Rebuttal Report

to

“Technical Memorandum – Evaluation of Methanol and Other Study Compounds From the South Lakes Dairy Located in Pixley, California Using the USEPA Surface Isolation Flux Chamber Technology, December 2007” by Dr. C. E. Schmidt,

and

“Quantification of Methanol Emissions, South Lakes Dairy, Tulare County, California, December 2007” by Thomas R. Card and Charles E. Schmidt

Prepared for
Center on Race, Poverty and the Environment
for use in
Association of Irritated Residents v. Fred Schakel Dairy, et al.

Prepared by

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January 25, 2008

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Introduction

The purpose of this report is to rebut the expert report entitled “Technical Memorandum – Evaluation of Methanol and Other Study Compounds From the South Lakes Dairy Located in Pixley, California Using the USEPA Surface Isolation Flux Chamber Technology, December 2007” by Dr. C. E. Schmidt and the expert report entitled “Quantification of Methanol Emissions, South Lakes Dairy, Tulare County, California, December 2007” by Thomas R. Card and Charles E. Schmidt, in Association of Irritated Residents v. Fred Schakel Dairy, et al., No. 1:05-CV-00707 OWW SMS. I respond to the report by Schmidt in Section I, and the report by Card and Schmidt in Section II. My opinion is summarized in Section III. Attached to this report are two appendices, Appendix A which includes results of my own research providing support for my opinions, and Appendix B which includes published references to support my opinions.

The defendant’s expert Dr. Chuck Schmidt and his associate Harold Litwiler were allowed to visually observe and document via handwritten notes, photographs, and video, the sampling conducted by myself and my associates Marty Rhoades and Edward Caraway on October 18-19, 2007. I offered the defendant’s expert the opportunity to collect duplicate samples at that time, but they declined. The defendant’s experts returned to conduct their own sampling on October 22-23, 2007. Plaintiff counsel and I asked for split sampling of any sampling by defendant’s experts but counsel for the defendant refused. Neither I nor any of the plaintiff’s experts were allowed to visually observe and document the defendant’s sampling event or take duplicate samples. Since I was not allowed the same level of review as defendant’s experts, this rebuttal report is limited and based solely on the written material provided to myself as part of that report, and not on actual conditions observed on-site on the date of sampling by defendant’s experts.

I. Rebuttal to “Technical Memorandum – Evaluation of Methanol and Other Study Compounds From the South Lakes Dairy Located in Pixley, California Using the USEPA Surface Isolation Flux Chamber Technology, December 2007” by Dr. C. E. Schmidt.

I. a. The authors sampled methanol, ethanol, and acetaldehyde using USEPA Method TO-15, which uses evacuated canisters. Koziel et al. (2005) demonstrated that canister methods have poor recoveries of VOCs, and that the percent recoveries decrease with increasing holding time in the canister (i.e. analyte concentrations decrease with time). For example, Koziel reported sample recoveries of only 2.7% for acetic acid (which has a molecular weight of 60 compared to 46 for ethanol and 32 for methanol) after a 24 hr holding time from SUMMA canisters, meaning that 97.3% of the compound was lost. In contrast, direct sampling methods such as SPME fibers and sorbent tubes were found to have minimal losses over time (Koziel et al., 2005). The defendant’s experts collected summa canister samples on 10/22/07 and 10/23/07. Samples were analyzed between 10/29/07 and 11/16/07, which was 7 to 24 days after sampling. I did not see that the defendant’s experts collected any field spikes as part of their QA/QC program, thus it is impossible to assess how these potential losses would affect measured emission rates.

I. b. In Table 1 of the Schmidt report, there is a column listing flame ionization detector (FID) in ppmv. I could find no reference of the FID in the text of the report, nor any interpretation of the FID results. I found it unclear in the report whether the FID was only used on the first four samples, and the lagoon sample, or whether it was used throughout the project. All other samples are listed as “NA” or “Not applicable.” If there is other FID data, it should be presented in Table 1, and the purpose and conclusions of the FID measurements should be discussed along with a comparison to previous FID measurements collected at other dairies as presented in the expert’s previous report (Card and Schmidt, 2006).

I. c. On Page 11 of the Schmidt report, a statement is made that measurements were made using the “USEPA **recommended** surface flux chamber technology.”

It is my understanding that the USEPA funded the original study as reported in Kienbusch (1986). However, I do not believe that the USEPA has formally recognized the flux chamber technology as the “recommended” or preferred method of measuring emission rates from animal feeding operations, nor that the selection of 5 L/min as the sweep air flow rate is the regulatory approved flow rate for measuring emissions at animal feeding operations. The USEPA funds many grants and projects every year, but they are usually clear that this does not imply endorsement. The Kienbusch (1986) report has a notice at the front of the report that states that the document is a preliminary draft, and that it “should not at this stage be construed to represent Agency policy.” Even if it were an EPA approved or recommended technology in 1986, there has been considerable knowledge gained on CAFO emissions since that time, enough to cast doubt on the appropriateness of flux chambers as the sole method of determining emission rates from CAFOs.

It is my opinion that the “USEPA flux chamber,” or “Kienbusch chamber” in the size and dimensions presented in the Kienbusch (1986) report, is but one method of measuring emission rates from area sources. A variety of flux chamber and wind tunnel sizes and dimensions have been used to measure emissions from animal feeding operations, in addition to ambient monitoring coupled with computer modeling to predict emission rates at the source.

The Kienbusch (1986) report suggests a sweep air flow rate of 5 L/min for a chamber with enclosed surface area of 0.13 m^2. The Kienbusch chamber has a volume of 30 L. Because one turnover volume is 30 L, then at 5 L/min, this equates to a turnover rate of 0.167 turnovers per minute (i.e. 5 L/min divided by 30 L/turnover = 0.167 turnovers/min).

Kienbusch (1986) states that most VOC emissions from contaminated soils are “generally believed to be controlled by the diffusion rate of the chemical compound through the air-filled pore spaces of the soil.” If a constant flux of VOCs were diffusing through the soil surface (i.e. such as VOCs diffusing through the soil surface from a subsurface landfill), then the sweep air flow rate would not affect emission calculations. However, emissions of VOCs and other volatile compounds (i.e. ammonia) from most area sources at animal feeding operations are not diffusion limited, rather they are "evaporation" or "vapor pressure" limited, meaning that wind speed plays a big factor in the amount of VOC emissions (Rhoades et al., 2005). In my opinion, a more appropriate sweep air flow rate would be one that simulates wind velocities in actual field conditions, definitely higher than 0.167 turnovers per minute and probably more in line with the 5.9 to 18.8 turnovers per minute suggested by Cole et al. (2007).

To further illustrate this point, I quote from Rhoades et al. (2005) "Chambers are relatively small and easy to move. However, they alter the microclimate of the NH_3 source, and so flux estimates made with chambers will usually differ from fluxes that occur without the chamber (Fowler et al., 2001). These differences in flux estimates may occur because of differences or changes in radiation balance, temperature, turbulence (wind speed and vertical profile), pressure, and the soil-atmosphere NH_3 concentration gradient (Fowler et al., 2001). In addition, some gases such as NH_3 may adsorb/desorb on the surface area of the chamber and the tubing. Several studies have been done to evaluate the performance of these enclosure methods. Ryden and Lockyer (1985) found that use of an enclosure method could provide a reliable measurement of NH_3 flux for treatment comparisons. However, they cautioned that air speed through the tunnel greatly affected the rate of NH_3 loss. Using wind tunnels, Meisinger et al. (2001) found that increasing air speeds from 0.5 to 1.0 m/s resulted in increasing NH_3 emission estimates. Using a variety of static chambers, several studies have indicated that ammonia emissions from a field surface increase as air flow rate increases up to 15 turnovers per minute (Watkins et al., 1972; Whitehead and Rastrick, 1991; Kissel et al., 1977). This is due in part to the fact that high ammonia concentrations in the chamber atmosphere at low sweep air rates inhibit release of NH_3 from the field or lagoon surface."

