

Measurement of airborne volatile fatty acids emitted from dairy cows and their waste using sorbent tubes sampling and thermal desorption/GC-MS analysis

(in collaboration with Dr. F. Mitloehner, UC Davis)

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Summary:

Measurements of seven airborne volatile fatty acids (VFAs) potentially emitted from dairy cows and their wastes will be collected using sorbent tubes and analyzed on a thermodesorption (TDS)/GC-MS system equipped with a PTV (programmed temperature vaporizer) inlet. Air samples will be collected at the enclosed UC Davis livestock air quality research facilities using Carbotrap 300 sorbent tubes. Air samples will be shipped on dried ice and analyzed within 14 days of sampling using automated TDS-GC-MS at the National Soil Tilth Laboratory in Ames, Iowa. Quantitation of the following VFAs will be performed in SIM (selected ion monitoring) mode: acetic, propionic, isobutyric, butyric, isovaleric, valeric, and hexanoic acids. Four sampling and analysis events will be conducted between August 2004 and April 2005 along with concurrent sampling for VOCs with summa sampling canisters. The final report, including the description of methodology, calibrations with standards, and results will be delivered to Dr. Frank Mitloehner (UC Davis). Dr. Frank Mitloehner will coordinate the use of facilities at UC Davis.

Methodology:

Air sampling for VFAs will be conducted at the exhaust manifolds from four large scale (70 X 40 ft) animal chambers that are being used to compare three air emission mitigation treatments for dry-lot corrals compared to a standard dry-lot corral treatment control. Treatments will include frequent manure harvest, bedding (feces/urine separation), and urease inhibitor. Sampling for VFAs will be conducted using 4 tubes for each treatment (16 samples total). Air samples will be collected simultaneously on 4 tubes per chamber using 1 portable sampling pump.

Sampling times for this study will range from 1 min to 1 hr, depending on actual concentrations encountered in the chambers and the air sampling flow rates used. In addition, 4 tubes will be used as trip blanks and 4 will be used to test for sorbent tube breakthroughs. These tubes could also serve as backup tubes. The total of tubes used in one sampling event will be 24. There will be 4 sampling events spaced approximately 2 months apart starting in August 2004 and ending approximately in April 2005.

In addition, VFA from cows and their waste will be measured simultaneously with other VOCs (Dr. Mitloehner's lab) during four sampling events (using 16 sorbent tubes) in two controlled environmental chambers. Air samples will be collected from an environmental chamber in 4-plicates at (a) empty chamber, (b) chamber with cattle, (c) chamber with cattle and manure, and (d) chamber with manure. This portion of the testing and analysis will be completed by February 2005.

Test Sampling Matrix

Location	Treatment	Samples	Approximate Sampling Date (s)
Drylot Chamber	Manure harvest	4 (concurrent)	Aug-Dec 2004
Drylot Chamber	Bedding treatment	4	Aug-Dec 2004
Drylot Chamber	Urease inhibitor	4	Aug-Dec 2004
Drylot Chamber	No treatment	4	Aug-Dec 2004
Field Blanks	Not applicable	4	Aug-Dec 2004
Enviro. Chamber	Empty chamber	4	Nov-Feb 2005
Enviro. Chamber	Chamber w/cattle	4	Nov-Feb 2005
Enviro. Chamber	Cattle & manure	4	Nov-Feb 2005
Enviro. Chamber	Chamber & manure	4	Nov-Feb 2005

All air samples will be collected on 178 × 6 mm diameter glass multi-bed thermal desorption tubes, Carobotrap 300 (Supelco, Bellefonte, PA). All tubes will be conditioned using a protocol as recommended by the manufacture (Supelco). The tubes will be conditioned on a Gerstel Tube Conditioner unit (Gerstel, Inc. Baltimore, MD) at 350 °C for 2 hours with a flow rate of 50-70 mL min⁻¹.

