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Comparison of Partial Reactive Organic Gases (ROG) Emission Factors from a Dairy and Beef Feedlot

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Abstract. Emission factors are fundamental tools for estimating the total emission of certain criteria pollutants from a particular source at a given time. In this work we performed a new protocol similar to EPA method TO-14A, suggested by Capareda et al. (2005) in determining ROG emissions from animal feeding operations. Fourteen (14) ROG were tentatively identified and quantified from the dairy and beef feedlot located at Central Texas and Texas Panhandle, respectively during summer of 2006. The compound groups found include ketones, aldehydes, alcohols, volatile fatty acids, benzothiazole, phenols and p-cresol. We found that the relative amounts of ROG in the dairy were much higher than in the beef feedlot and the volatile fatty acids (VFAs) group being more dominant than the other compound groups. Cattle wastes (i.e. manure and urine), milk and some dairy produce are considered as major contributors of biogenic ROG and could be the main reason for the difference. Meanwhile, acetic acid was selected among the volatile fatty acids and its concentration and emission factor were determined for both the sampling locations. It was found that the average emission factor of acetic acid in the dairy open feedlot (ca. 775 kg 1000-hd^{-1} yr^{-1}) was more than four times the magnitude of emission factor in the beef cattle openlot (ca. 186 kg 1000-hd^{-1} yr^{-1}). However, the analysis and characterization of the data using the suggested protocol does not include the full suite of ROG emissions from the dairy and beef cattle feedyards.

Keywords. ROG/VOC, volatile organic compound, emission factor, dairy, beef feedlot, Method TO-14A, biogenic ROG, acetic acid, VFA

Introduction

Volatile organic compounds (VOCs), which often times is referred to as reactive organic gases (ROGs), play a major role in the formation of photochemical oxidants in the atmosphere. The reaction of VOC with ultraviolet energy from sunlight in the presence of NOx could produce ozone (O_3), a federal criteria pollutant as listed by the US Environmental Protection Agency (US EPA) (Copper and Alley, 2002). Not all identified VOC are ROG, some are non-reactive hydrocarbons which may not significantly contribute to ozone formation. According to Monari et al. (1996) most of the measured individual VOC are expressed as the sum of non-methane hydrocarbons, and these measurements do not give information on the photochemical reactivity of the hydrocarbon mixtures.

Biogenic sources of VOC such as those contained in grass and hay (silage) are a major part of a cow's diet. These biogenic sources are converted to VOC through metabolism (enteric fermentation) and later emitted from the cow's wastes (i.e. feces and urine) or accumulated in the cow's milk if not completely metabolized (Ciccioli et al., 2004). VOC emissions from large cattle and dairy farms are often hard to accurately quantify, therefore an emission factor, usually expressed in kilograms VOC per head per year, is used to estimate the total production of VOC from a particular source. However, different VOC emission factors are being implemented in different parts of the country since the EPA (AP-42) does not mention a standard for VOC emission factors from cows. In Idaho for instance, an emission factor of 7.3 kg (16.0 lbs) of VOC per dairy cow per year is used. This factor was based on the research done by the South Coast Air Quality Management District (ICAFOAQS, 2002). A farm having 1000 dairy cows is estimated to produce about 7.3 metric tons (8 tons - US) of VOC per year (DEQ Report, 2003).

Odors in dairies and cattle feedlots are often associated with VOC emissions. Sweeten and Miner (1993) conducted an experiment on the intensities of odor in cattle feedlots. A portable scentometer was used to measure odor intensities which typically ranged from 31 to 170 dilutions to threshold (DT). The highest odor (101 DT) was observed three days after feedlot runoff had occurred and provided organic loading into the pond. The lower reading was observed after the partial stabilization of the volatile solids in the holding pond contents. In a parallel study done by Rabaud et al. (2002), the volatile organic compounds in ambient air from industrial dairies were successfully correlated with odor by the method of thermal-desorption GC-olfactometry-mass spectrometry. The method simultaneously provided compound identification, quantification and olfactory information. Thirty-five VOC were observed in the dairy with concentrations that varied from 0.08 to 747.76 μg m^{-3}. These compounds include acids, esters, alcohols, aldehydes, ketones, halogenates, amines and hydrocarbons. Some compounds having very strong odor intensity indicated the presence of odor-causing VOC with high concentrations (Rabaud et al, 2002).

The characterization of reactive organic gases (ROGs) from different sources (anthropogenic and biogenic) involves a series of procedures to acquire more accurate results. Although there are already some standardized methods (i.e. EPA TO-14A and ASTM D5466) for determining ROG emissions in ambient air, specific methods are still needed for uncharacterized and complex sources such as dairies (Higashi et al., 2004). The US Environmental Protection Agency (US EPA) first published Method TO-14 as a supplement to the "Compendium of methods for the determination of toxic organic compounds in ambient air (EPA 600/4-89-018)," in 1989, while the most recent update and revision, Method TO-14A, was published ten years later which was in 1999. Capareda et al. (2005) suggested a new protocol in quantifying ROG emissions in animal feeding operations (AFO) by introducing some modifications on the procedures of Method TO-14. All elements essential to Method TO-14 (i.e. the use of flux

chamber, pumps, GC and GC detectors) were present except for the air sample storage in gas canisters. The new protocol showed promising results in determining ROG fluxes, emission rates and emission factors from ground level sources which may have confirmed the appropriateness of the procedures used in the protocol.

Summary of EPA Method TO-14A

The US EPA Compendium Method TO-14A ("Determination of Volatile Organic Compounds (VOCs) In Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography") typically uses initially evacuated canisters and pump-ventilated sample lines when collecting air samples from the field. The gas canisters used for air sample storage should be specially-treated: leak-free, stainless steel pressure vessels of desired volume, with valve and passivated interior surfaces. The cost of gas canisters required for the method (i.e. TO-can^{TM} canisters) typically range between $290 and $1,067 depending on the capacity and other added features (Restek Corp., 2007). After the samples have been collected, the canisters are properly labeled with a chain-of-custody (COC) form and later transported to a predetermined laboratory for analysis. At the laboratory, the canisters are attached to the analytical system that involves the use of a high-resolution gas chromatograph (GC) coupled to one or more GC detectors. The GC could use either non-specific detectors or specific detectors. The non-specific detectors specified in Method TO-14A include, but are not limited to, the nitrogen phosphorus detector (NPD), the flame ionization detector (FID), the electron capture detector (ECD), and the photo-ionization detector (PID). Whereas, the specific ones include the linear quadrupole mass spectrometer (MS) operating in either the select ion monitoring (SIM) mode or the SCAN mode, or the ion trap detector. Each detector has different advantages and disadvantages from one another which may include cost, sensitivity, and range of compounds that can be identified.

