Volatile Organic Compound emissions from dairy cows and their excreta

Frank Mitloehner, PhD
Air Quality CE Specialist
Animal Science, UC Davis
Estimating Emissions from Animal Feeding Operations

Bill Schrock; US EPA
NRC findings

• “A critical requirement for estimating appropriate emission factors is a statistically representative survey of emissions from a class of AFOs over several iterations of the time period to be presented” (NRC 2004; pg. 100)

• NRC Finding 8: Estimating air emissions from AFOs by multiplying the number of animal units by existing emission factors is not appropriate…” (pg. 102)

• NRC Finding 9: Use of process-based modeling will help provide scientifically sound estimates of air emissions from AFOs for use in regulatory and management programs.” (pg. 103)

• Further reading on EF (pg. 242 pp)
NRC findings (pg. 103)

- “The (NRC) committee recommends the use of process-based modeling approach to predict emissions from both individual AFOs and regions. A process-based approach would involve analysis of the farm system through the study of its component parts.”
- It (the process-based model approach) would integrate mathematical modeling and experimental data to simulate conversion and transfer of reactants and products through the farm enterprise”.
- Mass balance (N, S, and C)
- Site specific
Process-Based Simulation Models Should Replace Emission Factors

- Accounts for site-specific design and management practices as variables and reflects interactions between emission sources
- Reflects mass balance constraints
- Scale specific (e.g., individual AFOs or regional/national scale)
Research Needs Are Significant

• Health and environmental impacts
  ...to understand which emissions are most harmful

• Standard measurement protocols
  ...so that research results can be directly compared

• Process- based emission simulation models
  ...to replace emission factors

• Transport and fate of emissions
  ...to better understand significance on local, regional, and national scales

• Best management practices to reduce emissions
  ...to understand the applicability, cost, and performance of emission control practices

Bill Schrock; US EPA
NRC findings and recommendations vs. specific regulatory needs in California?
What do we know about VOCs?

- VOC = approx 700 individual reactive gases (also referred to as ROG)
- Precursors in the formation of ozone
- VOCs vary in reactivity (e.g., freon forms more ozone than benzene)
- Several labs (e.g., West TX A&M, ISU) have measured VOCs (odor research)
- California research focus is on VOC contribution to ozone formation and not on odor forming potential (need for speciation of reactive hydrocarbons)
- Therefore, methods and equipment used in CA differ significantly to those used in other states
What do we think to know about VOCs?

- Dairy cows produce 12.8 lbs of VOC annually
- Emissions from 700 cows
  - 4.5 tons/year VOCs, which is equivalent to 60,000 cars (based on 12.8 lbs EF based on Benedict and Ritzman, 1938 study)
Cows rival cars as smog producers

The Valley's 2.6 million cows emit tons of gases that turn into pollution, but it's difficult to quantify just how much.

The barnyard is passing the freeway in a race few people even know about - making smog gases.

Everyone knew cars made these gases, but cows? Indeed, plumes of gases waft from San Joaquin Valley dairies where prodigious amounts of livestock waste are stockpiled. By 2005, cows will lead cars in venting this so-called "reactive organic gas," a main ingredient of smog.
What do we need to know about VOCs?

- Methods to measure speciated VOCs
- Dairy processes that lead to VOC production
- Speciated VOC compound lists from dairy processes
- Computations of identified VOCs with their specific reactivity to assess ozone forming potential
Volatile Organic Compound emissions from dairy cows and excreta
# Collaborators & Funding

Environmental Protection Agency IX ($75,000), SJVAPCD ($10,000)

<table>
<thead>
<tr>
<th>UC Davis</th>
<th>Dr. F. Mitloehner, Dr. B. Flocchini, T. Cassel, Dr. R. Higashi, Dr. E. DePeters, Dr. P. Robinson, Dr. J. Fadel</th>
</tr>
</thead>
<tbody>
<tr>
<td>UC Berkeley:</td>
<td>Dr. A. Goldstein, Dr. S. Lyn Shaw</td>
</tr>
<tr>
<td>Stanford:</td>
<td>Dr. M. Webber (Pranalytica), Dr. D. Baer, Dr. T. Owano (LGR)</td>
</tr>
<tr>
<td>Harvard:</td>
<td>Dr. M. Gupta (LGR)</td>
</tr>
<tr>
<td>Iowa State:</td>
<td>Dr. J. Koziel,</td>
</tr>
<tr>
<td>USDA-ARS:</td>
<td>Dr. S. Trabue</td>
</tr>
</tbody>
</table>
Objective