Conditioned tubes will be sealed with Teflon faced lined septum and end caps (Supelco, Bellefonte, PA), wrapped with aluminum foil. A 4 mL vial containing activated carbon with a filter paper in place of the septum will be placed in the transportation container to insure a VOC-free environment for the desorption tubes. A small cooler filled with dry ice will be used to keep the samples cool during overnight air shipment.

All samples will be analyzed within 14 days from the time of sampling. All samples will be allowed to equilibrate to room temperature before analysis. After analysis the sorption tubes will be conditioned as previously specified for 2 hours in order to clean them before collecting the next field samples. All samples will be analyzed on the Gerstel TDSA (Gerstel, Inc.) interfaced with Agilent 6890/5973N (GC-MS) (Agilent, Inc. Wilmington, DE. **Table 1** lists important instrument parameters for the Gerstel TDSA, Gerstel CIS4 (PTV in-let), GC and MS.

Table 1. Analytical instrument conditions for the analysis of air samples collected with sorbent tubes.

Gerstel TDS2				
Splitless Mode				
TDS Oven	Temperature	Ramp	Hold Time	Total Time
Temp. program	(°C)	(°C min ⁻¹)	(min)	(min)
Initial:	25	---	0.5	0.5
Final:	275	60	3.3	8.0
Transfer Line	300			
Gerstel, CIS 4 (PTV)				
Solvent Vent Mode, Glass bead/Carbotrap C packed inlet, Split Ratio 20:1				
TDS Oven	Temperature	Ramp	Hold Time	Total Time
Temp. program	(°C)	(°C sec ⁻¹)	(min)	(min)
Initial:	-80	---	0.2	0.2
Final:	280	12	3.0	3.7
Flow Rates	mL min ⁻¹			
Vent Flow	40			
Split Flow	10			
Agilent 6890 GC				
Column oven temperature	Temperature	Ramp	Hold time	Total time
program	(°C)	(°C/min)	(min)	(min)
Segment 1	20	---	0.5	0.5
Segment 2	240	11	5.0	25
Column	HP-FFAP	30m x 0.25mm x 0.25µm		
Carrier gas	Chromatographic Helium: 99.9999% pure			
	Flow mode: Constant flow			
	Flow: 1.0 mL/min ⁻¹			
Agilent 5973N (MS)				
Mode	SIM			
Masses Monitoring	43,47,53,60,73, and 74 m/z			
Ionization Type	Electron Impact			
Electron Energy	70 eV			
Resoultion	0.7-0.9 amu			

Sample chromatograms will be processed using a compound table with retention times. Minimum requirements for peak identification will require that the SIM identification and GC column retention time.

Measured concentrations of 7 target VFAs from each treatment will be reported in the final report. These concentrations could be then combined with measured air flow rates, environmental parameters, and animal data to estimate emission rates of VFAs from dairy cattle.

Budget:

A total of \$10,000 is requested for these experiments. These funds will be used for travel to UC Davis, shipping costs, analysis cost, materials/supplies, and salaries.

PROPOSAL BUDGET SUMMARY

DIRECT COSTS:

1. Labor & Employee Fringe Benefits (provide detailed breakdown by task and employee on separate sheet [including subcontractors])	\$ _____
2. Equipment (provide detailed breakdown on separate sheet)	\$ _____
3. Travel & Subsistence	\$ __1,100__
4. Electronic Data Processing	\$ _____
5. Photocopying/Printing/Mail/Telephone/FAX	\$ _____
6. Materials and Supplies	\$ __2,600__
7. Chemical Analyses (96 samples at \$50/per sample) on separate sheet)	\$ __4,800__
8. Miscellaneous (shipping of tubes/pumps to UC-Davis)	\$ __400__
TOTAL DIRECT COST:	\$ __8,900__

INDIRECT COSTS:

11. Overhead (%11 at USDA-ARS)	\$ __1,100__
12. General & Administrative Expenses (specify rate)	\$ _____
13. Other Indirect Costs (please specify)	\$ _____
14. Fee or Profit (specify rate)	\$ _____
TOTAL INDIRECT COST:	\$ __1,100__
TOTAL DIRECT AND INDIRECT COST:	\$ __10,000__