The Rhoades et al. (2005) research quoted above deals with volatile ammonia. A graph from the Rhoades paper showing how ammonia emission rate varies with sweep air flowrate is shown in Figure 1.

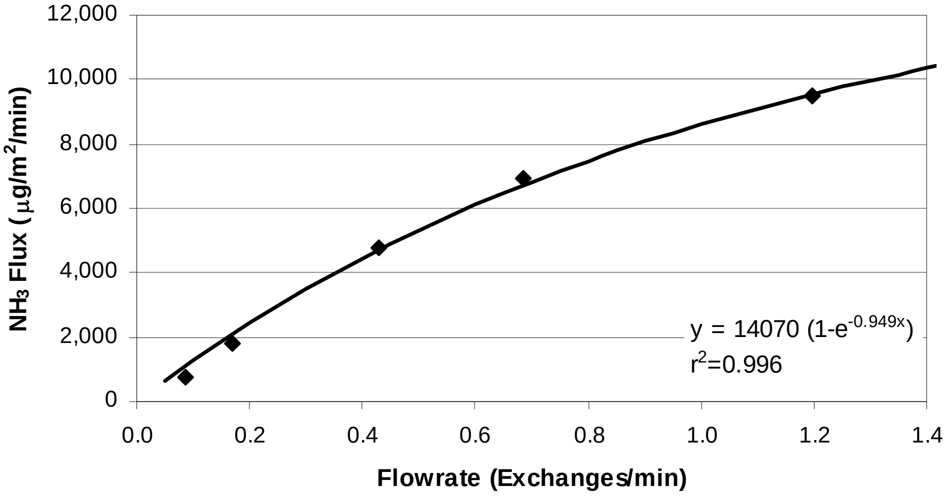

Figure 1. Graph showing NH_3 emission rates from a Texas dairy open lot pen at different sweep-air exchange rates (from Rhoades et al., 2005).

For the above example, the measured emission rate of ammonia at the Kienbusch (1986) flow rate of 0.167 turnovers per minute is about 2,000 µg/m^2/min. A doubling of the flowrate (i.e. to about 0.4 exchanges/min) results in an approximate doubling (or 100% greater) of the measured emission rate. Thus, air flow rate has a critical impact on measured emission rates for ammonia.

I have conducted recent research in a laboratory with a small wind tunnel (same wind tunnel used on the South Lakes Dairy Project) looking at how sweep air flow rate affects emissions of VOCs from manure and lagoons (Parker, unpublished data, referenced in the Parker (2007) and Parker (2008) reports, and scheduled for presentation at the 2008 International ASABE meeting in summer 2008). The results of the VOC emission data are similar to the findings of the NH_3 emissions, with VOC emission rates increasing with increasing sweep air flowrate. My research results show that emissions of low molecular weight VOCs are more affected by air flow rate at the lower flow rates (i.e. less than 5 turnovers per minute) than heavy molecular weight VOCs, but that all measured VOCs are highly dependent on sweep air flow rate. An example of how sweep air flow rate affects VOC emissions from simulated open lot manure conditions is shown in Figure 2 below.

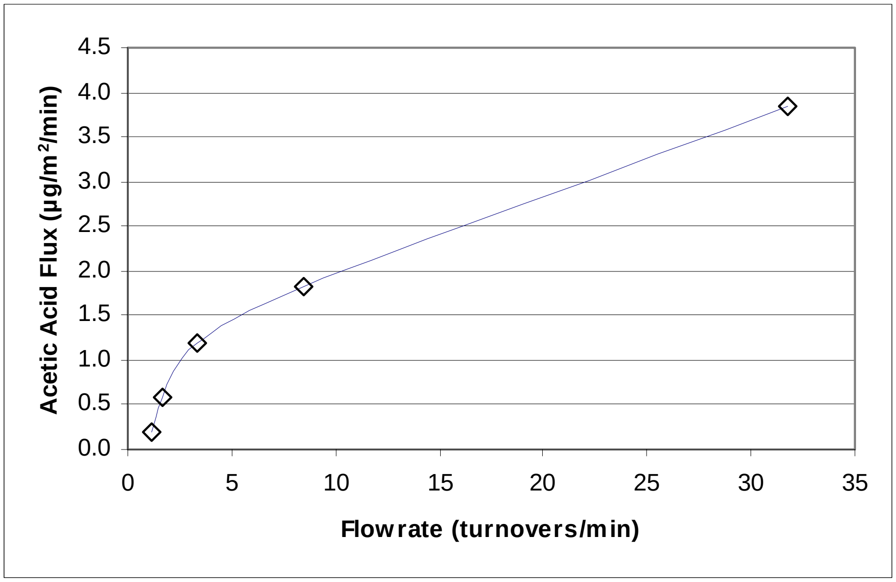

Figure 2. Graph showing acetic acid emission rates from 30% moisture content beef manure at different sweep-air exchange rates.

In Figure 2, the lowest measured flow rate for this particular experiment was 1.2 exchanges per minute, which for the geometry of the wind tunnel, equates to a velocity of 0.4 m/min or 0.014 miles per hour, still a very low wind velocity as compared to typical field conditions.

An example of how sweep air flow rate affects simulated lagoon conditions is shown in Figure 3.

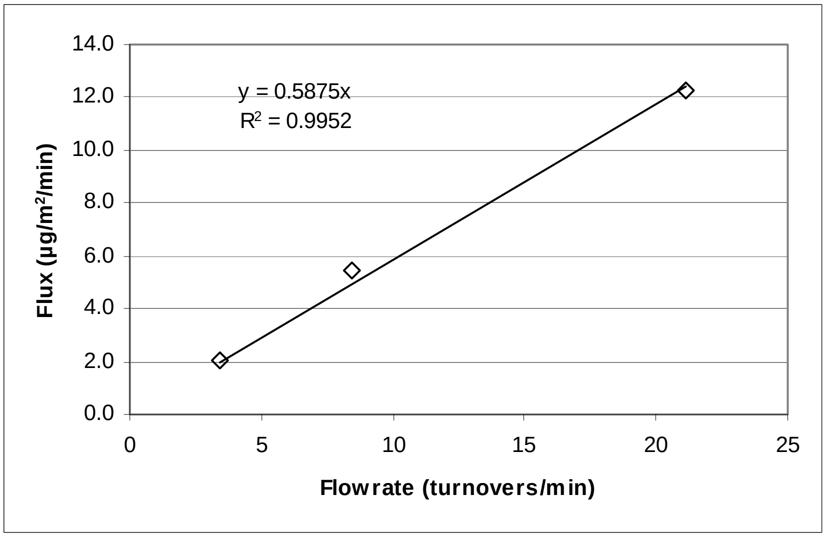

Figure 3. Graph showing acetic acid emission rates from anaerobic dairy lagoon effluent at different sweep-air exchange rates.

Similar to the previous results, a doubling of the sweep air flow rate results in an approximate doubling of the measured emission rate. In Figure 3, the lowest measured flow rate for this particular experiment was 3.3 exchanges per minute, which for the geometry of the wind tunnel, equates to a velocity of 1.0 m/min or 0.038 miles per hour, again a very low wind velocity as compared to typical field conditions.

Additional results and graphs showing how sweep air flow rate affects VOC emissions from beef manure, dairy lagoon effluent, dairy barn flush effluent, and beef cattle feedlot pond effluent from Parker (unpublished) are shown in Appendix A.

For comparison, the results of the effect of sweep air flowrate on methanol and ethanol emissions from the feed and silage at the South Lakes Dairy (Parker, 2007; Parker, 2008) have been graphed as shown below in Figures 4 and 5. The exchange rates of 0.85, 1.7, and 3.4 correspond to velocities of 0.26, 0.52, and 1.03 m/min (0.010, 0.019, and 0.038 mph), respectively.

