CHARACTERIZATION OF BIOGENIC NON-METHANE VOLATILE ORGANIC COMPOUNDS FROM CONFINED ANIMAL FEEDING OPERATIONS

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Samples were collected and analyzed in a field study to characterize C2-C12 volatile organic compounds (VOCs) emitted at six swine facilities in Eastern North Carolina between April 2002 and March 2003. Two sites employed conventional lagoon and field spray technologies, while four sites utilized various alternative waste treatment technologies in an effort to substantially reduce gaseous compound emissions, odor, and pathogens from these swine facilities. More than 100 compounds, including various alcohols, aldehydes, ketones, phenols, and sulfides, were positively identified and quantified by Gas Chromatographic/Flame Ionization Detection (GC/FID) analysis and confirmed by Gas Chromatographic/Mass Spectrometry (GC/MS). GC/MS analysis of one particularly complex sample collected assisted in providing identification and retention times for 17 sulfur type VOCs including dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide as well as many other VOCs. Carbonyl sulfide and carbon disulfide were positively identified by GC/MS analysis but were not identified by GC/FID due to their particular compound characteristics. Highest VOC concentration levels measured at each of the facilities were near the hog barn ventilation fans. Total measured VOCs at the hog barns were typically dominated by oxygenated hydrocarbons, i.e., ethanol, methanol, acetaldehyde, and acetone. Dimethyl sulfide and dimethyl disulfide, recognized as malodorous compounds, were determined to have higher concentration levels at the barns than the background at every farm sampled. Hazardous air pollutants acetaldehyde and MEK were measured at levels higher than their respective U.S. ambient background concentrations in many instances. Acetaldehyde was measured at levels above its reference concentration in many of the samples.

INTRODUCTION

Swine production increased dramatically in North Carolina between 1987 and 1997, making the state the second largest producer of hogs in the United States, with a population of ~10 million animals [1]. In recent years, contract arrangements for production have aided the expansion of hog operations by providing the capital necessary for swine operations to adopt new technologies and achieve major growth [2]. More hogs are confined to smaller areas, thereby increasing amounts of odorous and potentially harmful compounds due to a higher amount of excretion.

In response to environmental concern, the North Carolina Attorney General determined that the development of "Environmentally Superior Technologies" (ESTs) would serve well the public interest of North Carolina, with the objective of reducing potentially hazardous emissions from these swine facility sites[3]. Project OPEN (Odors, Pathogens, and Emissions of Nitrogen) was established in December 2000 in an effort to evaluate various alternative waste treatment technologies (i.e., ESTs).

Emissions of compounds such as methane and ammonia from swine facilities have been well documented [4,5,6,7,8]. This study focuses exclusively on the characterization of C_2-C_{12} volatile organic compounds (VOCs) present in the ambient air at various swine facilities located in the eastern region of North Carolina and may be regarded as a survey to determine various gaseous compounds. Some of these compounds are associated with unpleasant odors in this type of rural environment. VOC sample collection strategy was designed to assess VOCs from suspected emission sources at the various potential ESTs and conventional swine farm locations. Samples were collected at the housing areas as well as the technologies (i.e., storage lagoons) at all sites.

VOCs have been reported from several swine farms in Eastern North Carolina to investigate odor complaints [9]. The compounds detected in this study include various paraffins, olefins, aromatics, ethers, alcohols, aldehydes, ketones, halogenated hydrocarbons, phenols, and sulfides. Sulfides and phenols have long been associated with odor problems at swine facilities [10,11]. Results presented consist of the high C_2-C_{12} VOCs levels observed from the ventilation fans at the hog confinement barns. Concurrently collected samples of background air are included to more clearly determine the VOCs resulting from hog barn activities.

METHOD

Experimental Research Site Descriptions

Samples were collected at five different farms and one laboratory site located in Eastern North Carolina. Four sites utilized various ESTs to treat animal waste while two sites maintained a conventional waste treatment technology. With the exception of one site, ReCip, each farm was sampled during two different seasons. Each site and related waste treatment technology is briefly described below:

Barham Farm is a 4,000 head farrow to wean operation located near Zebulon, North Carolina (35.70°N, 78.32°W, 130m MSL). Each hog barn contained a fan ventilation system, sometimes referred to as tunnel ventilated. This site utilized a covered in-ground ambient digester as a potential alternative waste treatment system. The in-ground ambient digester may be considered as a primary treatment lagoon (4,459 m^2) that had an impermeable polypropylene covering over its surface. All the emitted gases including methane and other organic gases were collected under the cover and periodically extracted and delivered to a generator system where the gases were converted to electricity. The effluents from the hog barns were initially directed to the primary lagoon with the impermeable cover and the effluent then flowed through a single outlet pipe into a secondary storage lagoon (19,398 m^2). Here, the liquid waste was treated via a de-nitrification/biofiltration process. The treated wastewater was then used for two purposes: to flush fresh effluent from the hog barns and as a spray over agricultural crops for nutrient enrichment purposes [12].

