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SANTA BARBARA • SANTA CRUZ

AGRICULTURAL AIR QUALITY RESEARCH CENTER  
Frank Mitloehner, Ph.D., Director  
Air Quality CE Specialist  
Department of Animal Science  
2151 Meyer Hall  
1 Shields Ave  
Davis, CA 95616  
(530) 752-3936

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**DAVID CROW**

Air Pollution Control Officer (APCO)  
San Joaquin Valley APCD  
Fresno, CA

Dear Mr. Crow,

During the DPAG deliberations, I have released preliminary data from our VOC studies at UC Davis and UC Berkeley (Allen Goldstein). I am pleased to inform you that the project scientists involved in these studies have completed the analysis of all compounds. A full report will be released to the main funding agency (EPA IX) in September 2005 and a manuscript submitted for peer review. At this point, I want to share with you some of the key points as we now have a more complete understanding of these emissions than we did in April.

Before I report on the findings, allow me to reiterate our analytical limitations: the majority of our obtained values are based on PTR/MS, GC/MS, and laser-based spectroscopy (i.e., CH<sub>4</sub>) technologies. PTR-MS uses a chemical ionization method in which H<sub>3</sub>O<sup>+</sup> ions are allowed to react with a gaseous sample. If a given compound in the sample has a proton affinity greater than that of water, the proton is transferred to the compound, which can then be detected. Many classes of VOC have proton affinities larger than that of water (166.5 kcal/mol), including alcohols, aldehydes, aromatics, ketones, alkenes, nitriles, sulfides, and acids and can be measured accurately. The PTR/MS by its design does not measure alkanes, some alkenes, and halogenated compounds because their proton affinity is less than that of water. However, these compounds can typically be detected by use of a GC/MS.

Please note that certain types of organics (e.g., Volatile Fatty Acids, VFAs) may be difficult to detect with the PTR/MS due to their 'stickiness', or tendency to adsorb or condense onto surfaces. This is a typical problem for many analytical systems, and the PTR/MS is generally superior over most other systems due to extensive use of Teflon surfaces in contact with the sample and short residence times in the plumbing. VFAs are partly removed in the chamber tubing and plumbing before actually reaching the PTR/MS. However, if the concentrations are high enough we can still detect them. In the present experiments we were able to detect and quantify acetic acid, despite the system not being optimized for VFA analysis. The PTR/MS results must clearly be taken as a lower limit on the acetic acid fluxes. The only other VFA we observed was propionic acid; if others exist they are below our detection limits due to losses. As you know, the

PTR/MS was not intended to be the primary measure of VFAs. The primary VFA assay in our research was by means of sorbent tubes and GC/MS thermo-desorption analysis (USDA-ARS and Iowa State University). As I explained in my letter from July 8, 2005, we were not able to obtain inlet and outlet concentrations using this methodology. The 'grab samples' that we had taken, indicated considerably higher concentrations than those obtained by the PTR/MS.

Our methods did not include measurement of ethanol.

### **Chamber results (enteric fermentation)**

As you might recall, the main objective of our study was to compare the present 12.8 lb VOC emission factor that is based on the chamber study by Ritzman and Benedict (1938) and the EPA manual (1980) with a controlled and modern study also conducted under chamber conditions.

The present emission factor of 12.8 lb/cow/yr is based on the following assumptions and/or findings:

- 1) A cow produces 160 lbs/cow/yr of Total Organic Gas,
- 2) 70% of the TOG is methane,
- 3) 20% of the TOG is ethane,
- 4) 2% of the TOG is acetone (non-reactive),
- 5) 8% of TOG (12.8 lbs) is reactive (based on EPA manual, 1980) and considered reactive VOC.

Our work at UC Davis shows considerably different results (e.g., mid lactating cows & waste):

- 1) A mid lactating cow produces 299.54 lbs/cow/yr of Total Organic Gas,
- 2) 99.36% of the TOG is methane (297 lbs/cow/yr),
- 3) No ethane was detected,
- 4) 0.54% of the TOG is reactive (equals 1.63 lb/cow/yr) and considered reactive VOC,
- 5) 0.04% of the TOG is acetic acid (using PTR/MS).

As you see from the above values, our final data suggest that the numbers that I reported to you in April for VOCs were somewhat higher. As I stated during the April meetings, we intentionally and conservatively erred on the high side with our preliminary report. The most common VOC compounds we have found (aside from the non-reactive acetone) were methanol, acetic acid, dimethyl sulfide, and trimethyl amine. These made up about 74% of the total VOCs.

We realize that VFAs are part of a compound group that is of greatest interest to the District. We did find, as expected, acetic acid in inlet and outlet air using the PTR/MS. We have well established that acetic acid is by far the most prevalent VFA compound related to dairy cattle. Our PTR/MS analysis yielded a range of acetic acid from 0.02 to 0.13 lbs/cow/yr (mid lactating cow = 0.13 lb/yr). Because of the limiting factors mentioned above, this must be considered an underestimate. The acetic acid numbers measured using the PTR/MS were considerably lower than the numbers proposed by the District using our preliminary data (which are based on outlet concentration data only). In my view, the discrepancy cannot simply be attributed alone to reduced sensitivity and/or stickiness to surfaces in the PTR/MS method.

The district's proposed emission factor for VFAs (i.e., acetic acid) from enteric fermentation (based on extrapolated data from my study) is approx. 64 times higher than the highest concentration we have measured with the PTR/MS.

The discrepancy between both methods (derived from the same study) highlights the great level of uncertainty with respect to quantification of VFAs. In my view, this uncertainty can only be addressed by conducting additional VFA studies designed specifically for the purpose of emission rate quantification.

Sincerely,

A handwritten signature in black ink, appearing to read 'Frank Mitloehner', written in a cursive style.

Frank Mitloehner, Ph.D.