Note to researchers:

The Dairy Permitting Advisory Group is very appreciative of the groundbreaking research you have performed in analyzing VOC emissions from dairies in the San Joaquin Valley. The questions below are not intended to disparage anyone's research techniques or conclusions, but are meant to broaden and strengthen the DPAG's understanding of those techniques and conclusions.

We are asking that you supply us with answers to these questions so that we may determine how to best use the information gathered during your research to establish the best possible emission factor or factors for VOC emissions from dairies. We are not intending to create additional work for you however, so if the answers to these questions are present in a written report of your work, please merely supply us with the report and supply the necessary references so that the answers can be easily found. We also understand that some of the questions may not be within the area of your expertise or knowledge. If this is the case, please do not hesitate to say so, and decline to answer.

Thank you on behalf of the DPAG,

Dave Warner
DPAG Chair and
Director of Permit Services
San Joaquin Valley APCD

DPAG Questions Regarding Current VOC Emissions Research

General Questions

1. In a couple of paragraphs, please describe how the VOC samples were collected?
    a) How might results between methodologies (limitations, applications, etc.) be compared? Is there a preferred method for determining VOC emissions from a specific process?
2. How were sample VOC concentrations measured (e.g., GCMS using TO-15)?
    a) It appears that the EPA TO-15 method is central to identifying and quantifying the VOC/ROG emissions from dairy animals and their excreta in the Mitloehner, Krauter and Schmidt studies. What variations or modifications were made to the standard TO-15 method?
    b) Does TO-15 include the five ROGs identified in the 1980 technical manual from EPA (that is, ethyl alcohol, isopropyl alcohol, propyl acetate, ethyl amine, trimethyl amine) that was used as the basis of the interim emission factor? It does appear that ethanol and

isopropyl alcohol are included on the list, but what about the last three?

3. We are aware that the test methods do not identify all VOCs present. However, it is not clear whether the test methods quantify the mass of those unidentified VOCs. Please explain whether the results of your tests include a reporting of the mass emission rate of all VOCs. If the test results include the mass emissions rate then explain how the results might be biased by not knowing the identity of all VOCs. If the test results do not include the mass emissions rate, then please explain the potential significance of this under-reporting of VOCs.
    a) What are the expected relative reactivity's, as well as just mass, for the unknowns
    b) Please explain the uncertainty in the mass of VOC measured.
    c) Do any aspects of the data (e.g. negative results, high variability, outliers) indicate that some of the results may be questionable?
    d) What types of QA were performed (field blanks, reagent blanks, duplicate samples, etc.)?
    e) Is your method for determining emission rates an approved standard for testing? Has it been used on other source-types?
    f) Describe, in detail, how the total mass of Total Non Methane Hydrocarbons, Total Non Methane Non Ethane Organic Compounds, etc. are calculated. Are the estimation methods consistent from researcher to researcher?
4. In your opinion, how might diurnal and seasonal temperature and weather changes affect results?
5. What information about ambient conditions and management practices was collected during the tests?
    a) What information was collected about the process during testing (presence of feed, feed types, how many cows use feed lanes, maintenance practices, irrigation rate, lagoon loading rate, solids content, etc.)?
    b) Were samples of tested material (manure, feed, etc) collected to establish the nature of material sampled or for later additional analysis?
    c) Was moisture or age of the tested material determined, if so what was it?
6. How were emission rates determined from concentration measurements?
    a) Please provide the specific information needed for calculations, and provide samples of your calculations. We are interested in seeing how emission rates are determined from concentrations, and then how emissions factor (per cow) are calculated from emissions rates.
    b) How were averages determined if there were samples with non-detect levels of specific compounds?
    c) What emissions rates were found? Provide a table and indicate whether these rates are final or approved. How are emissions rates

that were calculated from measured concentrations during the research related to emissions from individual sources from dairy operations?

d) Are there VOC emissions from dairy operations that are not represented in your test results? (e.g., see list of potential emissions points at end of questions; enteric emissions; land application of manure; test results on flush lane might not be representative of scrape or vacuum systems, or of flush systems using different flush frequencies; etc.)
e) If specific emission factors were developed, what exactly is the basis for those emission factors? For example, when calculating the lagoon emissions, is the entire herd size being used as the basis or was the number of cows who actually contribute their manure to the lagoon established and used as the basis for the calculation? (
f) Does it make sense to adjust emission factors for type of cow (milk cows, dry cows, heifers, calves) or breed (Jersey, Holstein, Guernseys)? (Animal Units? Manure production?)
g) How would you define an average cow, upon which to base emissions, versus other bases for emission factors?
h) How might differences in dairy management practices affect emissions?

