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New Protocol for the Determination of Reactive Organic Gases in Animal Feeding Operations

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Abstract. *A new protocol was used to measure the quantity of reactive organic gases (ROG) being emitted from animal feeding operations (AFO) such as feed yards, dairies and poultry houses. The protocol makes use of a portable gas chromatograph (GC) that is brought to the field where actual measurements are taken in conjunction with the EPA flux chamber sampling protocol. To have the analyte concentrations come within the detection limits of the instrument, the GC is equipped with an EPA TO-14 purge and trap pre-concentration device that can introduce gas samples at a rate of 100ml/min. Once the analytes are trapped, they are desorbed and directed to the column for immediate separation. Installed were two traps, a carbosieve trap sensitive to highly volatile compounds and the Tenax GR trap sensitive to most other hydrocarbons. Two columns were also used to separate polar and non-polar substances. In addition, two detectors - a photo ionization detector (PID) for molecules with carbon double bonds and aromatics and a flame ionization detector (FID) to detect most other hydrocarbons, were installed. With this setup, flux and emission factors for ROGs from ground level area sources can be estimated more readily. This method eliminates problems associated with the use of Tedlar bags and gas canisters. This paper presents preliminary results on the appropriateness of methods used to determine ROG fluxes, emission rates and emission factors from ground level areas sources.*

Keywords. Volatile organic compounds, reactive organic gases, measurement protocol, gas chromatograph, ground level areas source, animal feeding operations.

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Introduction

Volatile organic compounds (VOC) emitted from anthropogenic and biogenic sources react in the troposphere in the presence of NO_x and sunlight to lead to photochemical formation of ozone (NRC, 1992). Ozone is one of five primary criteria pollutants regulated through the National Ambient Air Quality Standards (NAAQS). Some VOCs (for example, propylene) are reactive in the atmosphere, whereas others (for example methane) are inert. Some VOCs are hydrocarbons (contain only hydrogen and carbon) but others may be aldehydes, ketones, chlorinated solvents and others (Cooper and Alley, 2002). Reactive organic gases (ROG) comprise a fraction of VOCs. The published reports quantifying ROG emissions from concentrated animal feeding operations (CAFOs) are limited and puzzling due to the fact that not all VOCs are ROGs.

ROGs come in very minute concentrations but their impact on odors may be significant. Odorous compounds are not regulated but are considered a nuisance. Thus, technically, the importance of ROG emissions should only be evaluated on the basis of their effect on ozone formation. The ozone forming potential of ROGs emitted from AFOs are unknown at this stage. Currently, there is no standard protocol to measure ROG. The most common procedure for measuring VOC is to collect the gas in Tedlar bags or gas canisters and transporting the sample to the laboratory for analysis. The most sensitive laboratory instrument for ROG analysis and characterization is the gas chromatograph with mass spectrometer (GC-MS). More recently, the use of proton transfer reaction – mass spectrometer (PTR/MS) has been reported (Mitloehner, 2005).

This study will begin the tedious task of accurately measuring and quantifying ROG compounds responsible for creating tropospheric (close to ground) ozone in representative animal feeding operations in Texas.

Goals and Objectives

The main goal of this work is to develop an effective but innovative procedure for establishing ROG level in representative animal farms.

Specific Objectives

1. To develop a methodology to measure ROG in animal feeding operations such as feedyard and dairies such that fluxes could be measured directly and emission factor calculated readily;
2. To evaluate the effectivity of the protocol used in this study for ROG concentration determination and compare it with existing techniques;
3. To utilize a process-based approach for reporting emission factors; and
4. To propose a method to estimate the emission factor by accounting for the relative reactivity of the ROGs in ozone formation.