Grinnells Laboratories is located on the North Carolina State University campus in Raleigh, NC (35.47°N, 78.40°W, 107 m MSL). It should be taken into account that this site was located in a non-rural area. This site utilized a Ganet-Fleming Belt System that consisted of the retrofit installation of a conveyor belt type apparatus in the swine production facility to convey the manure wastes generated therein. The process separated the liquid wastes and the solid wastes as they were deposited inside the production facility. The solids were then managed through a gasification process, which involves the burning of a substance in a low-oxygen environment to convert complex organic compounds to gases. The gases were collected and used to make fuel-grade ethanol. The liquids received further treatment via a sequencing batch reactor. There is no storage lagoon located at this site [13].

Howard Farm, located near Richlands, NC (34.84°N, 77.50°W, 5 m MSL), utilized a "Solids separation/Constructed Wetlands" system as its potential waste treatment system. Effluents from the hog barns were directed initially to a solid separator where the solid waste was separated from the liquid waste. The solids were then removed to an off-site facility and liquid waste was put into two outer lagoon cells (outer cell 19,366 m^2; inner cell 10,256.3 m^2). As the wastewater traveled around the cells, it encountered the constructed wetlands, which treated the wastewater effluent through microbial utilization and the root substrate of the wetland plant species. The treated wastewater was then filtered into a finishing lagoon (7,428 m^2) where it was used in a manner similar to Barham Farm, i.e., the wastewater was recycled to flush more effluent through the hog barns and as a spray for agricultural crops. Containment houses located on the property utilized a fan ventilation system [14].

ReCip, located near Rose Hill, NC (34.84°N, 77.96°W, 30 m MSL), encompassed two cells, or treatment basins filled with media, that alternately drained and filled on a recurrent basis. The draining and filling cycles created aerobic, anaerobic, and anoxic conditions within the cells, providing both biotic and abiotic treatment processes to provide nitrification, denitrification, and phosphorous removal. This treatment process was prefaced by solids separation. One lagoon (2601.3 m^2) was used for containment of solids and another lagoon (2717.4 m^2) was utilized for treated wastewater. The hog barns on this site maintained an open-air natural ventilation system rather than fan outlets [15].

Stokes Farm and Moore Brothers Farm operate a conventional (i.e., lagoon and spray) technology as the primary means of handling effluent. This method of waste treatment is the same type that is currently used by most farms in North Carolina. Effluents flow from the hog barns into an on-site storage lagoon. This wastewater is then used to flush effluent from the houses and as spray over agricultural crops. Stokes Farm is located near Greenville, NC (35.43°N, 77.48°W, 17 m MSL). The storage lagoon is 15,170 m^2 and the hog barns utilize a natural ventilation system. Moore Brothers Farm is located in Jones County near Kinston, NC (35.14°N, 77.47°W, 13 m MSL). The storage lagoon is 30,630 m^2 and the confinement houses on site employ fan ventilation.

Sample Collection and Sampling Strategies

Ambient air samples were collected in 6-Liter electropolished stainless steel SUMMA canisters, evacuated to a sub-ambient pressure of <0.05 mm Hg. During sample collection, the valve on the canister was opened slowly over a timeframe of ~4 minutes and then fully opened on the order of 1 minute, thus allowing for a ~5 minute point sample to be collected.

Samples were collected during the 12:00-13:00 Eastern Standard Time (EST) period at various suspected source areas including lagoons, barn ventilation fans, and at "strong" odorous areas, determined through sense of smell, for each particular site. Simultaneous samples were collected at upwind and downwind locations on the farms in an effort to determine VOCs originating from the farm.

VOC Sample Analysis

The canister samples were taken to the National Exposure and Research Laboratory (NERL) of the US Environmental Protection Agency (EPA) located in the Research Triangle Park, NC, where they were analyzed using gas chromatographic (GC) procedures. All samples were analyzed by GC flame ionization detection (FID) combined with a cryogenic preconcentration approach. The GC column was a 60m x 0.32mm ID fused silica column with a 1μm liquid phase thickness (J & W Scientific, Folsom, CA). The GC column was temperature programmed and consisted of a -50°C initial temperature for two minutes followed by temperature programming to 200°C at a rate of 8°C/minute. After a 7.75 minute hold period, the column temperature is programmed to 225°C at 25°C/minute rate and held at that temperature for 8 minutes. This temperature programming sequence provided separation of the C_2-C_{12} compounds and conditioned the column for proceeding samples. Liquid nitrogen is used as the cryogen to obtain sub-ambient temperatures.