7. If VOCs are associated most with smell (p.69 NRC report), and waste lagoons do smell, are the methods of measurement missing some VOCs or semi-volatiles from the lagoons?
    a) Is it possible that fresh manure releases the most volatile VOCs & older manure releases semi-volatiles?
    b) Has anyone analyzed semi-volatiles?
8. Was N_2O measured? If so what were the results?
9. How well, in your opinion, do the 3 different studies represent the different types of dairies in CA?
    a) Geographically?
    b) In terms of size?
    c) In terms of practices (frequency of cleaning corrals for example)?
    d) Feed given to animals?
    e) Type of dairy cows/dry cows?
    f) Climate/seasonal variations?
    g) How are the emission factors affected due to the above-mentioned variables and differences in dairy type, location, etc.
    h) What constitutes enough evidence that a compound is being emitted by dairy animals and their excreta?
        a. For example, in seven sampling events it appears Krauter found only two compounds consistently – acetone and ethyl acetate. According to the spreadsheet posted on the ARB web site, Mitloehner found 13 VOC compounds in enteric and excreta emissions, but it is unclear how many sampling

events this includes. Multiple sampling events with repeated measurements of the same compounds might increase our confidence that these compounds can be expected; does he have more data to report?

b. What amount of methane did he measure? Schmidt reported during the symposium that he identified and quantified 18 VOC compounds. However, does this represent only one sampling event? It appears that of the compounds found by Mitloehner and those found by Schmidt, only five compounds were identified and quantified by both researchers. How can this be explained?
c. What is the ratio of methane versus VOC?

ROG & Amine Emissions from a Northern CA Flushed Lane Dairy – Dr. Schmidt

1. What specific types of processes were tested? (open corrals, flush lanes, etc.)
2. At what specific locations were samples taken? (e.g. Lagoon inlet and outlet, top of manure pile, etc). On what basis were the locations chosen?
3. Describe specific events that may have affected emissions (e.g., it has been reported that a lagoon was drawn down by 25% and that corrals were scraped a day prior to testing). How do you believe these events may have affected the quantity of emissions data generated?
4. Has anyone compared VOC emissions from freshly cleared corrals vs. corrals due for cleaning (in other studies)?
5. How are the emissions measured from the solid manure representative of solid manure from CA dairies since the pile measured at the dairy was apparently very small? (Explain calculation) Were you able to determine the average age of material in the pile or identify how recently the pile had been worked in ways that might stimulate or release additional emissions? Part of this question may have been answered in General Question 5.c
6. Explain how an ambient environment is simulated or duplicated in the use of a flux chamber on top of a sample? What are the factors that take place and how can we be sure that the environment has not significantly been altered?
7. For sampling in the flush lane, for what portion of the sampling period did the test chamber have manure within or beneath the test chamber?
8. Define types of categories on the TNMHC pie chart. We suggest the use of industry-standard terminology.
9. There is an apparent discrepancy between the number of cows reported under your study and the number of cows reported under Krauter's study. What was your number based on? Describe what you did to count cows or how was the number of animals at the facility determined? Have you followed up on this discrepancy?
    a) Can the numbers be verified through written documents?

b) How did you differentiate between the ages of the animals?