The moisture content for the air samples were lowered during analysis by a Nafion® dryer (if applicable) and the VOC were then concentrated by a cryogenically-cooled trap. The temperature of the trap is raised to revolatilize the VOCs originally collected in the trap. The collected VOCs were then injected into the GC and separated on a column then detected by one or more of the detectors mentioned earlier for identification and quantification.

In this work, we performed the new protocol suggested by Capareda et al. (2005) in determining ROG emissions in animal feeding operations (AFO). A report on the comparison of partial emission factors of ROG/VOC (in kg 1000-hd^{-1} yr^{-1}) for dairy and beef feedlot in Texas was also presented. The US EPA method TO-14 flux chamber was used to collect a known volume of air samples from the site. The method used in the air sampling still follows the EPA method TO-14A for determining VOC in ambient air. A gas chromatograph coupled with a purge and trap system and a combination of two non-specific detectors (FID/PID) were used to analyze the partial ROG/VOC concentrations directly from the sampling field (open lots and compost piles).

The ROG sampling events were done during the warm weather (summer) under specific conditions present and were limited only in some parts of Texas (Texas Panhandle and Central Texas). The results of the partial ROG emission factor calculations may not be valid for a different time of the year and for a different location.

Objectives

The following were the objectives of this research:

1. Perform a new protocol (suggested by Capareda et al., 2005) in determining reactive organic gases (ROG) emissions from beef cattle and dairy feedyards that still satisfies EPA's requirements for Method TO-14A.

2. Identify and quantify a dominant ROG (acetic acid) from both feedyards using the suggested protocol.
3. Estimate and compare the emission factor (in kg-1000hd^{-1}-yr^{-1}) of the identified ROG from the beef cattle feedyard and dairy.

Methodology

Suggested New Protocol Performed for the Determination of ROG in Dairy and Beef Feedyards

A. Sampling Location and Time

A feedyard located at the Texas Panhandle was chosen as the sampling site for determining ROG emissions for beef cattle. Figure 1 shows an aerial photo of the beef feedlot as well as the selected sampling locations on it. The air sampling was done for five consecutive days between the hours of 9:00 am and 8:00 pm (while the sun is still up) during warm weather (May, 2006). The beef feedlot held around 40,000 head of cattle, which were mainly raised for meat production. On the other hand, a dairy farm (Fig. 2) was selected in Central Texas for ROG sampling. The dairy had around 3500 head of cattle which mainly composed of milking cows and heifers. The dairy also had a milking facility located near the farm entrance. The ROG emission samplings at the dairy were also done for five consecutive days between the hours of 9:00 am and 8:00 pm during warm weather (June, 2006).

The four corner pens of the beef feedlot's open lot (total of around 400 pens) starting from the southwest corner (moving in a clockwise manner), were selected as sampling locations (Fig. 1). The approximate area of each sample pen and the number of cattle in each pen was 2000 m^2 (20000 ft^2) and 200, respectively. The soil can be described as very dry and fine textured (dusty) with portions having scattered cattle feed, feces and urine. ROG samplings were also done on the composting piles of the beef feedyard (with soil characteristics of coarse textured, loosely packed and dark-brown in color). Meanwhile, only three (3) pens from the dairy's open lot (Fig. 2), having the same soil (surface) characteristics as in the beef feedyard, were chosen for ROG sampling due to time constraints. The dairy open lot had a total of 16 large pens. The approximate area of the sample pen in the dairy was 7500 m^2 (80000 ft^2) while around 200 dairy cows were occupying each pen. One sampling was performed on the composting piles and another sampling was done on the concrete floor outside the milking facility.

B. Sampling setups and procedures

The sampling setups and procedures used for the determination of volatile organics or reactive organic gases (ROGs) in a dairy or beef cattle feedyard were similar and a schematic diagram is shown in Fig.3. The flux chamber was placed at a random sequence inside the pre-selected sites. Before the sampling was initiated, the flux chamber was laid flat on the ground first while a volume of zero grade air (analytical systems that contained <0.2ppbv of targeted VOCs were acceptable) was provided to create a certain flux of air inside the chamber. Then, air samples were drawn from the flux chamber through Teflon tubes with the use of a positive displacement pump. The volume of air samples drawn from the field were regulated by mass flow controllers connected to the pump. The ROGs were then concentrated into a series of adsorbent traps connected to the GC before injecting into the GC column. The excess air was purged out of the GC while the injected samples were analyzed in the system.

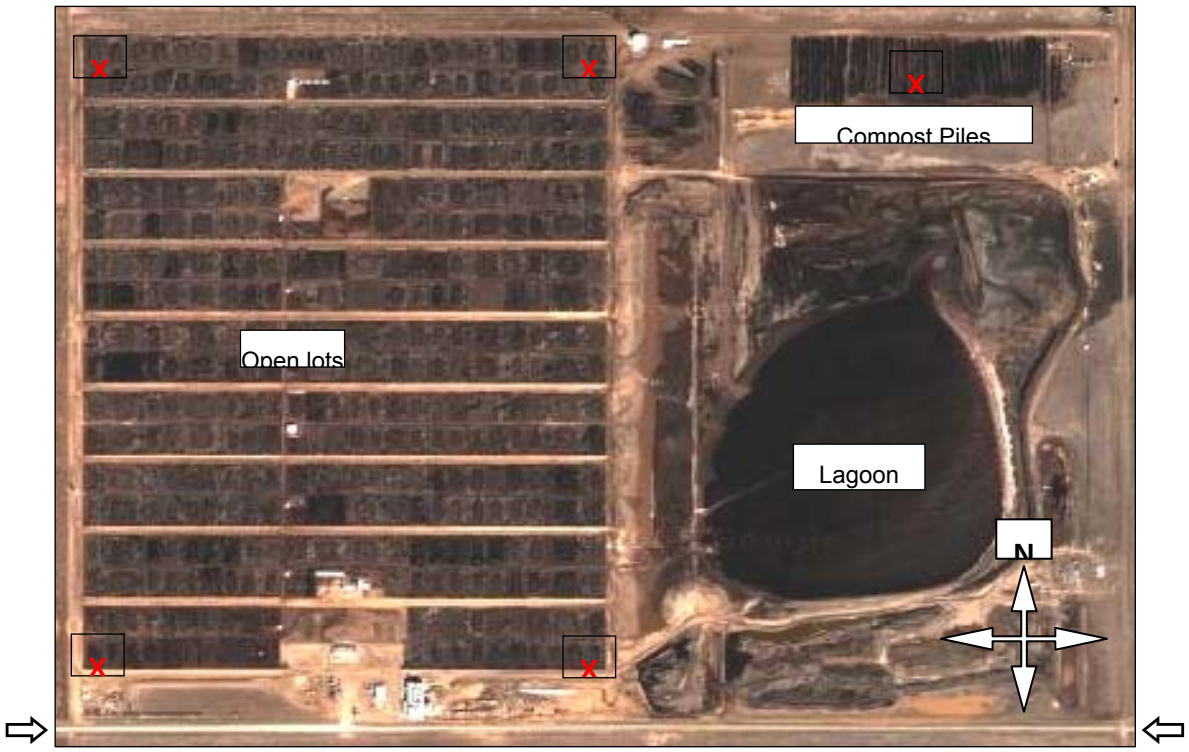

Figure 1. An aerial photograph of the beef cattle feedlot located at the Texas Panhandle. The sampling sites are marked with an “X.” (Photo from Google Maps)

