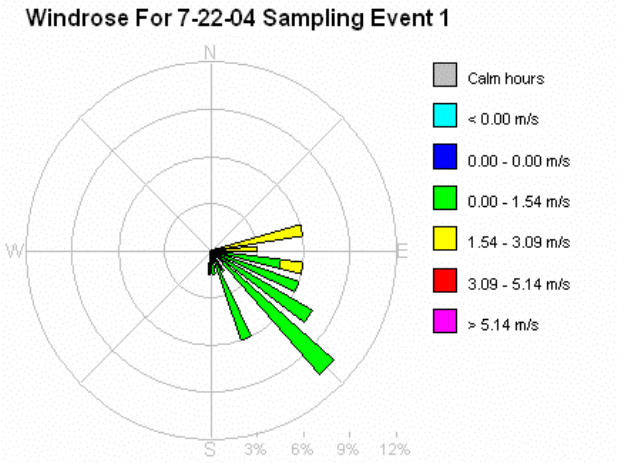
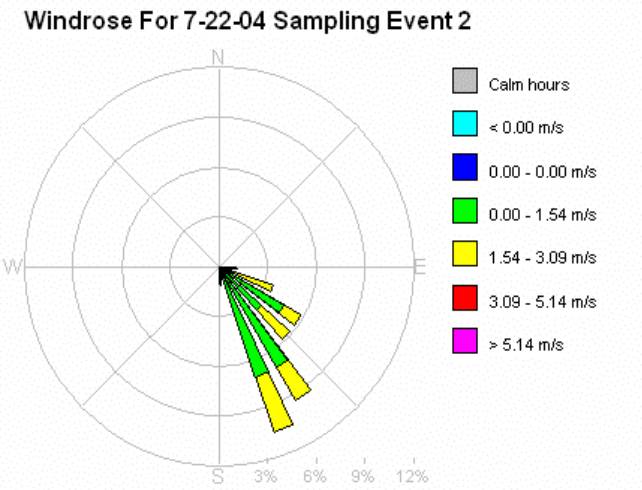


Table 4. Kings County dairy emission rates for July 22, 2004. Sampling and analysis by EPA-TO-15 methods. Wind data is collected continuously from the upwind sampling location and is reported in 5 minute averages.

7-22-04 test 2 1330 to 1600

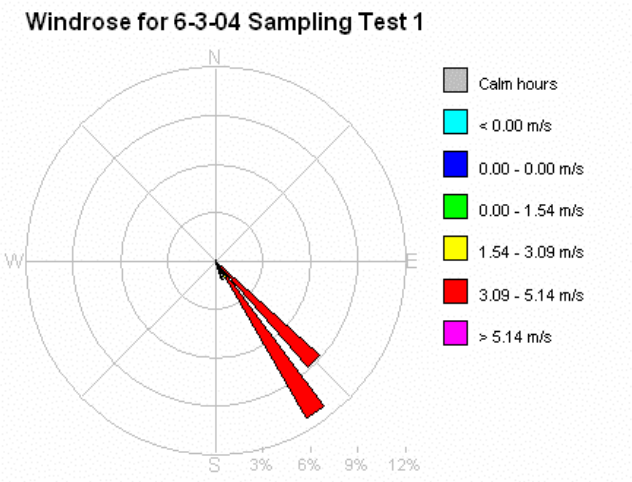
Kings Dairy	Measured TO-15 Concentration	Net TO-15 Concentration	Emission Rate
	µg/m^3	µg/m^3	#/hd/yr
Freestall	78.7	24.6	1.5
Trt Lgn	85.5	36.8	0.3
Storage Lgn	61.8	21.5	0.9



The first sampling period, 1100 to 1330 on July 22, 2004 did not have the consistent wind direction of the previous day and, therefore, cannot be modeled with the same level of confidence. The lower value for the animal housing area (Free stall) is most likely due to the fact that for some of the sampling period, the wind was not passing over the free stalls that were sampled. The lagoon samples were also compromised. The individual values may not be representative of the designated dairy locations but the samples were still collected from within the dairy and the emission rates can still be considered as examples though with less certainty. The second sampling episode on July 22, 2004 was conducted under much more suitable wind conditions so the data in Table 4 can be considered more valid than Table 3. The component emission rates and the sum of 2.7 lb./head/year are quite similar to the values modeled from the previous day, shown in Table 2.

A sample from the Merced County dairy was successfully modeled for June 3, 2004. Though the sampling was done six weeks prior to the Kings dairy, the weather conditions were similar and the results can be compared with some confidence.

Table 5. Merced County dairy emission rates for June 3, 2004. Sampling and analysis by EPA-TO-15 methods. Wind data is collected continuously from the upwind sampling location and is reported in 5 minute averages.