Rationale/Significance

The urgency of this research study arises from serious challenges being faced by animal feeding operations in some states (e.g. California) in responding to new regulations that will limit emissions of ROGs. These new regulations use as bases the federal and state (i.e., SB700 in CA) requirements to bring areas classified as ozone non-attainment into attainment and the time-lines set by EPA. The California Air Resources Board (CARB) uses an emission factor for ROG of 5.8 kg/hd/year (12.8 lb/hd/yr). This emission factor was based on a 1938 publication

(Ritzman and Benedict, 1938) which reported the total methane production for a cow to be 200 grams CH_4 in 24 hours (72.7 kg/head/year or 160 lbs/head/year). This result was determined from observation of 10 adult cows of Holstein and Jersey strains. In 1977, Keller and Cowherd conducted a study for the EPA on livestock and found that 8% of the total organic gases (TOG) are reactive and include ethyl alcohol (2%), isopropyl alcohol (2%) propyl acetate (2%), ethylamine (1%) and trimethylamine (1%). The remaining 92% supposedly consisted of methane (70%), ethane (20%) and acetone (2%) which were designated as non reactive VOC. Taking 8% of 72.7 kg/hd/year (160 lb/hd/year) gives 5.8 kg/hd/year (12.8 lb/head/yr) and this value became the emission factor for ROG in the State of California. Note that 72.7 kg/hd/yr (160 lbs/head/year) comprised emissions of methane only and not TOG. Clearly, there is an error in the calculation.

There are problems associated with current methods of measuring ROG. These include the following:

1. Gas canisters are expensive and may cost between $410-$755/unit depending on the capacity of from 1 to 15 liters (Restek Chromatography Products, 2005). Continuous 24-hour sampling would require a large number of gas canisters thus could not be performed if samples and containers are limited,
2. Conventional air sampling methods using gas canisters are often not sensitive enough to detect volatile organic compounds because of low concentrations. In addition, simple syringe injection may not provide enough sample volume to detect a substance appreciably due to the very low level of concentration of VOCs (Spinhirne et al., 2002),
3. Cryo-trapping is also a method of concentrating VOC/ROG samples (e.g. TO-15) and uses liquid nitrogen to condense the VOC but some problems have been identified (Higashi and Cassel, 2004) and exposing a high pressure cylinder containing a hydrocarbon mixture to low temperatures results in heavier molecules falling out of the gas mixture to condense or stick to the interior walls of the cylinder (Scott Specialty Gases, 2004).
4. Other inherent problems reported in literature include, among others, adsorption on walls of Tedlar bags or canisters (Koziel et al., 2004), gas emission losses during transport and reaction among gases during storage.

A more practical method to measure VOC/ROG and eliminating the problems enumerated above would involve bringing the gas-measuring instrument to the field. There are hundreds of compounds with varying volatilization characteristics and detection threshold limits. Some compounds have low detection threshold but have greater impact as odor nuisance. The detection threshold varies from 0.0026 to 0.5 ppm. A gas chromatograph would be able to detect those low limits but a large volume of sample is necessary in most instances. Thus this study made use of a portable GC equipped with purge and trap. The latter was used to increase the amount of gas sample injected into the unit.

Materials and Methodology

The overall sampling protocol for this study follows the EPA method TO-14. However, instead of samples being taken to the lab for GC analysis, the GC was transported to the field and actual gas emissions associated with flux chambers were directed to the GC. This protocol eliminated the use of expensive canisters or cryogenic traps to store gas samples. The protocol still made use of a few gas canister units to collect gas from the field for cross checking of data gathered from the field and for compound identification through an independent laboratory using GC-MS system.

Method TO-14 Dual Trap Air Concentrator

The Method TO-14 Air Concentrator was equipped with a vacuum pump and two independently heated adsorbent traps (for light and heavy volatiles). Gaseous and semi-volatile compounds were concentrated on to a chemically inert Tenax GR adsorbent. Highly volatile compounds with low boiling points (i.e., hydrogen sulfide and dimethyl disulfide) require the use of strong adsorbents. A Carbo-molecular sieve was used for this purpose for efficient compound capture. The use of single adsorbent will never provide for the capture and subsequent release of all malodorous and other VOCs present in air samples. The gas was sampled directly from the source. The vacuum pump was operated for several minutes or more to pass 100 ml/minute of gas through the traps, where the organics are retained. Several liters or more may be concentrated, depending on the detection limit required. Once the analytes were trapped, they were desorbed and directed to the column for separation.