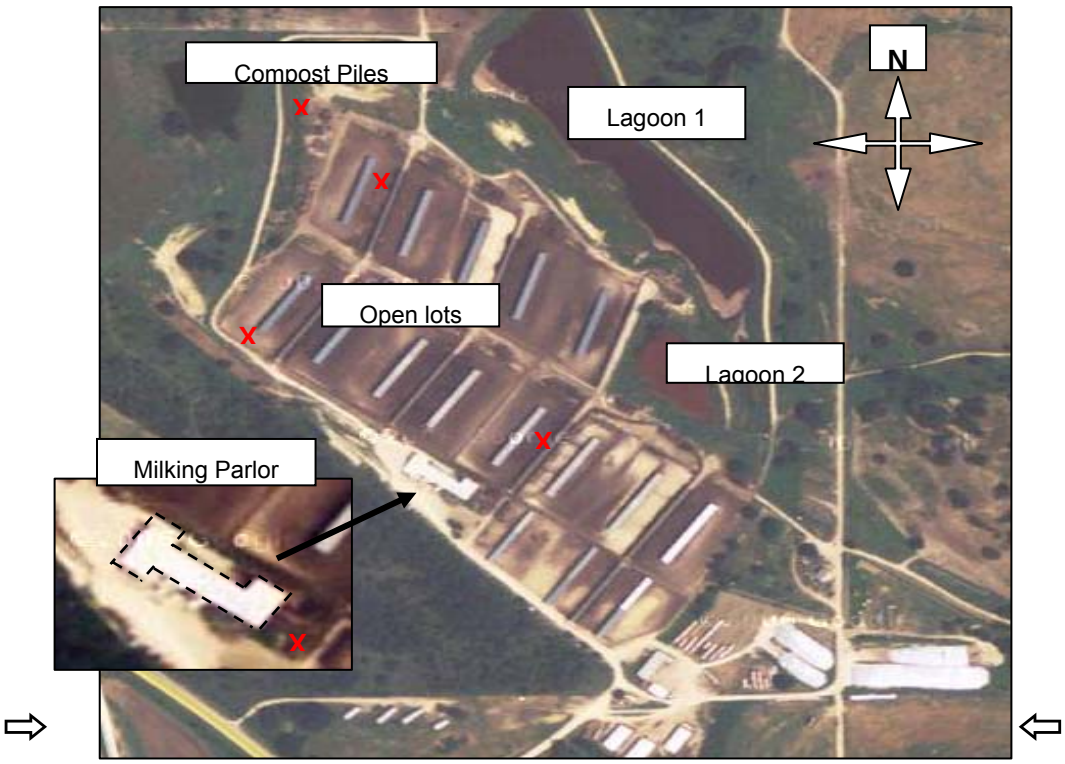

Figure 2. An aerial photograph of the dairy feedlot located in Central Texas. The sampling sites are marked with an "X." (Photo from Google Maps)

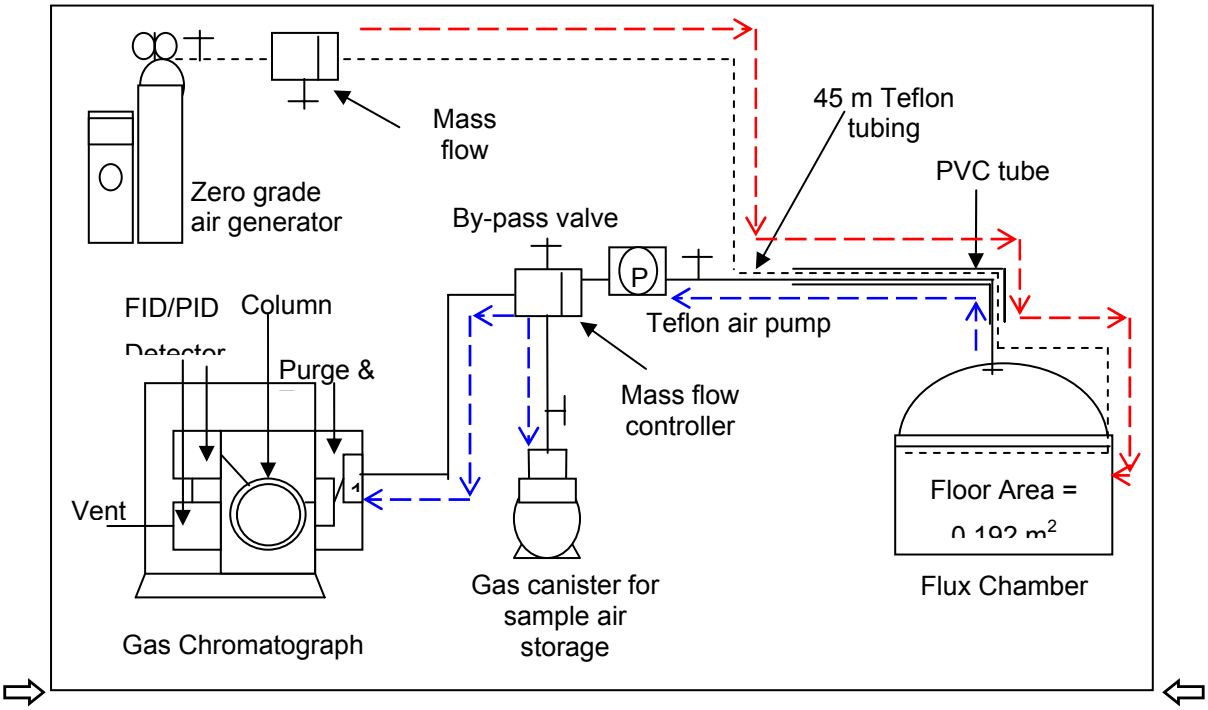

Figure 3. The schematic setup for VOC/ROG field measurements.