10. Why is acetone represented twice in the table?
11. In your presentation slide #29 (titled 'Dairy Emissions Phase 2 Summer Emissions) presented at the symposium, you identify and quantify 20 separate compounds, including ammonia, which is not an organic gas, and methane and acetone, which are not classified as ROG. The other 17 compounds add up to approximately 3.3 lbs. per year. Were any other organic gases identified and quantified individually? If so, what were these compounds, and what were the quantities?
12. How does the information described in the previous question reconcile with the figures in slide #29 of "TNMHC as hexane = 3.6 lbs/cow/year" vs. "TNMHC as methane = 19.4 lbs. hd/year" ? How were these TNMHC totals calculated and did they consider/include the 3.3 lb. total of the compounds above?
13. How did you come up with the 3.6 vs.19 lb/hd-yr numbers and what was the significance of reporting them as hexane or methane?
14. Slide #30 in your presentation indicates 3.6 to 19 lbs. ROG/cow/year were found. Is this a range or the same data interpreted two different ways based on the molecular weight of hexane versus methane? If the difference is not simply explained by the difference in molecular weight from hexane to methane, please clarify the exact basis of the variation.
15. Please provide the age (number of days) and moisture content of all solid manure sources tested-storage piles, freestall bedding, solid separator solids, piles in corrals, etc. Part of this question may have been answered in general Question 5.c
16. Where within the freestall barns were measurements taken-appears to be freestall beds, on rubber mats within flush lanes and on concrete within flush lanes? How many repetitions were taken of each source within the freestall barn source and how was the number for the source derived?
17. Dr. Mukhtar spoke specifically of accuracy problems in ammonia testing using the flux chambers due to moisture within the system-is this an issue when measuring VOC? If so, how did you ensure that moisture was not entering the system in areas such as the flush lanes and lagoon surface?
18. What type of feedstuffs were included in the milk string feed ration tested in the feed bunks? Specifically what types of wet and liquid feeds were included?
19. How were sites selected? Were these representative of the facility?
20. What was the animal activity in the area the previous 24-48 hours?
21. Were samples random or within a specific area?
22. Your conclusion is that ethanol is the dominant ROG species from feed. If acetic and propionic acids were not measured then it may be misleading to identify that ethanol is the dominant ROG. What types of wet/moist feed were fed? How long had the feed been in the feed bunk prior to sampling?
23. What is the anticipated source of acetone, benzene, and toluene? What would be the source for benzene and toluene?

Monitoring & Modeling of ROG @ California Dairies – Dr. Krauter

1. Have you been able to decipher what caused some of the emissions data to be 10-fold higher when compared to the majority of the results obtained?
2. At what specific locations were samples taken? On what bases were the locations chosen? What is the rationale of choosing the distances from emissions source to the sampling locations? Were sample locations consistent from dairy to dairy?
3. The ISCST model is designed to give a conservative estimate of concentration based on a given emission rate. Is there a concern that once you back-calculate from an emission concentration to an emission rate, the results are biased in the opposite direction (i.e., lower emissions rate)? How do you address that? What's the uncertainty of the method?
4. What are the limitations of the modeling? Is it possible that, based on things like changes in wind direction or loft caused by heating soils, emissions from certain areas of the dairy were not measured?
5. How well are the plumes characterized? Are there effects of buildings and trees that vary between sampling sites? Are the assumptions of the model equally true in each place? Could you explain the measurements and instruments used to define the transport characteristics of each location.
6. Enteric emissions alone (based on Mitloehner's study) are higher than the lower end of the range of total emissions measured in your study. Does this cast doubt on the results of your tests, or are there parameters that potentially explain this discrepancy?
7. Any thoughts as to why emissions are lower from Kings County Dairy when compared to Merced Dairy? There are more emission units (settling basins), but perhaps management practices are a factor? Or, do the sampling points not capture all emissions from the dairy?
8. There is significant variation in the data results provided-both within the Merced dairy across different time periods and days as well as between the Merced dairy and the Kings dairy-what information can you provide as to the daily activities going on at the dairy at the times of measurement that could account for some of the differences?
9. There is an apparent discrepancy between the number of cows reported under your study and the number of cows reported under Schmidt's study. What was your number based on? Describe what you did to count cows or how was the number of animals at the facility determined? Have you followed up on this discrepancy?
    a) Can the numbers be verified through written documents?
    b) How did you differentiate between the ages of the animals?
10. What was the time of day of sampling, duration of sampling, and potential activity on dairy to impact sampling. (part of this question may have been answered by general question #5)
11. What was the number of sampling events?