Detectors: Photo Ionization Detector (PID) and Flame Ionization Detector (FID)

A flame ionization detector (FID) was the primary detector of the portable GC and can detect numerous hydrocarbon related compounds. The FID is a nonspecific hydrocarbon detector with a sensitivity that, in general, is linearly proportional to the number of carbon atoms in a VOC molecule (Ackman 1968). A photoionization detector (PID) was used as an additional detector for molecules with carbon double bonds and aromatics. It is sensitive down to 10 ppb level and is nondestructive and thus was used in series prior to the FID detector to report multiple chromatograms from a single injection. The use of PID/FID combination has the advantage of simultaneous hydrocarbon speciation.

Columns: MTX-1 and MTX-Wax

Two columns were used in this study, the general-purpose non-polar phase (60 m MTX-1, Restek Corp.) detector and the general-purpose polar phase column (60 m MTX-Wax, Restek, Bellefont, PA). MTX-1 is ideal for solvents, flavor compounds and most petrochemicals. MTX-Wax is ideal for fatty acids methyl esters (FAMEs), solvents, BTEX (benzene, toluene, ethyl-benzene and xylene) and other flavor compounds. There is only one column oven on the portable GC and the use of different columns was done independently.

Experimental Design

Field Sampling Protocol

The general field sampling protocol involved the following steps:

a. Preparation of equipment to be used (high performance gas chromatograph with accuracy in the ppb level).
b. Setting up of capture containers (gas canisters were used to compare data gathered from the field sampling with those in the laboratory)
c. Identification of sampling areas (blocked area sources, at least 4 homogeneous blocks)
d. Identification of sampling times (diurnal variations)
e. Identification of operational variations (wetting of pens, scraping of pens, etc.)

The specific field sampling protocol is as follows:

a. The flux chamber was randomly placed in the pen complete with external protection from the cattle. The conveying Teflon tube (45 m) was lined-up on the ground with another external protection (hard black PVC tube).
b. Air flow was drawn from the flux chamber at a volumetric flow rate of 2 liters per minute.

c. The gas chromatograph was sampling at a rate of about 100 ml/min for 10 minutes through the traps. In this study a sampling period of 20 minutes was also used to provide 2 liters of sampled gas for comparative purposes.
d. The traps were heated and the collected sample was automatically injected to the gas chromatograph
e. Blanks were run after some sampling episodes to ensure that the traps are properly cleaned before another set of runs is implemented.
f. The chamber was positioned at another randomly selected site and the procedure was repeated.
g. At some specific areas in the pen, preferably those with numerous compounds detected and with relatively higher concentrations, gas canisters were filled up with sample air and brought back to the laboratory for analysis.

ROG Emission Level Characterization

The gas chromatograph is a powerful and sensitive instrument to measure minute concentrations of VOC/ROG compound if the proper detector and protocol are used. The resolution is excellent and numerous compounds can be identified in one sampling injection. By directly injecting a sample into the GC while in the field, any losses or deterioration in the state and concentration of each compound would be minimized. The only difficulty will be the stability of the gas chromatograph in the field and the possible effect of uncontrolled environmental conditions of the ambient air being sampled (moisture, temperature, etc.). This was avoided by installing the GC in an air-conditioned trailer complete with accessories, sample conditioning and gas standards. Ports that were utilized from flux chamber work were used to direct samples to the GC.

With the above set-up, gas concentrations could be reported using the following reporting units:
a. In standard absolute and relative units (ppm and $\mu g/m^3$)
b. From flux measurements ($ug/m^2/s$)
c. Emission factors estimation (kg target compound/head/day for a given season)

In the future, the identified compounds will be evaluated according to their level of reactivity in ozone formation and factors will be used to account for this reactivity.