The upper (hemispherical dome) portion of the flux chamber used in the field was made of Plexiglas or polymethyl methacrylate (PMMA), while the bottom (cylindrical skirt) part was made of stainless steel as shown in Fig 4. The two portions were flanged together by 6.35 mm (1/4 in.) steel bolts. The total floor area or footprint area of the flux chamber is 0.192 m^2. Two conveying Teflon tubes, about 45 m long by 0.635 cm (i.d.) each, were connected to the flux chamber (one on the very top and one on the side) while four small holes were spaced evenly on the Plexiglas top. The Teflon tubes were inserted in a hard black PVC tube (2.54 cm i.d.) for external protection from the sun and the cattle. The Teflon tubing connected on the side of the flux chamber provided the zero grade air flow at 5 L min^{-1}. The compressed zero grade air used in the sampling was purchased from Praxair (Part No. AI 0.0Z). The compressed air has O_2 content between 19.5 % and 23.5 % while the total hydrocarbons (THC) were less than 0.5 ppm. The Teflon tube connected at the very top portion of the chamber was used to convey air samples from the flux chamber to the GC. A small pump coupled with mass flow controller was used to draw air at a volumetric flow of 2 L min^{-1}. Of the 2 L min^{-1} of air drawn from the flux chamber, about 100 mL min^{-1} was being directed to the purge and trap system of the GC for about ten (10) minutes, thus having a total sample volume of one liter fed into the traps.

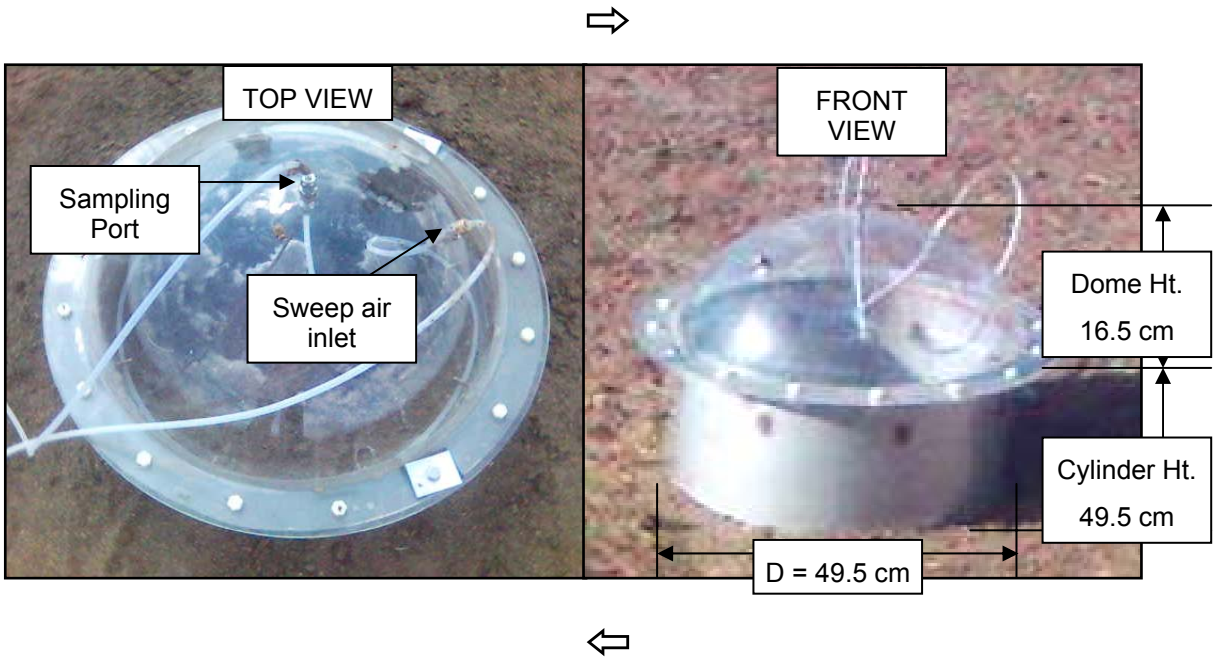

Figure 4. Details of the flux chamber used for air sampling.

There were two traps installed in the system that both satisfy the EPA TO-14 purge and trap pre-concentration requirements. The first trap was the Tenax™-GR trap which is sensitive to most other hydrocarbons while the second trap was a Carbosieve™ trap which is sensitive to highly volatile compounds. The collected ROGs were heated on the traps and were automatically injected into the GC column. The GC used was a portable type manufactured by SRI Instruments (Model No. 8610C) and is capable of temperature programming. The GC was equipped with two non-specific detectors - a “photo ionization detector (PID) which responds to

all molecules whose potential is below 10.6 eV, including aromatics and molecules with carbon double bonds" (SRI Instruments) and a flame ionization detector (FID) which is a mass sensitive hydrocarbon detector, a nearly universal response to organic compounds (vapors containing CH groups), with typical sample detection limits corresponding to 10^{-14} g carbon-s^{-1} with a linear response range of 10^6 to 10^7 orders of magnitude (Karger et al., 1973). The GC column used was a non-polar, 100 % dimethyl polysiloxane phase, stainless steel treated capillary column (MXT®-1), 60 m long, 0.53 mm (i.d.) and 5.0 µm film diameter (d.f.). The carrier gas used was He flowing at 100 mL min^{-1}. The compound peaks were recorded and analyzed through a computer installed with PeakSimple Chromatography Data System Software (Ver. 3.29). Blank samples were ran before starting the actual air sampling at each location to make sure that the column was clean and functioning well.

While performing the suggested new protocol for ROG determination, air samples were also collected from the selected sampling locations and were stored in gas canisters. The gas canisters were sent to an analytical laboratory (Micro-Analytics Laboratory at Round Rock, Texas). This procedure was done to make quantitative comparisons of the ROG emissions determined while performing the suggested protocol with the results found in the analytical laboratory which follows the EPA Method TO-14A procedures.

C. Analytical Procedures

A known volume of air sample from the dairy and beef feedyards was conveyed into the GC's purge and trap system through the Teflon tubes. A summary of the processes involved in the purge and trap system is shown in Table 1. After collecting enough air samples from the field (10 min) and concentrating the volatile compounds in the trap, both the traps (Tenax™ GR and Carbosive™) were heated to 200 ^{0}C. The heated samples were automatically injected into the GC column after trapping and the components were detected by the FID and PID with temperatures set at 100 ^{0}C and 150 ^{0}C, respectively. The GC column temperature program used was the following: initial temperature of 40 ^{0}C held for 12 min and was increased to 200 ^{0}C at 10 ^{0}C min^{-1}, and was maintained at 200 ^{0}C for another 15 min.