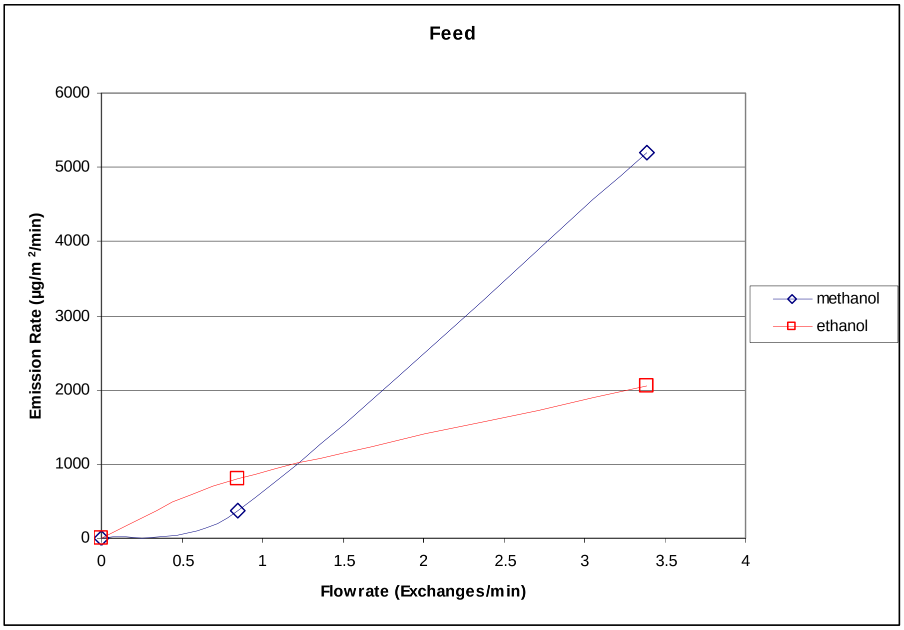

Figure 4. Graph showing methanol and ethanol emission rates from South Lakes Dairy feed in freestall barn at different sweep-air exchange rates, as measured with the wind tunnel.

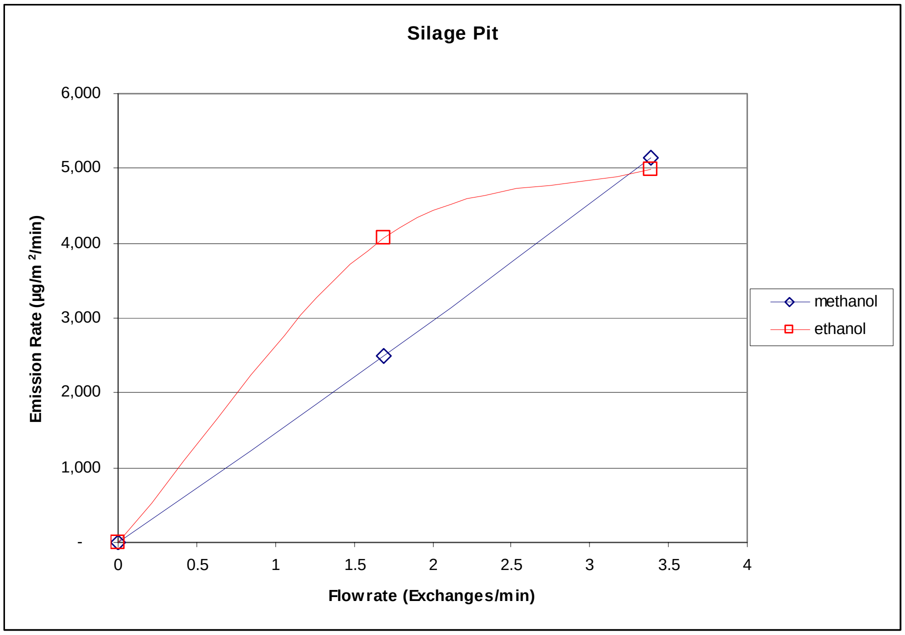

Figure 5. Graph showing methanol and ethanol emission rates from South Lakes Dairy corn silage pit at different sweep-air exchange rates, as measured with the wind tunnel.

The results shown in Figures 4 and 5 for methanol and ethanol follow the same trends as the previously presented VOC results, and demonstrate that sweep air flowrate has a great effect on measured alcohol emission rates. In general, a doubling of the flowrate results in an approximate doubling of the measured methanol emission rates.

There has been some debate as to the proper sweep air flowrate to simulate emission rates during field conditions. Using a mass-balance approach, Cole et al. (2007) reported that turnover rates of 5.9 to 18.8 were required with flux chambers to obtain ammonia fluxes equal to 95% of those from simulated field conditions for an entirely open source. Cole et al. (2007) also reported emissions were 2.7 to 8.0 times higher from the open source as compared to emissions at 0.5 turnovers/min.

Given that methanol has a vapor pressure of 98 mm Hg at 20°C, ethanol has a vapor pressure of 59 mm Hg at 20°C, and ammonia has a vapor pressure of 115 mm Hg at 20°C, then I would expect methanol and ethanol to behave similarly to ammonia, meaning that emission rates should be measured at 6 to 18 turnovers per minute, far greater than those measured by either myself or the defendant’s experts. Based on the results shown in Figures 4 and 5 alone, this suggests that the true methanol or ethanol emission rates are likely 2.7 to 8 times greater than the emissions presented in both the Card and Schmidt (2007) and Parker (2008) reports.

Similarly, Smith and Watts (1994) evaluated how sweep air flow rate affects odor emissions from cattle feedlots. Because odor is just a perception to one or more VOCs, then these results would be comparable to VOC emissions. Smith and Watts (1994) stated that if a wind tunnel is to be used to determine actual surface emission flux rates, “then a tunnel wind speed which equates to ambient conditions must be used.” They referenced several instances of how wind speed or sweep air flowrate directly impacts measured emission rates, with emissions decreasing as flowrate and velocity decreased.

The average wind speed during the sampling at the dairy from 8:30 AM October 18 to 8:30 AM October 19 was 5.9 km/hr (3.7 mph or 98.3 m/min). It might be argued that the wind speed in the barns is reduced because of the sheltering effect of the barn, fences, and animals themselves, but this is why the dairy installs electric fans. Fans and misters are often used to cool the cattle in an effort to increase dry matter intake and subsequent milk production (Brouk et al., 2001). The fans are used to increase the wind speed and offer a cooling effect on the cattle. Fans were observed in operation while we were sampling within the freestall barns on October 18, 2007 and can be seen in the photo below (Figure 6).

Figure 6. Photo taken during sampling of manure in the freestall barn. Notice overhead electric fans on both the left and right sides. Photo taken October 18, 2007.

On the date of sampling, October 18, 2007, I measured an air velocity profile within the freestall barn with the fans running using a portable hot wire anemometer (reference page 2 of the field notebook, Appendix B of 12/17/07 report). That velocity profile is shown in Figure 7. The velocity profile showed an air velocity of 1.1 m/s (66 m/min) measured 30 cm (1 ft) above the concrete pavement in the barn.