Preliminary Results and Discussions

ROG Measurement Set-up

The schematic for the ROG measurement set-up for this study is shown in Figure 1. Source emissions were measured using a flux chamber. Air was drawn from the flux chamber to the GC with a known volumetric flow rate of 2 liters/min. While air emissions from the chamber were conveyed through Teflon tubing (approximately 45 m in length), a sample was taken by the purge and trap system on the GC to concentrate the compounds sampled in the two types of traps discussed earlier. Of the 2 li/min flow through the flux chamber, about 100 ml/min is fed through the purge and trap for about 10 minutes, thus injecting a total volume of one liter in the trap. If the detection level is quite low, more gas sample will be fed through the traps (sampling time increased to 20 minutes). After the trapping period, the traps were heated and gases were injected into the column. After injections, the traps were further heated to clean up some residual compounds that were not directed through the GC. The exhaust gases were purged out of the system. Two columns were used independently of each other to differentiate polar

compounds and non-polar compounds. The use of the PID detector is mandated in several EPA methods (TO-14 and 8021) because of its sensitivity and selectivity.

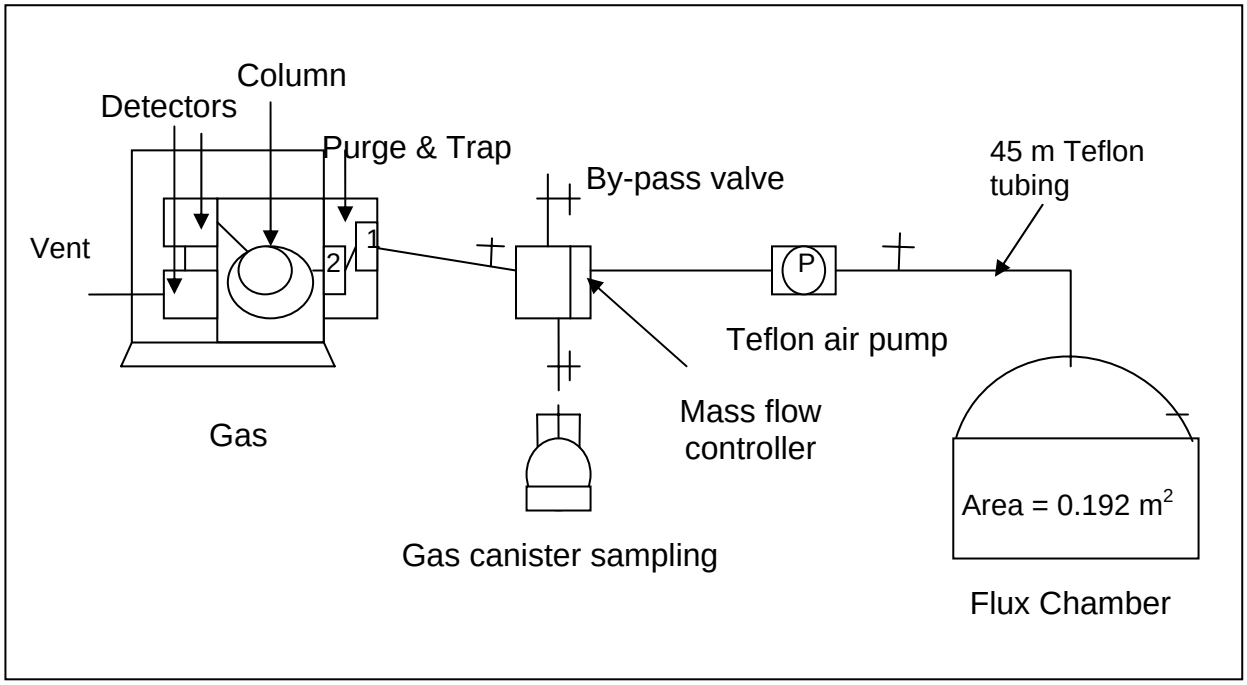

Figure 1. Schematic of ROG measurement setup.