D. Characterization and Quantification of ROGs

The chromatograph peaks were tentatively identified based on existing literatures for dairies (Rabaud et al., 2002, Capareda et al., 2005) as shown in Table 2. The identification was done by initially matching the retention times of the known compounds with the unidentified peaks from the sample chromatographs. The analyses were confirmed by selecting a specific compound of interest from the previously identified list of compounds and injecting a volume of a known standard into the GC following the same procedures done in the field. Acetic acid was chosen from the list of initially identified compounds from the samples. Acetic acid with ≥99.7 % (GC/T) purity from Sigma-Aldrich were prepared at increasing concentrations of 500, 1000, 3000, and 5000 ppm (parts per million) and were injected in the GC to determine their corresponding peak areas. The plot of the peak area against concentration of acetic acid was used to interpolate the total concentration of acetic acid in the field samples.

The gas chromatographic results from the analytical lab were also used to confirm the compounds in the air samples that were tentatively identified based on literatures. Other compounds that were left unidentified were just labeled as unknown. The identified compounds were grouped together according to their classifications (aldehydes, ketones, alcohols, volatile fatty acids, aromatics and others) and the total percentage for each group was calculated.

E. Emission factor computation

The emission factor for the selected compound (acetic acid) on each specific location was computed based on the determined mass concentration of the compound from the air samples. Afterwards, the average emission factors of acetic acid were computed for the whole open lot and compost piles of the dairy and beef feedyard. Equation (1) was used in converting the concentration of acetic acid from parts per million (ppm) to mass concentration (in μg m^{-3}) while assuming standard conditions (25 ^{0}C, 1 atm). Equation (2) provided means in calculating the gas emission flux in μg m^{-2} min^{-1} while Eq. (3) gave an output of the gas emission rate in kilogram of compound emitted per head of cattle in a year and the emission factor in kilogram for a thousand head cattle per year. After computing all the emission factors from the selected sites, a comparison in terms of the quantity of compound emitted in a year were done for the dairy and beef feedlot.

Table 1. Summary of the processes involved in the purge and trap system.

Event	*Event Function*	*Time (s)*
D "ON"	Pump/Shaker "ON"	0.1
D "OFF"	Pump/Shaker "OFF"	10.0
C "ON"	Trap 2 heat "ON"	11.0
F "ON"	Trap 1 heat "ON"	11.1
G "ON"	Valve in "INJECT"	12.0
G "OFF"	Valve in "LOAD"	17.0
E "ON"	Purge gas "ON"	17.1
C "OFF"	Trap 2 "OFF"	30.0
F "OFF"	Trap 1 "OFF"	30.1
E "OFF"	Purge gas "OFF"	30.2

Table 2. Summary of standards used in the tentative identification and quantification of airborne compounds from a dairy feedyard[a] (Rabaud et al., 2002).

Name	CAS No.	MW (g/mol)	d	Mp (C)	Bp (C)	$V_{initial}$ (uL)	V_{final} (mL)	Conc (ppm)	Neat t_r (min)	Des. t_r (min)
Standard Solution 1: Acids in Methanol										
Formic acid	64-18-6	46.03	1.220	8.4	100.7	250	25	12.20	3.352	4.725
Acetic acid	64-19-7	60.05	1.049	16.6	117.9	250	25	10.49	4.010	5.218
Propionic acid	79-09-4	74.08	0.993	-20.8	141.0	250	25	9.93	4.990	5.954
Vinylacetic acid	625-38-7	86.09	1.009	-35.0	169.0	250	25	10.13	5.793	6.879
Valeric acid	109-52-4	102.13	0.939	-33.8	186.0	250	25	9.39	6.641	7.653
Standard Solution2: Organic Compounds in Methanol										
Acetaldehyde	75-07-0	44.05	0.788	-121.0	20.8	1000	50	15.76	5.798	6.606

Ethanol	64-17-5	46.07	0.789	-117.3	78.5	1000	50	15.78	3.235	3.415
Isobutyraldehyde	78-84-2	72.11	0.794	-65.0	64.2	1000	50	15.88	3.839	4.015
2-butanone	78-93-3	72.11	0.805	-86.3	79.6	1000	50	16.10	4.110	4.556
2-methyl-butane	78-78-4	72.15	0.620	-159.9	27.8	1000	50	12.40	3.346	3.675
Pentane	109-66-0	72.15	0.626	-130.0	36.1	1000	50	12.53	3.461	3.857
Pyridine	110-86-1	79.10	0.978	-42.0	115.5	250	50	4.89	5.523	6.322
2,3-butanedione	431-03-8	86.09	0.981	-2.4	88.0	1000	50	19.62	4.038	4.407
Ethyl acetate	141-78-6	88.11	0.902	-83.6	77.1	250	50	4.51	4.239	5.000
1-nitropropane	108-03-2	89.09	0.993	-108.0	131.0	250	50	4.97	5.472	6.190
Cycloheptatriene	544-25-2	92.14	0.888	-79.5	117.0	250	50	4.44	6.014	6.895
Methylisobutyrate	547-63-7	102.13	0.891	-86.0	91.8	250	50	4.46	4.909	5.989
3-hexanol	623-37-0	102.18	0.819	NA	134.5	250	50	4.10	5.965	6.819
Benzaldehyde	100-52-7	106.12	1.050	-26.0	178.0	250	50	5.25	7.412	8.605
o-xylene	95-47-6	106.17	0.870	-25.2	144.4	250	50	4.35	6.871	7.936
Benzyl alcohol	100-51-6	108.14	1.045	-15.3	205.3	250	50	5.23	7.863	9.201
Acetophenone	98-86-2	120.15	1.033	20.5	202.6	250	50	5.17	8.131	9.509
trichloroethane	71-55-6	133.40	1.339	-30.4	74.1	250	50	6.69	4.611	5.222
Carbon tetrachloride	56-23-5	153.82	1.594	-23.0	76.8	250	50	7.97	4.780	5.448

[a]Retention times have been included for both the neat compounds injected by flash injection (neat t_r) and the compounds thermally desorbed and cryotrapped prior to separation (des t_r).