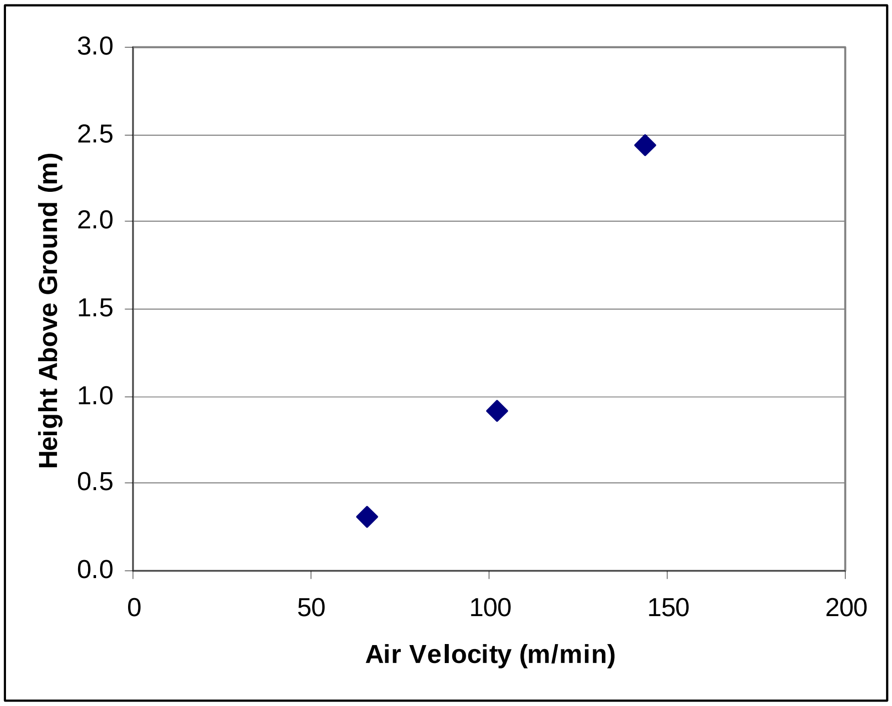

Figure 7. Air velocity profile measured using a portable hotwire anemometer in the freestall barn on October 18, 2007 with fans operating.

It is my belief that the results of the sweep air flowrate analyses, coupled with the mass balance approach presented later in this report, will give rise to a more accurate measure of the true emissions of methanol and other VOCs.

Based on my experience in conducting mass balance and field sampling at CAFOs, the results of my recent research, the published literature, and results obtained with the small wind tunnel on the South Lakes Dairy Project, it is my opinion that the concentrations and emissions measured with the Kienbusch "USEPA" flux chamber at the flow rates used (5 L/min = 0.167 turnovers/minute) are considerably lower than actual field emission rates, and thus provide a conservatively low estimation of actual emission rates from the dairy.

I. d. Appendix C of Schmidt (2007) reports the ethanol emission rates for the same samples on which methanol emissions were measured. The highest ethanol emission rate was measured in the "heifer cow bunker feed" (HC BF). The measured concentrations (231,527 and 246,447 µg/m^2/min in samples #207 and #208 for fresh feed and 109,662 µg/m^2/min in sample #215 for 4-hr old feed) are higher than any of the ethanol emissions measured in the support stock feed source (i.e the wheat silage which had measured ethanol concentrations of 6,982 and 52,301 µg/m^2/min for samples 211 and 212). Given that the heifer diet is a mixture of mostly non-alcohol emitting sources (heifer diet contains 6.3 lbs of wheat silage on a dry matter basis per Figure 3-2 of Card and Schmidt report), and assuming a typical dry matter intake of 25 lb/d for the heifers, then the heifer feed would be composed of 25% silage. Thus, if the feed were composed of 100% silage, the resulting ethanol emission rate from just the fresh silage would be 4 times higher, or about 960,000 µg/m^2/min. This means that there is either another high-alcohol emitting feed source on the dairy that was not measured, or that the measured alcohol emissions from the wheat silage are actually much higher than those presented in the report.

I. e. For the analysis of semi-volatile VOCs, the authors used EPA Method TO-13 which recommends a sampling volume of 300 m^3 (USEPA, 1999). The defendant's experts used an actual sampling volume of 0.030 m^3, which is four orders of magnitude less. As a result, the laboratory reported all semivolatile VOC concentrations as less than the method detection limit.

II. Rebuttal to "Quantification of Methanol Emissions, South Lakes Dairy, Tulare County, California, December 2007" by Thomas R. Card and Charles E. Schmidt

II. a. On Page 7 of the Card and Schmidt (2007) report, the authors state that "This leachate covered approximately 20% of the exposed paved area around the silage piles."

At the time of our sampling of the leachate area on October 19, 2007, there was considerably more than 20% of the exposed paved area occupied by leachate. The dairy was using almond hulls and shells to soak up the leachate, and although some of the hulls appeared dry on the surface, they were wet underneath and we documented VOC emissions from these dry top/moist underneath hulls. I observed that the area occupied by the leachate grew throughout the day as more leachate ran from the silage piles or bubbled up through the cracks in the concrete.

If leachate handling and operating procedures were different between the 10/19/07 Parker et al. sampling date and the 10/22-24/07 Schmidt et al. sampling dates, then those procedures and resulting conditions should be noted in the report.

II. b. On page 8, Figure 3-1, the authors present a methanol emission decay curve for production and non-production livestock, and use the weighted average methanol emission over the 24 hr period as the emission value in the calculation of site methanol emissions in Table 4-1 of their report.

Based on the hourly emissions in Table 3-1 of their report, I infer that the calculations are based on feeding the cattle twice per day, once at 4:00 AM and again at 11:00 AM. This matches up with what is stated in Ryan Schakel's deposition (pp. 35-37, 41) and Manuel Rodrigues' deposition (pp. 21, 25) in which they state that the milk cows and support stock are fed twice per day.

Though a minor error, the decay curve is flawed in that emissions were never measured at 24 hours post feeding. Schmidt measured at 17 hours post feeding, therefore, the decay curve shown in Figure 3-1 of their report should actually be only reported to 17 hours post feeding. I have presented a corrected decay curve in Figure 8 below.

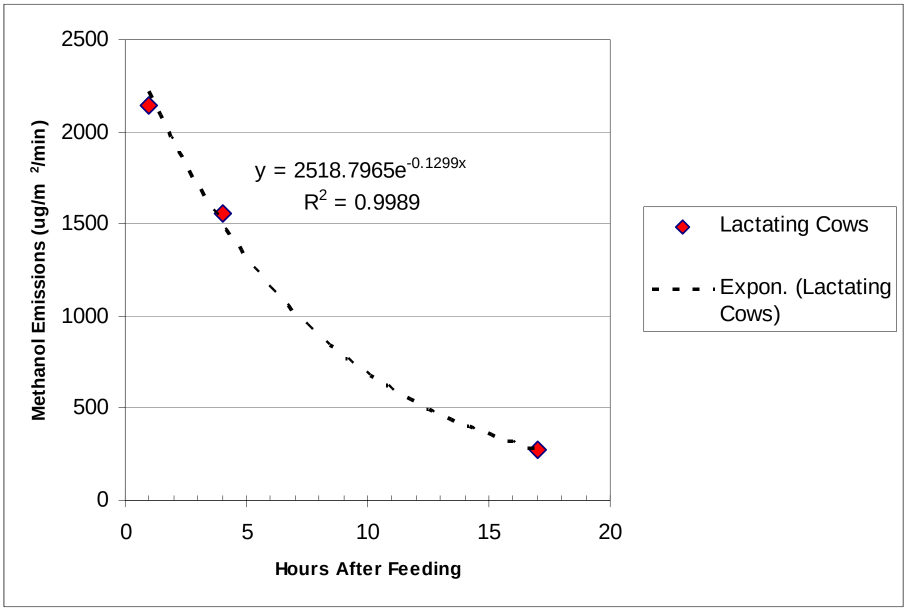

Figure 8. Corrected decay curve showing methanol emissions from lactating cows (adapted from Card and Schmidt, 2007).

Based on Schmidt's (2007) ethanol emission rates, I also prepared the decay curve for ethanol emissions from lactating cows, and it is shown in Figure 9.