Preliminary Results: Compound Identification

Figure 2 shows the chromatogram of sample taken from the gas canister showing the range of compounds that were detected. This sample was taken from a pen plot with dry surface between 10:30-10:40 in the morning. Gas collected from the gas canisters went through the flux chamber from the source and the 45 m of tubing (from pen surface to the mobile trailer). Compounds were identified using the solid phase micro-extraction (SPME) technique discussed by Spinhirne et al. (2002). The SPME fiber was exposed to the whole gas sample in the gas canister for about an hour. Table 1 shows the list of compounds identified for this particular test (1st three columns). Figure 3 shows another chromatogram taken from another pen surface with relatively wet (hot spot) surface (11:50 am - 12:00 noon) and the list of compounds detected is shown in Table 1 as well (last three columns). Common compounds found in both surfaces included the following: acetone, hexaldehyde, heptaldehyde, octyl aldehyde, p-cresol, and benzothiazole (highlighted in Table 1). Volatile fatty acid (VFA) predominated on dry surfaces (mainly acetic acid) and none were identified on relatively wet surfaces. Aldehydes as well as benzothiazole and p-cresol were identified in both surfaces. The latter are associated with odorous compounds. Close to half of the compounds detected on the wet surfaces were aldehydes (47.6%) while VFAs (30.8%) predominated on the dry surface (Table 2). Aldehydes represented about 20% of the whole sample in dry manure sample. Some condensates were visible on the inner surface of the flux chamber during the sampling of the wet sample.

Results from the field measurements using the portable GC will be reported once complete laboratory calibration procedures have been completed. Calibration runs using standard a TO-15 certified sample were unsuccessful since no compounds matched those taken from field

measurements. The pre-concentration and traps of the GC were able to detect some VOC/ROG compounds but not in the same order of magnitude as those identified using the SPME protocol. The main reason could be that the SPME tube is exposed to about 6 liter sample in the gas canister while the GC was only able to trap as much as 2 liters of sampled gas.

Table 1. Compounds identified from the gas canister sample taken from the dry and wet pen surfaces (The percentage composition of each compound from whole sample is provided).

Wet Manure Surface			Dry manure surface		
Peak #	Compound	% of Total	Peak #	Compound	% of Total
1	-	7.346	1		
2	CO_2	5.045	2	**Acetone**	2.615
3	**Acetone**	2.203	3		
4	-	1.187	4	3-methyl butanol	3.473
5	Methyl-ethyl ketone (MEK)	5.875	5		
6	Pentanal	3.856	6	**n-Hexaldehyde**	12.464
7	-	3.727	7	**Heptaldehyde**	3.606
8	-	2.189	8	**Octyl aldehyde**	3.789
9	1-Butanol	3.655	9	Acetic acid	21.782
10	**n-Hexaldehyde**	24.150	10	Propionic acid	3.135
11	-	0.276	11	Isobutyric acid	3.692
12	**Heptaldehyde**	3.688	12		
13		2.773	13		
14		2.042	14	N-butyric acid	2.137
15	**Octyl aldehyde**	9.395	15		
16	Dimethyl-trisulfide	3.327	16	2-ethyl hexanoic acid	0.809
17	-	2.568	17	Phenol	6.516
18	Nonyl aldehyde	6.461	18	**Benzothiazole**	3.479
19		1.802	19	**p-cresol**	9.923
20	**Benzothiazole**	4.445	20		
21	**p-cresol**	3.491			
22		0.498			

Table 2. Relative amounts of specific compound groups from whole sample.

Wet Manure Surface		Dry Manure Surface	
Compound Groups	% from whole sample	Compound Groups	% from whole sample
Ketones	8.078	Ketones	2.615
Aldehydes	**47.556**	Aldehydes	19.859
Alcohols	3.655	Alcohols	3.473
Benzothiazone	4.445	**VFA**	**30.827**
p-cresol	3.491	Phenol	6.516
Others	32.775	Benzothiazole	3.479
		p-cresol	9.923
		Others	23.308