CAS No. = Chemical Abstracts Service No., MW = molecular weight, d = molar diameter, Mp = melting point,

Bp = boiling point, V (initial/final) = initial and final injection volumes

Equation (1):

$$C_{ppm} = \frac{(volume \cdot of \cdot polluta\eta t \cdot gas)}{(total \cdot vol \cdot of \cdot gas \cdot mixture)} \times 10^6$$

$$C_{mass} = \frac{1000 \times (C_{ppm}) \times MW_p}{24.45}$$

Equation (2):

$$EFl_{acetic} = \frac{C_{mass} \times V_{fc}}{A_{fc}}$$

Equation (3):

$$ER_{acetic} = \frac{EFl_{acetic} \times 1000kg \times 1440 \frac{\min}{day} \times A_{pen}}{\#of \cdot hds} \times 365 \frac{days}{yr}$$

$$EF_{acetic} = ER_{acetic} \times \frac{1000hds}{1000hds}$$

where,

C_{ppm} = concentration of compound (ppm)

C_{mass} = concentration of compound per mass basis (μg m^{-3})

MW_p = molecular weight of compound at STP

EFl_{acetic} = gas emission flux of acetic acid (μg m^{-2} min^{-1})

V_{fc} = total volume of air supplied inside the flux chamber (m^3 min^{-1})

A_{fc} = foot print area of flux chamber (m^2)

ER_{acetic} = emission rate of acetic acid (kg hd^{-1} yr^{-1})

A_{pen} = area of pen (m^2)

EF_{acetic} = emission factor of acetic acid (kg 1000-hd^{-1} yr^{-1})

Results and Discussion

A. Preliminary Compound Identification

The new method suggested by Capareda et al. (2005) for determining ROG emissions from AFO was successfully performed in this research. The ROG samplings were done separately in the open lots of dairy and beef cattle feedyards. The air samples drawn from the standard EPA flux chamber were directly analyzed in the field using a portable gas chromatograph that was attached to a computer. The combination of Tenax GR and Carbosive traps were able to capture different types of compounds during the sampling period. Carbosive traps (Carbotraps), having specific affinity to compounds, sorbed highly volatile compounds of low molecular weights while the Tenax GR trap captured larger compounds with intermediate volatility (Rabaud et al., 2003).

The carbohydrate oxidation and fermentation during and after digestion in cows could have contributed a lot to the diversity of the compounds observed in this study (Rabaud et al., 2003). Fourteen (14) of the volatile organic compounds were tentatively identified and quantified base on their average estimated percentage from the injected sample volume in the GC (Table 3). These compound identifications were based on the retention time (the time when a certain peak elutes on the chromatogram) of the different volatile organic compounds reported in the literatures (Rabaud et al., 2002; Capareda et al., 2005). The tentatively identified compounds were also sorted into their respective compound groups (i.e. ketones, aldehydes, volatile fatty acids, alcohols, phenol, benzothizole and p-cresol). The fractions of each individual compound group are summarized in Table 4.

Based on preliminary analyses, the fractional amount of the identified reactive organic compound groups from the dairy open feedyard showed slightly higher values than in the beef feedlot. These include ketones, aldehydes, benzothiazole and p-cresol groups which have almost twice the fractional amounts for the dairy. The fraction of alcohols found in the dairy was also relatively high (ca. 4 % - v/v) while the alcohols found in the beef feedlot had very low concentration to an almost undetectable level. The high amounts of alcohols in the dairy feedyard could have been contributed mainly by the presence of lactating cows in the pens

(Filipy et al., 2006). On the other hand, only the volatile fatty acids group in the beef feedlot had slightly higher percentage (ca. 2 % more) compared to the dairy feedyard.

The volatile fatty acids (VFAs) group tends to dominate the ROG emissions on both open feedlots. The high percentages of VFAs from both sources (dairy and beef cattle) could be attributed to the presence of fresh cow manure and urine scattered inside the pen. These volatile organic compounds were directly associated with cattle wastes and their relative amounts depend greatly on the ambient temperature (Filipy et al., 2006). The floors of the pen were all made of earthen materials and the cow manures were just scraped-off occasionally when the cattle wastes accumulate on the floor surface. Volatile fatty acids have relatively low boiling points which could lead to having good chromatographic separation in the GC (Brotz and Schaefer, 1987). According to Rabaud et al. (2003), VFAs were also the ones that exhibited the greatest odor intensity for dairy cattle which could also indicate that the compounds have high concentrations.

Results from the analytical laboratory (Microanalytics Lab) measurement that follows EPA method TO-14A will be reported once the laboratory sends back the complete analysis of the ROG compounds found in the sampling sites. From then, a verification and comparison in terms of the variety and amount of compounds found with the application of the new protocol against the standard EPA method TO-14A will be performed.

B. Emission Factor Determination: Acetic Acid

Among the most commonly occurring reactive organic compounds found in the air samples, acetic acid (CH_3COOH) was chosen due to its abundance and presence on both sampling locations (dairy and beef feedlot). The relatively large amounts of acetic acid compounds in dairy and beef cattle feedlots were also reported in other literatures (Shaw et al., 2005; Rabaud et al., 2003).

The concentration of acetic acid in the air samples was estimated by the ratio of the (chromatographic) peak area of the standard acetic acid with a known concentration to the peak area of the sample. The molecular mass and density of acetic acid used in the calculations were 60.05 g mol^{-1} and 1.049 g ml^{-1}, respectively, and the atmospheric conditions were assumed to be at standard (25 ^{0}C and 101.325 kPa). The concentrations of acetic acid in parts per million by volume in air (ppmv) at a specific location were listed and summarized in Tables 5 and 6 (second and third columns) for beef cattle feedlot and dairy feedyard, respectively.

The average concentrations of acetic acid in the beef cattle feedlot were significantly higher in the east (right) side (i.e. northeast and southeast corners) than in the west (left) side. This observation could have been influenced by the prevailing wind directions (eastward) and the warm and dry weather conditions at the Texas Panhandle during the time of sampling as reported by the National Weather Service (NWS), NOAA in May 2006. Furthermore, the cattle were moved out of the southwest corner pen during the air sampling which might significantly affected the number of ROG that were detected as well as the measurements of their (ROG) relative amounts. Meanwhile, the remaining sampling pens contained the cattle while performing the air sampling and measurement.

The measured average concentrations of acetic acid in the dairy feedyard were much higher than those from the beef cattle feedyard. The pen located at the southeast (close to the center) part of the openlot registered the highest concentration of all the measured samples. The surface soil characteristics on the site (wet and muddy) coupled with the warm weather condition for June 2006 (NWS, 2006) at Central Texas could have affected the amount of acetic acid observed through the GC. In addition, the presence of large amounts of cattle wastes scattered all over the sampling site could have also contributed to the large emission of acetic

acid and other volatile compounds. Nonetheless, the high average wind speed (ca. 7 m s^{-1}) for both locations during the sampling period might also have limited the detection of the other more volatile ROG in the sites.

The emission factors of acetic acid for both sampling locations were calculated based on the equations provided earlier in the methodology (Table 5 and 6). The concentration (ppmv) of acetic acid was first converted to mass concentration (in μg m^{-3}). The footprint area of the EPA standard flux chamber (0.192 m^2) and the volumetric flowrate of zero-grade air (5 L min^{-1}) through the chamber were used to calculate the emission flux of acetic acid. The emission flux indicates the amount of compound being released in a certain area at a given time. The area of the sampling pen and the total number of cattle head inside the pen were the parameters used for estimating the compound's emission rate. The emission factors were computed per thousand head of cattle for both sites and are shown in Figures 5 and 6.