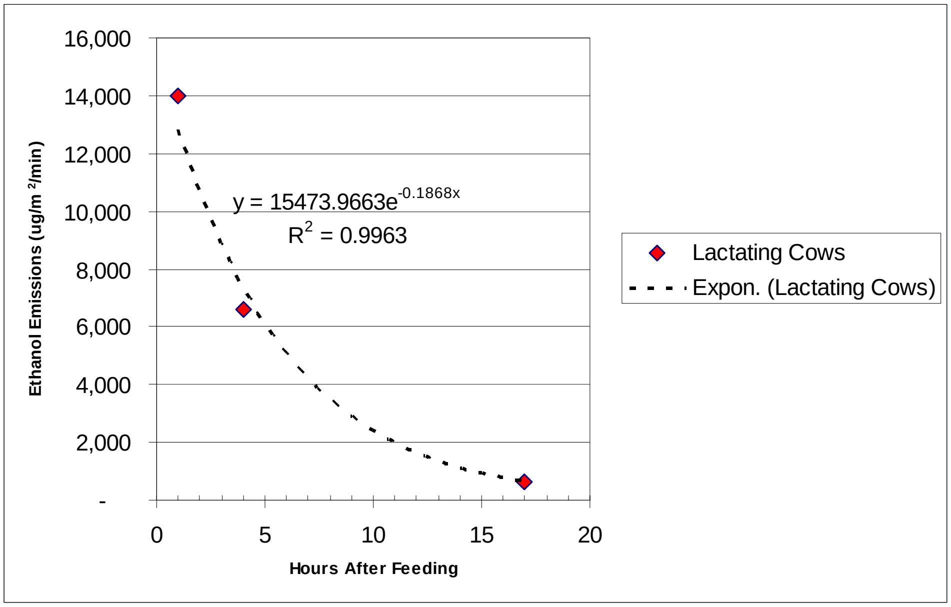

Figure 9. Decay curve showing ethanol emissions from lactating cows (from data in Card and Schmidt, 2007).

I agree with the general findings of the defendant's experts in that the decay curve shows that methanol (and other VOC) emissions decrease over time, however, **the primary thing that this graph shows is that most of the methanol in the feed has volatilized after 17 hours. The methanol emissions from the feed decrease over time as the concentration of methanol in the feed decreases.**

Because air sampling methodologies can give differing results depending on the type of sampling (i.e. flux chambers, wind tunnels, ambient with modeling, etc.) and the laboratory methodology (i.e. GC/MS with sorbent tubes, GC/MS with canisters, acid trapping, etc.), it is my opinion that whenever masses can be accurately measured before and after, that the mass balance approach gives a much higher confidence in actual losses of compounds to the air.

My opinions on the mass-balance approach are in agreement with a recent report prepared by a committee appointed by the National Research Council (NAS, 2003), which supports a "process-based" approach where relevant elements are followed through the animal feeding process, and the amount of air emissions that occur at each step are measured using a mass balance approach.

In dealing with nitrogen emissions from beef feedlots and dairies, it has been my experience that a mass balance should be used to determine if the reported emission rates are believable, or in other words, that they make common sense. For compounds that are not produced either at the site or by the animal, the mass balance approach can be used to determine the maximum possible emission rate (sulfur is an example, the maximum emissions of sulfur at a feedlot is determined by the amount of S in the feed). Overall mass balances on all VOCs at an AFO are more difficult because VOCs are actually generated both in the gut of the animal and after the manure leaves the animal. However, a mass balance approach makes full sense when dealing with emissions from feed in the freestall barn.

The following is a discussion of using the mass balance approach to determining alcohol losses from the feed in the freestall barns at the dairy. The general premise is to measure the alcohol concentration in the feed as delivered to the animals, measure the alcohol concentration in the feed at some later time period, and then calculate the losses of VOCs to the air. I have made these calculations as it pertains to the South Lakes Dairy using the decay curve proposed by Card and Schmidt as follows.

The decay curve shows that the emission rate decreases from an average of 2,140 $\mu g/m^2/min$ at one hr post feeding to an average of 274.5 $\mu g/m^2/min$ at 17 hrs post feeding. Thus, there is an 87.2% reduction in the methanol emission rate after 17 hrs. The methanol emission rate decreased because the methanol concentration in the feed decreased. I can approximate based on Henry's Law (Biokess and Edelson, 1981; Spanel et al., 2002), which states that the concentration in the vapor phase is proportional to the concentration in the liquid (i.e. feed) phase, that the methanol concentration in the feed also decreased by 87.2%.

Per Card and Schmidt, 2007, p. 7, the primary methanol (and ethanol) source in the feed is the silage. I did not quantify the alcohol concentration in the silage at the South Lakes Dairy (though I have requested the opportunity to do so in the future), so I will use typical published alcohol concentrations for this mass balance approach. Ethanol concentrations in corn silage are typically 1-3% of dry matter, while references on published methanol concentrations are limited. Johnson et al. (2003) reported ethanol concentrations in corn silage of about 0.75-1.86% of dry matter. Kung and Shaver (2001) reported typical corn silage ethanol concentrations of 1-3% of dry matter, while Kung and Stokes (2001) stated that ethanol concentrations can be as high as 5-6%. Kaiser et al. (1981) reported a corn silage ethanol concentration of 3.06% of DM, and methanol concentration of 0.17% of DM. Hart and Lamb (1914) published a corn silage methanol concentration of 0.05% on a wet weight basis, the methanol concentration on a dry basis would twice as big given typical moisture contents of silage.

If the emission rates decrease 87.2% over a 17 hr period, and I infer that methanol concentrations in the feed also decrease by 87.2%, then I can estimate the actual methanol losses to the air knowing the amount of silage that is fed.

Typical dry matter intake (DMI) values for dairy cows are well published. A lactating cow will have a DMI of about 20 kg/day, while a dry cow will have a DMI of about 12 kg/day (Robinson, unknown date; Harris, 1992; NRC, 2001).

To show these calculations, I will first calculate the “potential emissions” if cows do not consume any of the feed, but I assume it is still disturbed by the cattle and pushed up once per hour by the dairy personnel. The logic is as follows:

> Each lactating cow consumes 20 kg dry matter per day.
>
> Each lactating cow consumes 4.7 kg (10.4 lb) of corn silage per day (Card and Schmidt, 2007).
>
> The corn silage (CS) has an ethanol concentration of 1-3% of dry matter. I assume based on the reported emission rates that methanol emissions are about 15.2% of ethanol emissions (Schmidt reports fresh feed samples no. T15-105 and T15-106 have methanol/ethanol ratios of 16.1 and 14.4%, respectively, for an average of 15.2%). Thus, the methanol concentration in the silage as delivered to the bunk would be 0.15 and 0.45% of dry matter if the ethanol concentration were 1% and 3% of DM, respectively. Note that in my sampling, the feed samples in the freestall barn had a methanol/ethanol ratio of 38.8% (Table 4, revised report, 1/7/08).

> The potential methanol emissions from the feed can now be calculated, and I will use a range from low end to high end concentrations:
>
> Low end: 4.7 kg dry CS/day * 0.15% methanol * 87.2% lost = 0.00615 kg/cow/d
> High end: 4.7 kg dry CS/day * 0.45% methanol * 87.2% lost = 0.0184 kg/cow/d
>
> Low end: 0.0061 kg/cow/d * 5,800 cows * 365 d/yr = 13,019 kg/yr (28,643 lb/yr)
> High end: 0.0184 kg/cow/d * 5,800 cows * 365 d/yr = 38,953 kg/yr (85,696 lb/yr)

Of course, the above numbers are unrealistic because cows consume the feed and the quantity of feed in the bunks is continually decreasing after feed delivery. Thus, the amount of feed available for volatilization decreases with time after feeding. One thing that is certain is that feed is present for most or all of the 24-hr period, or else there would not have been feed present to measure the 24-hr feed sample. Also, Ryan Schakel and Manuel Rodrigues stated in their depositions that the dairy maintained feed on a 24-hour basis for milk cows and pushed up the feed once every hour.

To take into account the fact that cattle consume the feed, I have made an estimate of methanol emissions using the same assumptions as above, but assuming that the cattle eat an equal amount of dry matter over the 24 hr period. If 4.7 kg (dry weight) of corn silage is fed per day, then each cow would consume 4.7 kg/24 hr=0.1958 kg of silage per hour. Using the feed delivery numbers presented in Table 3-1 of Card and Smith (2007), I made a spreadsheet to better calculate the potential methanol emissions while taking into account the fact that feed disappears every hour, and the emission rate also decreases every hour. I assumed that 70% of the feed was delivered at hour 0, then the remaining 30% was delivered seven hours later.