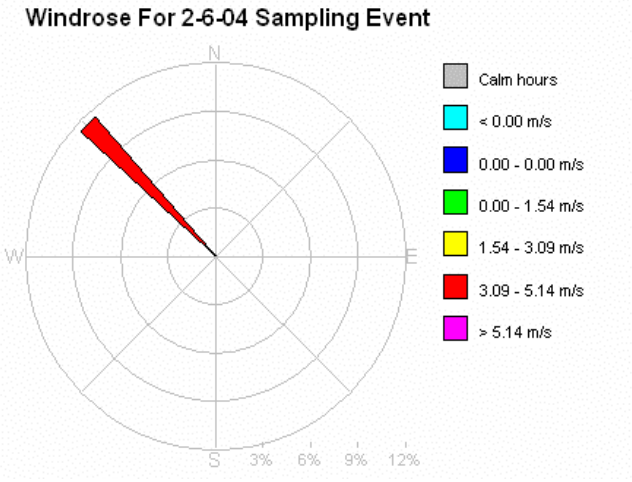


6-3-04 test 1 945 to 1230

Merced Dairy	Measured TO-15 Concentration	Net TO-15 Concentration	Emission Rate
	µg/m^3	µg/m^3	#/hd/yr
Lagoon	79.2	16.2	2.4
Freestall 1	101.1	21.3	6.3
Freestall 2	73.5	14.4	3.6

The emission rates shown in Table 5 for the Merced dairy reflect a different sampling pattern due to the different configuration of the dairy. The animal housing areas were not up-wind of the lagoon, which was a single, large facility unlike the sequential lagoons found at the Kings dairy. The Freestall 1 and 2 sampling sites were for the two distinct animal housing locations and can be averaged and added to the lagoon emission rate to estimate the emission rate from the whole dairy as equal to 6.9 lb./head/year. The only other sampling episode with sufficient data for modeling emission rates at the Merced dairy was in the winter on February 6, 2004. The wind conditions were not sufficiently consistent for the usual 2 hour sample because a weather system was moving through to the north, causing the wind to back through the day. A period of 30 minutes provided a consistent wind direction and the sampling canisters were filled in 5 minutes at the end of that period. The data from this winter sample was modeled and is shown in Table 6.

Table 6. Merced County dairy emission rates for February 6, 2004. Sampling and analysis by EPA-TO-15 methods. Wind data is collected continuously from the upwind sampling location and is reported in 5 minute averages.



2/6/2004 1100 to 1105

Merced Dairy	Measured TO-15 Concentration	Net TO-15 Concentration	Emission Rate
	µg/m^3	µg/m^3	#/hd/yr
Lagoon	139.6	39.4	1.5
Freestall 1	118.6	17.1	4.2
Freestall 2	109.7	20.1	3.8

The winter sampling period for the Merced dairy can be used to estimate a whole dairy emission rate in the same fashion as used for the June 6 sample at the same location. The free stall emission rates are averaged and added to the lagoon emission to get a total of 5.5 lb./head/year. That value is no more different from the June 6 emission rate than the July 21 and 22 emission rates were for the Kings dairy. It may be that the seasonal effect on emission rates that was expected to lower winter values does not apply to ROG emissions. An additional interesting factor regarding this sample is the fact that the wind direction was the opposite of the usual NW wind of the other sampling episodes. Though the wind direction was different and the sampling period was shorter, the values for the animal holding areas, lagoon and the estimate for the whole dairy were remarkably consistent with the other sample take at this dairy.

The ROG emission rates modeled from the five recent sampling episodes cannot be directly compared with those from the initial sampling at the Kings dairy in October, 2002 because the analysis for ROG in the collected samples was different. The samples taken in 2002 were analyzed by GC-FID and reported as Total Non-Methane HydroCarbon. TNMHC, as discussed above, is an overestimation of ROG because it measures everything in the sample and the results are reported in terms of an index compound. While some speciation of the gasses in the sample can be estimated, most are not identified. It is certain that a significant portion of the TNMHC modeled and reported in Table 1 is not an ozone precursor (ROG). A more specific method of analysis was needed to better separate the gasses in the samples for identification and quantification. The EPA-TO-15 provided that method as well as the sampling and QA/QC programs used for this study. The TO-15 analytical method uses a GCMS to separate and identify the gasses by molecular weight. The problem with the method is its reliance on a standard gas. Accurate quantification and precise identification requires a known amount of any gas of interest to be analyzed by the system for calibration. Unfortunately, the only standard gas that was available at the time of the sampling was one that was formulated for combustion products rather than dairy emissions. There are certainly ROG compounds in the samples that cannot be accurately quantified because they were not present in the standard gas. Therefore, the analytical results may underestimate actual ROG emissions. Since there are compounds in the standard gas that are not reactive and those non-ROG's are a significant portion of the identified and quantified gasses, the modeled emissions may, instead, be an overestimate. It is not possible to determine which is the greater error in the analysis, the missing ROG compounds or the identified gasses that are included but are not ROG's. A much more suitable standard gas has been ordered and will be used in subsequent analysis and modeling of samples collected from these same dairies.

References

1. Environmental Protection Agency. 1995. Users Guide for the Industrial Source Complex (ISC3) Dispersion Models Volume 2. EPA-454/B-95-003b. Office of Air Quality Planning and Standards; Research Triangle Park, North Carolina.

2. Environmental Protection Agency. 1999. Determination of Volatile Organic Compounds (VOC) In Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GCMS): Method TO-15, EPA-600/625/R-96/010b, U.S. Environmental Protection Agency; Research Triangle Park, NC

3. Krauter Charles, D. Goorahoo, C. Potter and S. Klooster, 2003. Ammonia Flux Profiles For Various Soil and Vegetation Communities in California. Proceedings of the EPA Emission Inventory Conference in San Diego California

4. Petersen, W.B. and E.D. Rumsey, 1987: User's Guide for PAL 2.0 - A Gaussian-Plume Algorithm for Point, Area, and Line Sources, EPA/600/8-87/009, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.