Results show that the emission factors of acetic acid from the dairy feedyard had higher magnitudes than those found in the beef feedlot. The average emission factor of the dairy cattle (ca. 775 kg 1000-hd^{-1} yr^{-1}) was more than four times the average emission factor of the beef cattle (ca. 186 kg 1000-hd^{-1} yr^{-1}). One of the main reasons could be that the difference in the feedlot's location (Texas Panhandle and Central Texas) and time period (May and June, 2006) had affected the characteristics of ROG in each sampling site. Another reason could be that dairy cows potentially emit higher amounts of acetic acid from their milk and wastes (Filipy et al., 2006). Even if there were also scattered cattle waste in the beef feedlot, the loose and extremely dry soil combined with the warm weather and high winds could have evaporated a large part of the acetic acid from the soil surface, thus the detected amounts of acetic acid were smaller than in the dairy. Based on the literatures (Koziel et al., 2004; McGinn et al., 2003; Rabaud et al., 2003), the relative fraction of acetic acid ranges from 37 % to 67 % of the total volatile fatty acids emission for cattle while the emission factor for VFAs was estimated to be about 0.24 to 0.65 kg hd^{-1} yr^{-1}. In the present study, the emission factor of acetic acid alone ranged from 0.13 to 0.24 kg hd^{-1} yr^{-1} for the beef feedlot and from 0.32 to 1.46 kg hd^{-1} yr^{-1} for the dairy feedyard. The results suggest that acetic acid was abundant in the sites where the sampling runs were performed.

Table 3. Summary of ROG tentatively identified from the open feedlots of dairy and beef cattle feedyards. (The percentage composition of each compound from the whole sample is also provided).

Dairy feedlot			*Cattle feedlot*		
Peak No.	Compounds	% Present	Peak No.	Compounds	% Present
1	-	1.660	1	*Acetone*	1.592
2	*2-Butanone*	3.031	2	-	1.458
3	*3-Methyl butanol*	1.994	3	-	4.070
4	-	4.235	4	-	2.248
5	-	2.128	5	-	1.822
6	*1-Butanol*	2.132	6	-	1.471
7	*Hexanal*	1.034	7	*Hexanal*	1.776
8	-	1.352	8	-	2.102

9	-	1.799	9	-	1.685
10	*Acetic acid*	1.086	10	-	2.365
11	-	2.471	11	*Acetic acid*	1.001
12	*Propanoic acid*	1.148	12	-	1.227
13	-	2.983	13	-	8.138
14	*Butanoic acid*	2.257	14	*Dimethyl trisulfide*	2.135
15	-	2.373	15	-	1.882
16	-	2.573	16	*Propanoic acid*	1.808
17	-	6.890	17	*Isobutyric acid*	2.729
18	-	2.557	18	*Butanoic acid*	4.035
19	-	3.200	19	-	2.811
20	*2-Ethylhexanoic acid*	4.389	20	-	1.308
21	-	1.211	21	-	3.096
22	*Phenol*	2.144	22	*2-Ethylhexanoic acid*	1.511
23	*Benzothiazole*	2.063	23	*Phenol*	1.984
24	*p-cresol*	1.466	24	-	3.709
25	-	1.483	25	*Benzothiazole*	1.244

- (Unknown compound)

Table 4. Relative amounts of specific compound groups from the whole sample.

Dairy feedlot		*Cattle feedlot*	
Compound Groups	% from whole sample	Compound Groups	% from whole sample
Ketones	3.514	*Ketones*	1.592
Aldehydes	3.640	*Aldehydes*	1.776
Alcohols	4.127	*Alcohols*	0.0
VFA	9.109	*VFA*	11.084
Phenol	2.144	*Phenol*	1.984
Benzothiazole	2.063	*Benzothiazole*	1.244
p-cresol	1.466	*p-cresol*	0.868

Table 5. Concentrations of acetic acid in all sampling locations at the beef cattle openlot.

Sampling	*Ave. Con'c*		*Efl*	*ER*	*EF*	*EF*
Location	ppm	(µg/m³)	(µg/m²/min)	(kg/hd/yr)	(kg/1000hd/yr)	(lb/1000hd/yr)
SW	0.4150	1019.33	26.54	**0.1395**	**139.52**	**840.95**
NW	0.4590	1127.28	29.36	**0.1543**	**154.30**	**930.01**
NE	0.7184	1764.45	45.95	**0.2415**	**241.51**	**1455.67**
SE	0.6281	1542.52	40.17	**0.2111**	**211.13**	**1272.58**
Average	0.56	1363.39	35.51	0.19	186.61	1124.80

Table 6. Concentrations of acetic acid in all sampling locations at the dairy openlot.

Sampling	*Ave. Con'c*		*Efl*	*ER*	*EF*	*EF*
Location	ppm	(µg/m³)	(µg/m²/min)	(kg/hd/yr)	(kg/1000hd/yr)	(lb/1000hd/yr)
SE	1.1581	2844.44	74.074	**1.460**	**1460.00**	**3212.001**
W	0.4279	1051.01	27.370	**0.539**	**539.46**	**1186.823**
NW	0.2599	638.31	16.623	**0.328**	**327.63**	**720.794**
-	-	-	-	**-**	**-**	**-**
Average	0.62	1511.26	39.36	0.78	775.70	1706.54