As stated above, because I don’t know the exact methanol concentration in the silage, I am giving a range of calculated potential methanol emissions based on silage methanol concentrations of 0.15 and 0.45% of dry matter obtained from published literature. To better quantify methanol concentrations in the future, I have requested that counsel for the plaintiff file the necessary documents to obtain physical samples of the silage if discovery reopens, and I will amend this report based on the results of that sampling if and when it is obtained.

Table 1 on the following page shows that, based on the mass balance approach and the decay curve of Card and Schmidt (2007), the methanol emissions would range from 20,668 to 62,004 lb/yr for initial silage methanol concentrations of 0.15 and 0.45%, respectively. This is for the silage fed to the lactating cows in the freestall barns only, and does not take into account any methanol emissions from the silage fed to the support stock or emissions directly from the silage storage area. I have presented similar numbers for ethanol emissions using the same mass balance approach in Table 2, with ethanol emissions ranging from 155,578 to 466,733 lb/yr.

The mass balance approach gives a definitive range of the actual alcohol emissions at the dairy from the feed in the freestall barns. A more accurate mass-balance estimation can only be made by knowing the actual methanol and ethanol concentrations of the silage at the South Lakes dairy.

Table 1. Spreadsheets showing the estimated range of *methanol* emissions using a mass-balance approach with the decay function data of Card and Schmidt (2007).

Initial methanol concentration in silage (% of DM) = **0.15%**

	Hour	Card & Schmidt Predicted emission rate (ug/m2/min)	Observed	% remaining per hr	kg eaten per hr	kg silage/cow left in bunk	kg methanol starting in bunk at start of hour	methanol lost to eating in the hour (kg)	methanol lost to decay in the hour (kg)	methanol left in bunk at end of hour (kg)	new methanol conc for next hour (%)
Feed Delivered	0	2519		0.8782	0.1958	3.29	0.00494	0.000294	0.000601	0.00404	0.131%
	1	2212	2140	0.8782	0.1958	3.09	0.00404	0.000256	0.000492	0.00329	0.1136%
	2	1943		0.8782	0.1958	2.90	0.00329	0.000222	0.000401	0.00267	0.0988%
	3	1706		0.8782	0.1958	2.70	0.00267	0.000193	0.000325	0.00215	0.0858%
	4	1498	1560	0.8782	0.1958	2.51	0.00215	0.000168	0.000262	0.00172	0.0744%
	5	1316		0.8782	0.1958	2.31	0.00172	0.000146	0.000210	0.00136	0.0645%
	6	1155		0.8782	0.1958	2.12	0.00136	0.000126	0.000166	0.00107	0.0322%
Feed Delivered	7	1015		0.8782	0.1958	3.33	0.00319	0.000063	0.000388	0.00274	0.0873%
	1	2212	2140	0.8782	0.1958	3.13	0.00274	0.000171	0.000333	0.00223	0.0760%
	2	1943		0.8782	0.1958	2.94	0.00223	0.000149	0.000272	0.00181	0.0661%
	3	1706		0.8782	0.1958	2.74	0.00181	0.000129	0.000221	0.00146	0.0574%
	4	1498	1560	0.8782	0.1958	2.55	0.00146	0.000112	0.000178	0.00117	0.0498%
	5	1316		0.8782	0.1958	2.35	0.00117	0.000098	0.000143	0.00093	0.0432%
	6	1155		0.8782	0.1958	2.15	0.00093	0.000085	0.000113	0.00073	0.0374%
	7	1015		0.8782	0.1958	1.96	0.00073	0.000073	0.000089	0.00057	0.0323%
	8	891		0.8782	0.1958	1.76	0.00057	0.000063	0.000069	0.00044	0.0279%
	9	782		0.8782	0.1958	1.57	0.00044	0.000055	0.000053	0.00033	0.0240%
	10	687		0.8782	0.1958	1.37	0.00033	0.000047	0.000040	0.00024	0.0206%
	11	603		0.8782	0.1958	1.18	0.00024	0.000040	0.000030	0.00017	0.0176%
	12	530		0.8782	0.1958	0.98	0.00017	0.000034	0.000021	0.00012	0.0149%
	13	465		0.8782	0.1958	0.78	0.00012	0.000029	0.000014	0.00007	0.0125%
	14	409		0.8782	0.1958	0.59	0.00007	0.000024	0.000009	0.00004	0.0102%
	15	359		0.8782	0.1958	0.39	0.00004	0.000020	0.000005	0.00002	0.0077%
	16	315		0.8782	0.1958	0.20	0.00002	0.000015	0.000002	0.00000	
	17	277	274.5			0.00	0.00000	0.000000	0.000000	0.00000	
							Totals	0.0026	0.00444		

Mass Balance Approximations:
0.00444 kg/d * 5800 cows * 365 d/yr = **9,395 kg methanol emitted/yr**
20,668 lb methanol emitted/yr

Initial methanol concentration in silage (% of DM) = **0.45%**

	Hour	Card & Schmidt Predicted emission rate (ug/m2/min)	Observed	% remaining per hr	kg eaten per hr	kg silage/cow left in bunk	kg methanol starting in bunk at start of hour	methanol lost to eating in the hour (kg)	methanol lost to decay in the hour (kg)	methanol left in bunk at end of hour (kg)	new methanol conc for next hour (%)
Feed Delivered	0	2519		0.8782	0.1958	3.29	0.01481	0.000881	0.001803	0.01212	0.392%
	1	2212	2140	0.8782	0.1958	3.09	0.01212	0.000767	0.001476	0.00988	0.3408%
	2	1943		0.8782	0.1958	2.90	0.00988	0.000667	0.001203	0.00801	0.2963%
	3	1706		0.8782	0.1958	2.70	0.00801	0.000580	0.000975	0.00645	0.2573%
	4	1498	1560	0.8782	0.1958	2.51	0.00645	0.000504	0.000786	0.00516	0.2233%
	5	1316		0.8782	0.1958	2.31	0.00516	0.000437	0.000629	0.00409	0.1936%
	6	1155		0.8782	0.1958	2.12	0.00409	0.000379	0.000499	0.00322	0.0966%
Feed Delivered	7	1015		0.8782	0.1958	3.33	0.00956	0.000189	0.001165	0.00821	0.2620%
	1	2212	2140	0.8782	0.1958	3.13	0.00821	0.000513	0.001000	0.00670	0.2279%
	2	1943		0.8782	0.1958	2.94	0.00670	0.000446	0.000816	0.00543	0.1982%
	3	1706		0.8782	0.1958	2.74	0.00543	0.000388	0.000662	0.00438	0.1722%
	4	1498	1560	0.8782	0.1958	2.55	0.00438	0.0003372	0.000534	0.00351	0.1495%
	5	1316		0.8782	0.1958	2.35	0.00351	0.000293	0.000428	0.00279	0.1296%
	6	1155		0.8782	0.1958	2.15	0.00279	0.000254	0.000340	0.00220	0.1122%
	7	1015		0.8782	0.1958	1.96	0.00220	0.000220	0.000268	0.00171	0.0970%
	8	891		0.8782	0.1958	1.76	0.00171	0.000190	0.000208	0.00131	0.0837%
	9	782		0.8782	0.1958	1.57	0.00131	0.000164	0.000160	0.00099	0.0721%
	10	687		0.8782	0.1958	1.37	0.00099	0.000141	0.000120	0.00073	0.0618%
	11	603		0.8782	0.1958	1.18	0.00073	0.000121	0.000089	0.00052	0.0528%
	12	530		0.8782	0.1958	0.98	0.00052	0.000103	0.000063	0.00035	0.0448%
	13	465		0.8782	0.1958	0.78	0.00035	0.000088	0.000043	0.00022	0.0375%
	14	409		0.8782	0.1958	0.59	0.00022	0.000073	0.000027	0.00012	0.0306%
	15	359		0.8782	0.1958	0.39	0.00012	0.000060	0.000015	0.00005	0.0232%
	16	315		0.8782	0.1958	0.20	0.00005	0.000045	0.000006	-0.00001	
	17	277	274.5			0.00	0.00000	0.000000	0.000000	0.00000	
							Totals	0.0078	0.01331		

Mass Balance Approximations:
0.01331 kg/d * 5800 cows * 365 d/yr = **28,184 kg methanol emitted/yr**
62,004 lb methanol emitted/yr

Table 2. Spreadsheets showing the estimated range of *ethanol* emissions using a mass-balance approach with the decay function data of Card and Schmidt (2007).