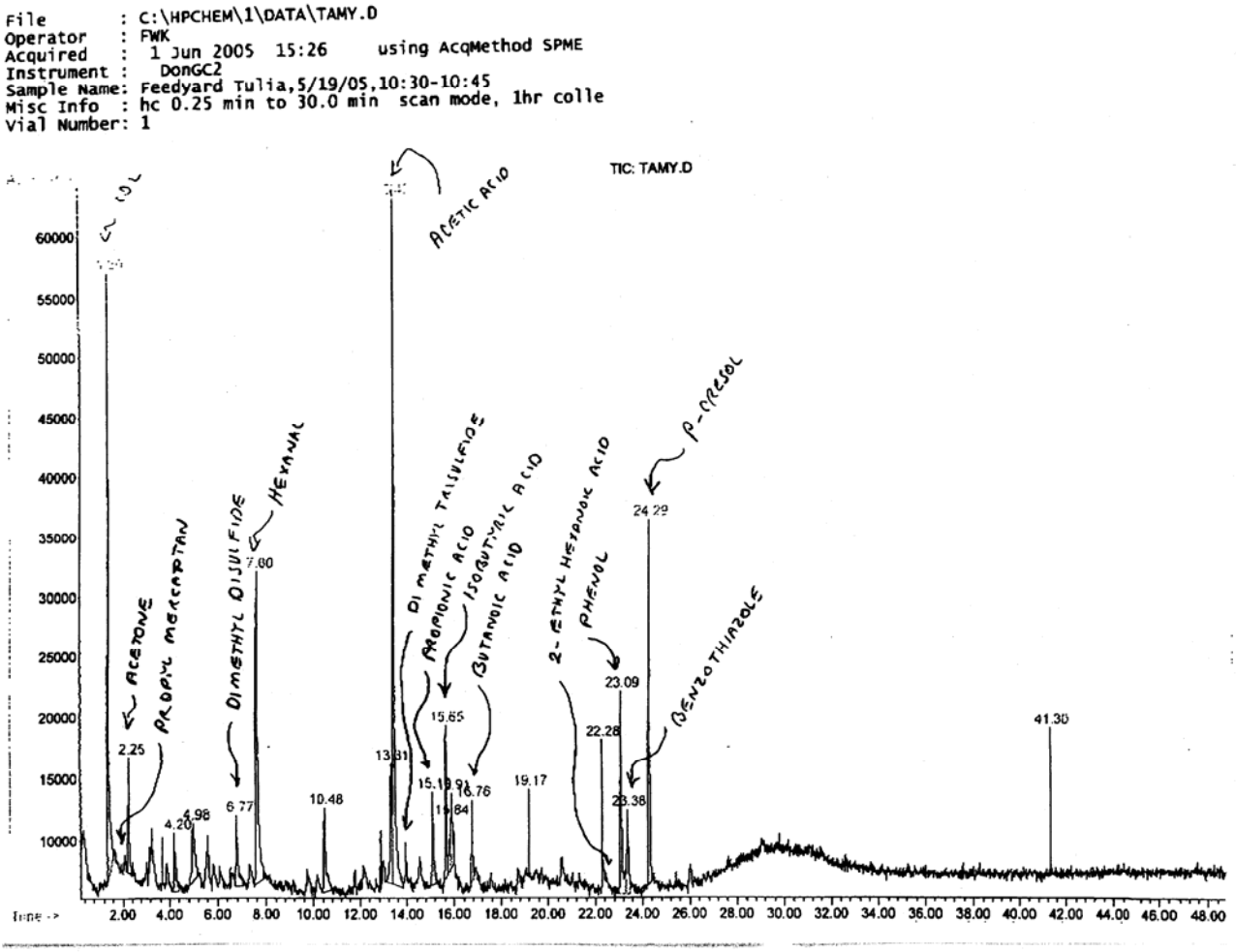

Figure 2. Chromatogram showing the range of compounds detected through the protocol used in this study with the flux chamber set on relatively dry surface.