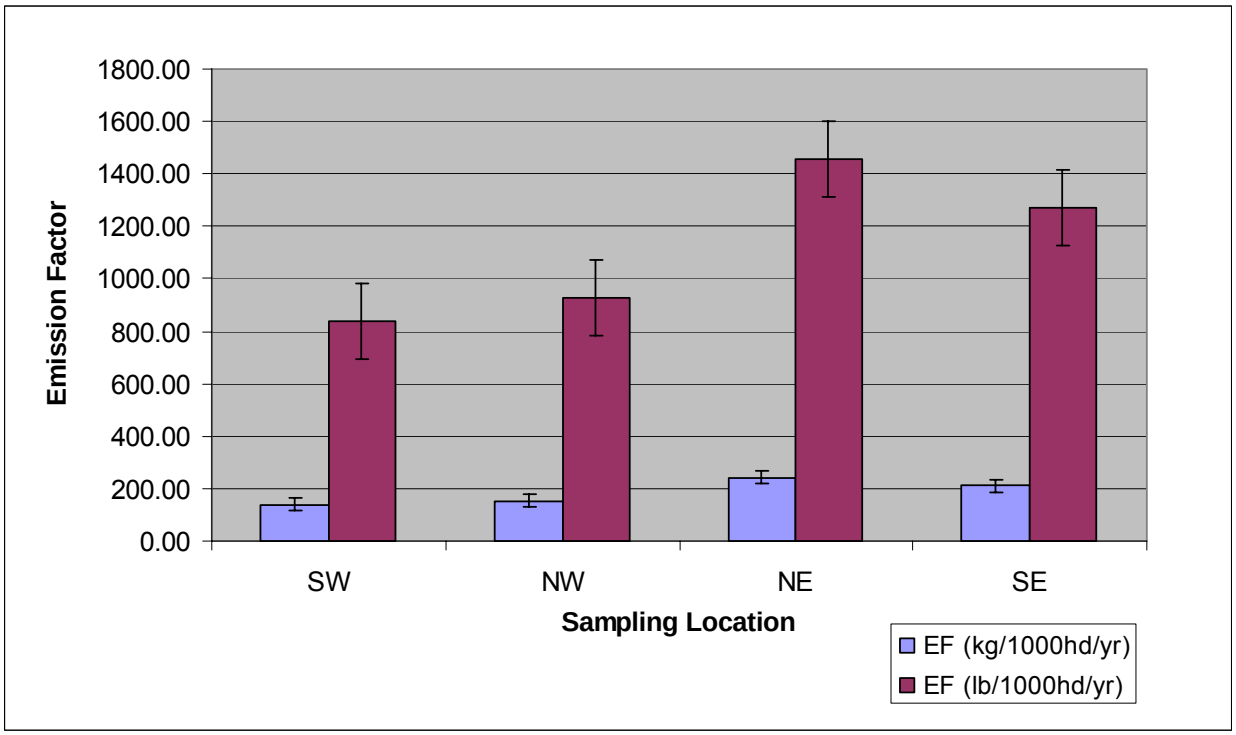

Figure 5. Emission factors of acetic acid from the different locations in the beef cattle openlot.

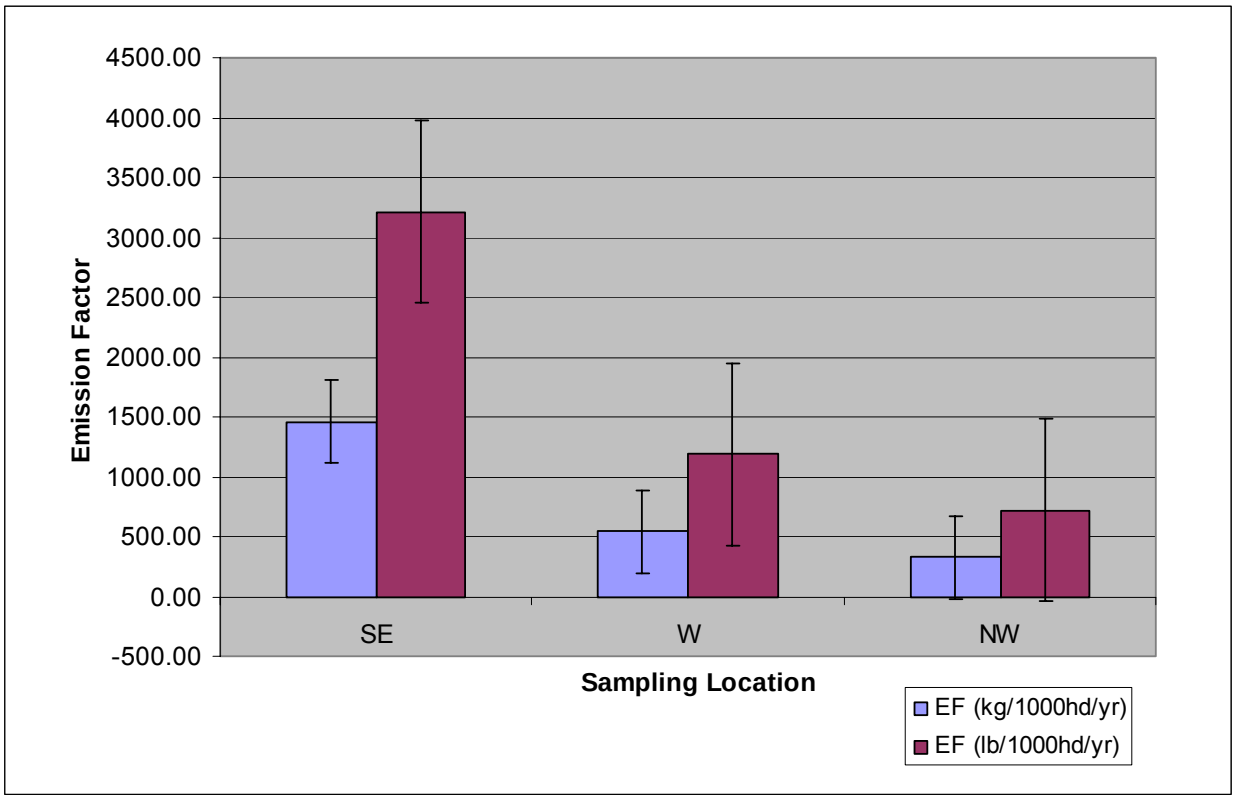

Figure 6. Emission factors of acetic acid from the different locations in the dairy openlot.

Conclusion

The research study was able to produce results by performing the new protocol for determining ROG emissions as suggested by Capareda et al. (2005). It should be noted that the data presented in this paper are just preliminary and the research are still on-going. Fourteen (14) of the reactive organic gases detected by the GC were tentatively identified and quantified base on their relative percentages in the whole injected sample volume. However, many other compounds in the chromatogram remained unidentified. The identified compounds were also sorted according to their respective compound groups. The results of the measurements from the analytical laboratory which follows the EPA method TO-14A are still expected for verification of the compounds and for quantitative comparison.

It was observed that the values of the relative percentages of ROG in the dairy feedyard have higher magnitudes than in the beef cattle feedlot. In addition, there was no alcohol compound found in the beef feedlot. One possible reason could be that the conditions of the site during sampling (very warm and dry) affected the amount of ROG emission in the air. On the other hand, the volatile fatty acid (VFA) group dominated the ROG found on both the sampling locations. According to the literatures (Rabaud, et al. 2003; Filipy et al., 2006), a large amount of

VFAs are sourced from the cattle wastes which were abundant on both locations during the sampling runs. Acetic acid is one of the volatile organic acids found on both sampling locations.

The emission factors of acetic acid from the dairy feedyard and beef cattle feedlot were determined in weight per 1000 head of cattle per year. The emission factor of acetic acid (ca. 775 kg 1000-hd^{-1} yr^{-1}) in the dairy feedyard was determined to be more than four times the emission factor in the beef cattle feedlot (ca. 186 kg 1000-hd^{-1} yr^{-1}). It was also observed that the values of emission factor for acetic acid found in this study could be higher than the reported values of emission factor for the whole VFA in some other literatures.

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