12. In your Presentation slide #22, titled “Individual TO-15 compound emissions (#/head/year) for Kings and Merced Dairies”, appears to contain a list of 61 compounds. Doesn’t TO-15 look at more compounds than that, over 70? Where are the rest?
    a) Of the 61 compounds listed, only two showed up in all sampling events: acetone (which is not a ROG) and ethyl acetate? Since animals and animal waste is a constant at dairies, should we conclude that compounds not showing up in all samples are not generated by the animals or the waste?
13. Mitloehner appears to also be doing TO-15, but there are only 56 compounds listed. Why? Is the data in the Excel spreadsheet on the web a result of one sampling event or the average of several? What compounds are we consistently seeing show up in multiple sampling events?
14. Have you evaluated the possibility or magnitude of consumption or dispersion of ROG between the site of emission and the site of detection. This would clearly underestimate emissions. Possible fates could be particle formation, gaseous deposition, etc.

VOC Emissions from Dairy Cows and their Excreta – Dr. Mitloehner

1. Illustrate the procedures/events of the entire study starting with an empty chamber. Include the following details:
    a. Day one: Was the chamber completely empty or was there any feed there?
    b. Day two: Did this day, the first day with cows in the chamber, include feed? Characterize the feed (e.g. grain, oats, hay, silage).
    c. Day three: On this day, measurements of cows and waste were taken. Was feed also included in the total measurement?
    d. Day four: Measurements of only waste was taken. Was the feed removed from the chamber on this day? If not, is there a way to differentiate the emissions from the waste and the feed?
    e. How often was the feed brought into or removed from the chamber on these days?
2. Please explain how you measured cows + waste separately from waste only, and how these separate estimates were combined and extrapolated into an emission factor.
3. There is a concern that fermenting feeds may be a significant source of emissions from dairies. Please characterize the feed type and quality sufficiently so that an assessment can be made of the likelihood that rotting or fermenting feed may have affected your study results.
4. Your study focuses on the urine, feces, and sweat of individual cows. The Dairy Permitting Advisory Group is tasked to quantify VOC emissions from dairies. Therefore, how do we integrate your data to include emissions from other sources on a dairy such as stored manure and lagoons?

5. Your study appears to also be doing TO-15, but there are only 56 (compared to 61 compounds from Krauter's study) compounds listed. Why? Is the data in the Excel spreadsheet on the web a result of one sampling event or the average of several? What compounds are we consistently seeing show up in multiple sampling events?
6. There are several instances within the data set provided where the inlet reading (background) for a given compound is significantly higher for "excreta" vs. "cows + excreta"-in some cases the inlet for "excreta" is higher that the outlet for "cows + excreta"-how do you account/explain this?
7. Was air scrubbed coming into the chamber? Looking at the acetone values, there is one ',' and one value for inlet. The outlet values on both days are not much greater than one of the inlet values. Why was the one inlet value so high or is this a low value? Inlet air quality appears to vary significantly.

On Farm Measurements of Methane & Select Carbonyl EF – Terry Cassel

1. Characterize the differences in test methods and results between yours and Fresno State's Study.
2. Do the overall emissions include emissions from the milking center?
3. Were emissions from manure piles included in the air samples?
4. What was the time of day of sampling, duration of sampling, and potential activity on dairy to impact sampling.
5. What were the number of sampling events?
6. What do the negative VOC emissions coming from the lagoon mean?
    a) Since the emissions estimates are calculated as differences between upwind and downwind measurements, what uncertainties are introduced into the calculation of the magnitude of the emission estimates? Should the emission estimate be shown as the range between the downwind measurement (as maximum possible attributable value) and the difference between upwind and downwind (calculated emission flux)?
7. What is the confidence level on the high VOC concentrations resulting in 800 lb/hd-yr emission rates? Explain the different possible reasons for these very high numbers.

Emission Points at a Dairy

Milking Center

- Milking parlor
- Cow holding area

Cow Housing and Feeding

- Freestalls

- Flush Lanes
- Open Corrals
- Calf hutches
- Feed lanes
- Enteric
- Feed in feed manger
- Silage Piles
- Bedding Material

Liquid Manure Management

- Mechanical separator
- Settling Basins
- Lagoon
- Storage Pond
- Liquid manure application to land
- Processing Pit

Solid Manure Management

- Manure Piles
- Emissions from manure disturbance
- Windrow composting
- Separated solids
- Solid manure application to land