Initial ethanol concentration in silage (% of DM) = **1.00%**

	Hour	Predicted emission rate (ug/m2/min)	Observed	% remaining per hr	kg eaten per hr	kg silage/cow left in bunk	kg ethanol starting in bunk at start of hour	ethanol lost to eating in the hour (kg)	ethanol lost to decay in the hour (kg)	ethanol left in bunk at end of hour (kg)	new ethanol conc for next hour (%)
Feed Delivered	0	15474		0.830	0.1958	3.29	0.03290	0.001958	0.005606	0.02534	0.819%
	1	12837	13,985	0.830	0.1958	3.09	0.02534	0.001604	0.004317	0.01942	0.6699%
	2	10650		0.830	0.1958	2.90	0.01942	0.001312	0.003308	0.01480	0.5475%
	3	8835		0.830	0.1958	2.70	0.01480	0.001072	0.002521	0.01120	0.4469%
	4	7330	6,596	0.830	0.1958	2.51	0.01120	0.000875	0.001909	0.00842	0.3643%
	5	6081		0.830	0.1958	2.31	0.00842	0.000713	0.001434	0.00627	0.2965%
	6	5045		0.830	0.1958	2.12	0.00627	0.000581	0.001068	0.00462	0.1388%
Feed Delivered	7	4185		0.878	0.1958	3.33	0.01872	0.000272	0.002281	0.01617	0.5160%
	1	12837	13,985	0.830	0.1958	3.13	0.01617	0.001011	0.002755	0.01240	0.4222%
	2	10650		0.830	0.1958	2.94	0.01240	0.000827	0.002113	0.00946	0.3452%
	3	8835		0.830	0.1958	2.74	0.00946	0.000676	0.001612	0.00717	0.2818%
	4	7330	6,596	0.830	0.1958	2.55	0.00717	0.0005519	0.001223	0.00540	0.2298%
	5	6081		0.830	0.1958	2.35	0.00540	0.000450	0.000920	0.00403	0.1871%
	6	5045		0.830	0.1958	2.15	0.00403	0.000366	0.000687	0.00298	0.1520%
	7	4185		0.830	0.1958	1.96	0.00298	0.000298	0.000507	0.00217	0.1232%
	8	3472		0.830	0.1958	1.76	0.00217	0.000241	0.000370	0.00156	0.0996%
	9	2880		0.830	0.1958	1.57	0.00156	0.000195	0.000266	0.00110	0.0802%
	10	2390		0.830	0.1958	1.37	0.00110	0.000157	0.000187	0.00076	0.0643%
	11	1983		0.830	0.1958	1.18	0.00076	0.000126	0.000129	0.00050	0.0511%
	12	1645		0.830	0.1958	0.98	0.00050	0.000100	0.000085	0.00032	0.0402%
	13	1364		0.830	0.1958	0.78	0.00032	0.000079	0.000054	0.00018	0.0311%
	14	1132		0.830	0.1958	0.59	0.00018	0.000061	0.000031	0.00009	0.0231%
	15	939		0.830	0.1958	0.39	0.00009	0.000045	0.000015	0.00003	0.0153%
	16	779		0.830	0.1958	0.20	0.00003	0.000030	0.000005	-0.00001	
	17	646	659			0.00	0.00000	0.000000	0.000000	0.00000	
							Totals	0.0136	0.03340		

0.03340 kg/d * 5800 cows * 365 d/yr =

Mass Balance Approximations:
70,717 kg ethanol emitted/yr
155,578 lb ethanol emitted/yr

Initial ethanol concentration in silage (% of DM) = **3.00%**

	Hour	Predicted emission rate (ug/m2/min)	Observed	% remaining per hr	kg eaten per hr	kg silage/cow left in bunk	kg ethanol starting in bunk at start of hour	ethanol lost to eating in the hour (kg)	ethanol lost to decay in the hour (kg)	ethanol left in bunk at end of hour (kg)	new ethanol conc for next hour (%)
Feed Delivered	0	15474		0.830	0.1958	3.29	0.09870	0.005875	0.016818	0.07601	2.456%
	1	12837	13,985	0.830	0.1958	3.09	0.07601	0.004811	0.012951	0.05825	2.0096%
	2	10650		0.830	0.1958	2.90	0.05825	0.003936	0.009925	0.04439	1.6424%
	3	8835		0.830	0.1958	2.70	0.04439	0.003216	0.007563	0.03361	1.3407%
	4	7330	6,596	0.830	0.1958	2.51	0.03361	0.002626	0.005726	0.02525	1.0929%
	5	6081		0.830	0.1958	2.31	0.02525	0.002140	0.004303	0.01881	0.8894%
	6	5045		0.830	0.1958	2.12	0.01881	0.001742	0.003205	0.01386	0.4165%
Feed Delivered	7	4185		0.878	0.1958	3.33	0.05616	0.000816	0.006842	0.04851	1.5481%
	1	12837	13,985	0.830	0.1958	3.13	0.04851	0.003032	0.008265	0.03721	1.2667%
	2	10650		0.830	0.1958	2.94	0.03721	0.002481	0.006340	0.02839	1.0355%
	3	8835		0.830	0.1958	2.74	0.02839	0.002028	0.004837	0.02152	0.8455%
	4	7330	6,596	0.830	0.1958	2.55	0.02152	0.0016557	0.003668	0.01620	0.6894%
	5	6081		0.830	0.1958	2.35	0.01620	0.001350	0.002760	0.01209	0.5613%
	6	5045		0.830	0.1958	2.15	0.01209	0.001099	0.002060	0.00893	0.4561%
	7	4185		0.830	0.1958	1.96	0.00893	0.000893	0.001522	0.00652	0.3697%
	8	3472		0.830	0.1958	1.76	0.00652	0.000724	0.001110	0.00468	0.2988%
	9	2880		0.830	0.1958	1.57	0.00468	0.000585	0.000798	0.00330	0.2407%
	10	2390		0.830	0.1958	1.37	0.00330	0.000471	0.000562	0.00227	0.1928%
	11	1983		0.830	0.1958	1.18	0.00227	0.000378	0.000386	0.00150	0.1534%
	12	1645		0.830	0.1958	0.98	0.00150	0.000300	0.000256	0.00095	0.1207%
	13	1364		0.830	0.1958	0.78	0.00095	0.000236	0.000161	0.00055	0.0933%
	14	1132		0.830	0.1958	0.59	0.00055	0.000183	0.000093	0.00027	0.0694%
	15	939		0.830	0.1958	0.39	0.00027	0.000136	0.000046	0.00009	0.0458%
	16	779		0.830	0.1958	0.20	0.00009	0.000090	0.000015	-0.00002	
	17	646	659			0.00	0.00000	0.000000	0.000000	0.00000	
							Totals	0.0408	0.10021		

0.10021 kg/d * 5800 cows * 365 d/yr =

Mass Balance Approximations:
212,151 kg ethanol emitted/yr
466,733 lb ethanol emitted/yr

II. c. On page 11 of the Card and Schmidt report, the authors state that "No measurements were made at the milk parlor based on the small surface area and that methanol had not been found their previously (Card and Schmidt 2006)."