• To measure speciated VOCs using different methods and instruments in dry and lactating cows and their waste

• To measure TNMNEOC, volatile fatty acids, as well as ammonia, methane, and carbon dioxide
Materials and Methods

Air

- 71 VOCs using GC/MS (concentrator)
- All oxygenated VOCs using PTR/MS (real time),
- TNMNEOC (total organic compounds) using GC/FID
- Volatile Fatty Acids (VFAs) using GC/MS thermodesorption
- Methane (real time)
- Ammonia using ion chromatography
- Carbon dioxide and water

Others

- Ambient temp, RH, air flow
- Animal behavior, video system
- Feed intake, body weight, milk parameters, respiration rate
Materials and Methods

Animal types and experimental setup

• Close-up dry cows
• Far-off dry cows
  – Day one: Measurements of empty chamber
  – Day two: Allow cows to adapt to chamber
  – Day three: Measurements of cows and waste
  – Day four: Measurements of waste only (no cows)
    • 3 measurement days per week over 6 wks
• Low producing lactating cows
• Medium producing lactating cows
• High producing lactating cows
  – Day one to four: cows and waste
    • 4 measurement days per wk over 6 wks
GC/MS with pre-concentrator

System identical with ARB instruments. VOC method: TO-15 to analyze 71 hydrocarbon VOCs (detections limit ppt).
LGR Methane Analyzer; real time monitoring, ppt sensitivity (laser based cavity-enhanced spectroscopy)
Ion Chromatography, Dionex (NH3)
Proton Transfer Reaction Mass Spectrometer (PTR-MS)

PTR-MS uses proton transfer reactions to ionize VOCs. Hundreds of organic species in complex matrices can be monitored on-line (detections limits pptv)

http://www.ptrms.com/ptrms/method.htm

UC Berkeley; Goldstein Group
Proton Transfer Reaction Mass Spectrometer (PTRMS):

\[ \text{VOC} + \text{H}_3\text{O}^+ \rightarrow \text{VOC H}^+ + \text{H}_2\text{O} \]

- Sample air
- calibration VOC mixes
- catalytically cleaned air

\( \text{CO}_2 \) and \( \text{H}_2\text{O} \) measurements:

- Sample air
- calibration mixes

UC Berkeley; Goldstein Group
GC/MS results

See Excel file...
Day of 2004

Acetone (ppb)

Dry Cows

Excreta

Lact. Cows

Excreta

UC Berkeley; Goldstein Group
Unknown Masses with Similar Time Profiles

Inlet
Outlet

m45 (ppb)
m63 (ppb)
m69 (ppb)
m83 (ppb)
m87 (ppb)
m101 (ppb)

340 342 344 346 348 350

Day of 2004

UC Berkeley; Goldstein Group
Result summary

- Data is **preliminary and studies are ongoing**
- Methodology is largely developed
- Measured VOC (TO-15) emissions are considerably lower than current ARB estimates
- Summing up emission factors of individual VOCs to one emission factor does not take differences in reactivity into consideration
- Cows themselves seem to emit more VOCs than their excreta (for most measured substances)
- Significant methane and ammonia emissions
- TNMNEOC and VFA results are currently being processed
Air Emissions Mitigation Techniques and Technologies for Californian Dairies

PI: F. Mitloehner
Co-PIs: R. Zhang, P. Robinson, J. Fadel, T. Harter

SWRCB
Mitigation Research Objectives

• Environmental management (e.g., water sprinkling of drylot pens, shade, frequent manure harvest from corrals, stocking rates)

• Nutritional management

• Manure management (e.g., manure storage covers, anaerobic digesters, aerators, pH control)

Measures: VOC, PM10, PM2.5, and NH3
Frank Mitloehner, PhD
Air Quality CE Specialist
Animal Science Department
University of California, Davis
(530) 752-3936
fmmitloehner@ucdavis.edu