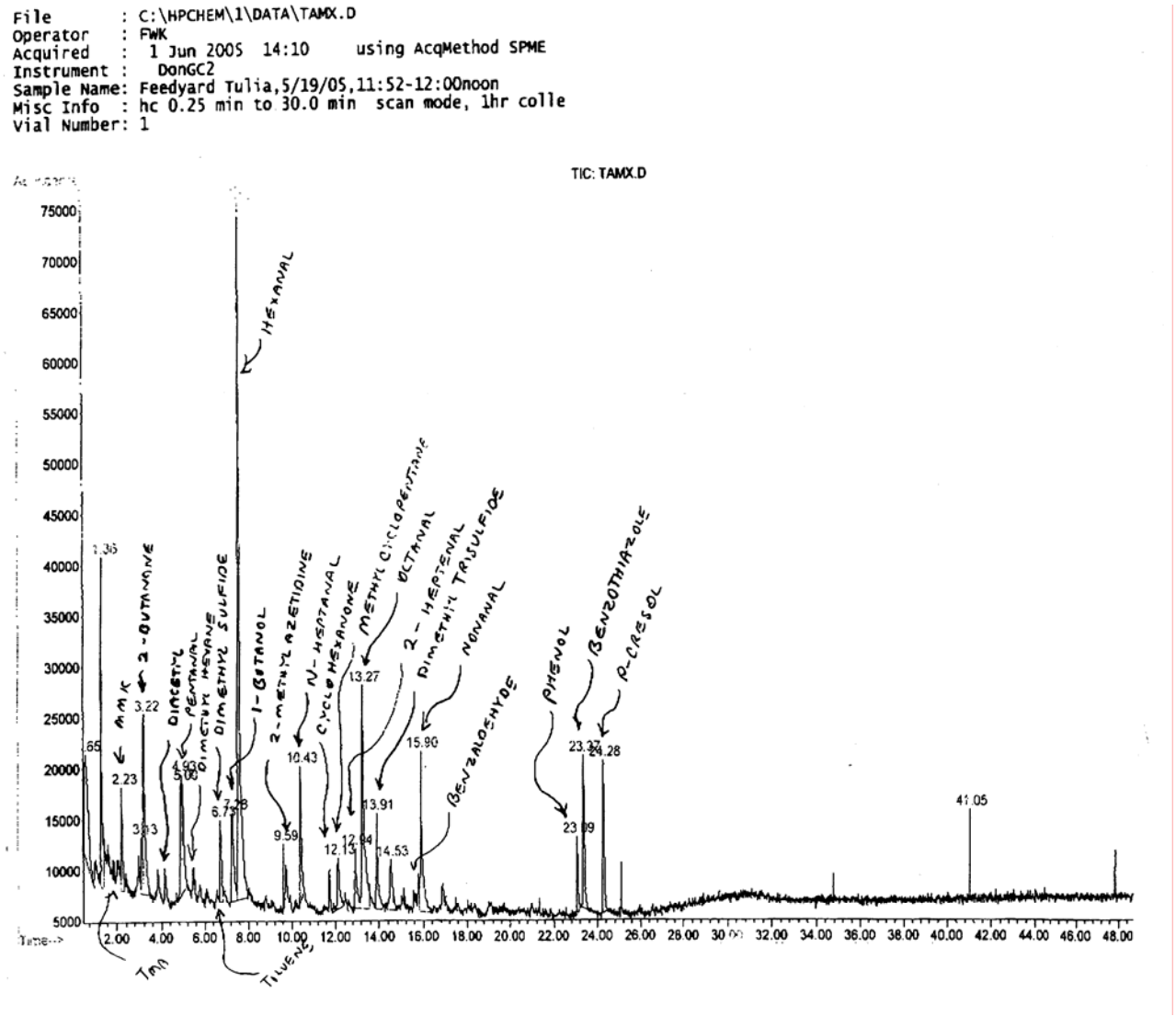

Figure 3. Chromatogram showing the range of compounds detected through the protocol used in this study with the flux chamber set on wet pen surface.

Summary of Preliminary Results and Conclusion

Some preliminary results generated from this study include the following:

1. It is possible to detect VOC/ROGs compounds from ground level areas sources using flux chamber through 45 m of Teflon tubing and a portable gas chromatograph.