I disagree with this statement for two reasons. First, the milking parlor is not a small surface area relative to the other surfaces that were measured and reported within their report. Secondly, it is probable that the reason methanol was not found in the milking parlor previously is that it was never measured there. I reported detection of methanol and other VOCs in two ambient samples collected within the milking parlor in my sampling reports (Parker, 2007; Parker, 2008). If methanol were found in flush alleys and open lot pens at previously sampled dairies, then logically methanol should be found in the milking parlor where manure is deposited on the ground surface similar to other locations. Enteric emissions would also be present in the milk parlor.

Any location that is occupied by cattle will have some VOC emissions. Most large dairies operate their milking parlors continuously, around the clock, and I assume the South Lakes Dairy to be similar. The milking parlor is not a small surface area relative to other measured sources on the dairy. The milking parlor, including the wash pens, is 808 ft (246 m) in length, which is longer than any of the eight barns. At any one time, there are potentially 100 to 200 cows being milked, with about 700 cows in the drip pens and another 700 cows in the wash pens (based on cow densities presented in the design drawings, Sheet DB-1, dated 4/2/03). Thus, the milking parlor will potentially house about 1,500 cows during times of milking. Several photos taken during the sampling of the ambient VOCs within the milking parlor on October 19, 2007 are shown in Figures 10 and 11 below. The design drawings give a total area for the milk house and parlor of 48,891 ft^2 (4,544 m^2), which is more than half the size of a single freestall barn. The milking parlor is a considerable area source and should be included in the calculation of total VOCs from the dairy. VOC emissions will result from the manure deposited in the milking parlor, and from enteric emissions while cows are within the milking parlor.

Figure 10. Photo taken during ambient sampling in the milking parlor showing cows just prior to being milked. Photo taken October 19, 2007.

Figure 11. Photo taken from the site of the ambient sampling location within the milking parlor, showing cows in the pen just prior to being milked. Photo taken October 19, 2007.

II. d. On page 11 of the Card and Schmidt report, the authors state that “No direct measurements were made from livestock respiration or flatulence. Previous work (Mitloehner 2006) has shown these emissions to be minor.” This statement is contradictory to what is presented in the Mithoehner (2006) report. In the Executive Summary of the Mitloehner (2006) report, item 4, Mitloehner states “Alcohols were measured at high concentrations. Both ethanol (EtOH) and methanol (MeOH) were produced during enteric fermentation (eructated gas). However, both EtOH and MeOH increased over time in correspondence with accumulating fresh waste.”

Scientists have been aware of methanol and ethanol emissions from ruminants (i.e. cattle) since the early 1970s (Bethea and Narayan, 1972; Vantcheva et al., 1970; Dewhurst et al., 2001), and from silage since as early as 1914 (Hart and Lamb, 1914) and 1962 (Morgan and Pereira, 1962). More recently, Spinhirne et al. (2004) used solid phase microextraction and GC/MS to measure VOCs in the breath of cattle. Though Spinhirne’s sampling device was not designed for alcohol detection and quantification, their results verify that cattle produce VOCs in their breath.

Mitloehner (2006) reported enteric methanol emission rates of 3.34 lb/lactating cow/yr and 1.95 lb/dry cow/yr as measured using a photoacoustic INNOVA 1412 instrument. Mitloehner also reported a total methanol emission rate (enteric and non-enteric) of 11.12 lb/lactating cow/yr and 3.09 lb/dry cow/yr.

Mitloehner’s total methanol emission rate includes both enteric, manure, and feed emissions. In Mitloehner’s study, the diet consisted primarily of grain, alfalfa, cottonseed meal, almond hulls and soybean meal with other minor ingredients. Because Mitloehner’s ration had no silage added, I would expect the alcohol contribution from the feed to be minimal. Thus, the primary sources would be the manure and enteric emissions. If there were no emissions from enteric, then all of the emissions would be from the manure, and vice versa. But Schmidt (2007) reported virtually no methanol emissions from the manure, which makes Card and Schmidt’s (2007) statement about enteric emissions contradictory. Schmidt (2007) reported emissions of methanol from two samples collected in the manure flush lane of 14.0 and 11.0 $\mu g/m^2/min$ (Schmidt report, Table 9), and Card and Schmidt (2007) used an average emission rate of 12.5 $\mu g/m^2/min$ for calculating methanol emissions from the flush lanes. It seems entirely implausible to believe that there were both zero enteric emissions and near-zero emissions from the manure based on Mitloehner’s publication.

To determine the emissions from each cow due to the manure flush lanes using the Schmidt (2007) numbers, I performed the following calculations:

Given there were about 5,800 lactating dairy cows in the freestall barns at the time of sampling, and the total flush lane area in the barns was reported as 26,949 m^2 (Card and Schmidt report, Table 2-1), then each cow would occupy 4.6 m^2 of flush lane space (26,949 m^2/5,800 cows = 4.6 m^2/cow).

Take average of two samples: (14.0+11.0)/2=12.5 µg/m^2/min
Convert to per cow basis: 12.5 µg/m^2/min * 4.6 m^2/cow = 57.5 µg/cow/min
Convert to annual basis: 57.5 µg/cow/min * 60 min/hr * 24 hr/day * 365 day/yr = 3.022E+7 µg/cow/yr

Convert to lb/yr: 3.022E+7 µg/cow/yr * 1 g/1E+6 ug * 1 lb/454 g = 0.066 lb/cow/yr

Thus, using the Schmidt (2007) report, I calculated that the flush lanes reportedly account for an annual methanol emission rate of 0.066 lb/cow/yr, which is 168 times lower than Mitloehner's published emission rate of 11.12 lb/cow/yr for both cows and waste (enteric and non-enteric), and 51 times lower than Mitloehner's 3.34 lb/cow/yr for cows (enteric) only.

In my opinion based on the published literature, the assumption that enteric emissions are minimal represents a gross underestimation of total methanol emissions from the dairy (i.e. 0.066 lb/lactating cow/yr compared to Mitloehner's 11.12 lb/lactating cow/yr). The magnitude of this assumption is great, as I estimated enteric methanol emissions were 23,924 lb/yr in my sampling report based on Mitloehner's numbers.

III. Summary and Conclusions

In summary, it is my professional opinion, as supported by the data presented herein, that the Schmidt (2007) and Card and Schmidt (2007) reports underestimate the true methanol emissions at the dairy for the following reasons:

1) The Kienbusch chamber at a sweep air flowrate of 5 L/min (0.167 turnovers/min) inhibits the volatilization of methanol and other VOCs and thus provides a conservatively low estimation of emission rates from the dairy. Recent research using a mass-balance approach has shown that a sweep air flowrate of 5.9 to 18.8 turnovers per minute is required to simulate emissions from an open source, and that measured emission rates are 2.7 to 8.0 times higher from an open source as compared to emissions made in a flux chamber at 0.5 turnovers/min.

2) The reporting of elevated alcohol emissions in the "heifer cow bunker feed," higher than the 100% silage, suggests there may be another high alcohol source present on the dairy.

3) The use of a methanol decay curve, which results in a lower calculated methanol emission rate, actually supports an overall methanol mass balance loss of 87.2%. Using this mass-balance approach, I estimate that the true methanol emissions from the feed in the bunks of the freestall barns ranges from 20,668 to 62,004 lb/yr. This is 3.8 to 11.4 times greater than Card and Schmidt's estimate of 5,446 lb/yr for the same feed source and corroborates the findings of item 1) above.

4) Using the same mass-balance approach for ethanol emissions from the feed in the bunks of the freestall barns gives ethanol emissions ranging from 155,578 to 466,733 lb/yr.

5) Based on published data, the failure to include enteric emissions provides a gross underestimation of total methanol emissions at the dairy by an estimated 23,924 lb/yr based on my calculations.

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Appendix A

Additional Results of VOC Emissions vs. Sweep Air Flow Rate

(Parker, Unpublished data, to be presented at the 2008 International ASABE Meeting in Summer 2008)

Appendix B

Copies of References