2. Compounds identified include aldehydes and ketones, alcohols, VFAs and other odorous gases of varying percentages depending upon surface types. VFAs predominate on dry surfaces while aldehydes predominate on wet (hot spot) surfaces.
3. The pre-concentration and traps of the GC were able to detect some VOC/ROG compounds but not those that were identified using SPME protocol. The main reason could be that the SPME tube is exposed to about 6 liter sample in the gas canister while the GC was only able to trap as much as 2 liters of sampled gas.
4. Future work will evaluate the reactivity of the ROG compounds measured and report an emission factor based on the potential of certain compounds identified to form ozone.
5. A method will be proposed to categorize compounds according to their reactivity and this will be used to further correct the emission factor. Thus, emission rates will not be translated directly into an emission factor but all factors affecting their potential to form ozone will be thoroughly evaluated.

More research work is needed to understand HRVOC emissions from CAFO. The process of O_3 formation is complicated because of variability in chemical formations. Data from several research studies may not be combined to generate a single emission factor due to different protocol used and conditions of tests surfaces. Emission factor should only be calculated from the highly reactive compounds that could be involved in the formation of ozone. No emission factor for HRVOC is being recommended in this report.

Future Work

Similar sampling tests will be conducted on another animal feeding operation (particularly a dairy) and the whole GC setup and the flux chambers will be brought to the field for actual ROG sampling work. Samples will also be collected from gas canisters and brought back to the lab for analysis to measure the differences of both methods. In addition, gas canister samples will also be sent to a certified laboratory for identification and analysis of the compounds present.

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References

Ackman, R.J. 1968. The Flame Ionization Detector: Further comments on molecular breakdown and fundamental group response. J. Gas Chromatography. 6:497-501.

Cooper C. D. and F. C. Alley. 2002. Air Pollution Control: A Design Approach. 3rd Edition. Waveland Press, Prospect Heights, Illinois.

Keller, R.M. and C. Cowherd. 1977. Identification and Measurement of Atmospheric Organic Emissions from Natural and Quasi-natural Sources. Report for EPA contract No. 68-02-2524, July 1977.

Koziel, J.A., J.P. Spinhirne, J.D. Lloyd, D.B. Parker, D.W. Wright, and F.W. Kuhrt. 2004. Evaluation of Sample Recovery of Malodorous Gases from Air Sampling Bags, SPME and Sampling Canisters. Paper presented at the 2004 ASAE/CSAE Annual International Meeting held from August 1-4, 2004 at Ottawa, Ontario, Canada. Meeting sponsored by

the American Society of Agricultural Engineers (ASAE), St. Joseph, MI. USA. Paper No. 044129.

Mitloehner, F. 2005. Volatile Organic Compounds Emissions from Dairy Cows and Their Excreta. Paper presented for the Livestock Emissions Research Symposium Organized by the California Air Resources Board (CARB), Fresno, CA. January 26, 2005.

National Research Council (NRC). 1992. Rethinking the Ozone Problem in Urban and Regional Air Pollution. National Academy Press. Washington D.C.

Restek Chromatography Products. 2005. Product Catalog. Bellefont, PA.

Ritzman, E.G. and F.G. Benedict. 1938. Nutritional Physiology of the Adult Ruminant. Carnegie Institute, Washington.

Scott Specialty Gases. 2004. Protecting Against Condensation Improves Calibration Accuracy. Scott Tech Newsline. Volume 1, Issue 5, Plumsteadville, PA, March 2004.

Spinhirne, J.P., J.A. Koziel, D.B. Parker, D.L. Williams, A.A. Cole and J. A. Sweeten. 2002. Screening for Volatile Fatty Acids in Agricultural Air Using Solid Phase Micro-extraction and Gas Chromatography – Mass Spectrometry. Paper presented at the 2002 Annual International Meeting of the ASAE held from July 28-31 at Chicago, Illinois, Sponsored by the ASAE St. Joseph, MI.