The GC/FID system was calibrated using 0.25 ppm propane in air NIST SRM (National Institute of Standards and Technology Standard Reference Material). Compound identification was determined using a CALTABLE consisting of more than 300 VOCs with corresponding column retention times.

A gas chromatograph equipped with a mass spectra detection system (GC/MS) (Hewlett-Packard Model 6890/5972, Avondale, CA) was used to verify compound peak identification. The GC/MS system served to both verify compound identification as well as to identify unknown compound peaks. Generally, 1-2 samples collected during each sampling campaign were selected for GC/MS analysis, based on the observed high peak concentration levels and/or the occurrence of unknown peaks.

RESULTS

Measurement campaigns for this study were conducted as the farms became steady-state with the individual technologies in place. Due to the nature of Project OPEN, the farms were available for sampling for about two week increments in each warm and cold season, resulting in some limitations of our sampling strategies. The data results presented here consist of one day sampling at each swine farm facility for both warm and cold seasons. Highest VOC concentrations were typically observed at the hog barn ventilation locations for all sites. These specific results provide the most suitable database to compare both composition and concentration differences between sites and for both seasons.

Identification of the VOCs with the GC Systems

Using a GC/FID approach, individual VOCs are identified by column retention time using a detailed CALTABLE containing known VOCs and their corresponding retention times prepared from the analysis of known VOC mixtures. At the outset of this study, the GC column retention times for many of the sulfur containing VOCs were unknown. A sample collected at the outlet of a pipe leading from the covered lagoon to the electric generator system at the Barham Farm during the April sampling period greatly assisted in the identification of many of these sulfur compounds. This pipe transported methane as well as other organic gases produced from a primary treatment lagoon fitted with an impermeable cover to a generator system that converted these gases to electricity. The GC/FID analysis results of this sample indicated a complex pattern of peaks, several of which were not in the existing CALTABLE. The sample served to demonstrate the complex VOC mixture produced by the treatment of hog waste that may be released to the ambient air.

Sulfides were of particular interest because many produce distinct malodors. Seventeen sulfur-type VOCs were identified, including thiophene, 2-methylthiophene, 3-methylthiophene, methyethyldisulfide, 2-ethylthiophene, 2,5-dimethylthiophene, 3-ethylthiophene, 2,3-dimethylthiophene, methylisopropyldisulfide, methylpropyldisulfide, methyl-sec-butyldisulfide, and dimethyl tetrasulfide and eventually added to the GC/FID CALTABLE to use for the other canister samples collected at the swine farm sites. The three largest peaks observed from the GC/FID at column retention times later than isobutane were dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide. These compounds represented 21.1, 17.7, and 24.4%, respectively, of the total concentration of all the GC compound peaks eluting from the column between isobutane and the last observed GC compound peak. Two other sulfur-containing VOCs also observed in the GC/MS results included carbonyl sulfideand carbon disulfide. Neither compound is expected to respond in the FID. Other VOCs identified in the sample by GC/MS included alkanes, alkenes, ketones, and aldehydes.

VOCs Observed at Hog Barns

Highest VOC concentrations generally observed at each of the six swine facilities were sampled at the barn ventilation locations. With the exception of Stokes, this location was directly in front of the fan ventilation systems. At the Stokes site, natural open-air barn ventilations are utilized rather than ventilation fans and samples collected next to or between the barns were selected for comparison. To better evaluate the VOCs coming from the barns, corresponding background (i.e., upwind) samples were simultaneously collected when the barn ventilation fans were sampled. Measurements from the ReCip site were not included in this analysis because no concurrent background sample was collected.

It is expected that the observed VOC composition at the ventilation outputs consists of background ambient air combined with VOC sources within the barn facility. Ideally, activities within the hog barns at each of the different site locations are expected to be uniform; however, it should be noted that the number of animals as well as the animal weights, size, and type (i.e., farrowing or finish) vary from barn to barn as well as farm to farm and could affect observed VOCs measured.

Figure 1 depicts the percent contribution of the various characteristic types of identified VOCs observed at the hog barns. Percentage values were determined by summing the individual VOCs into the various compound types and ratioing these groups to total identified VOC. Oxygenated VOCs appear to be the most abundant compounds

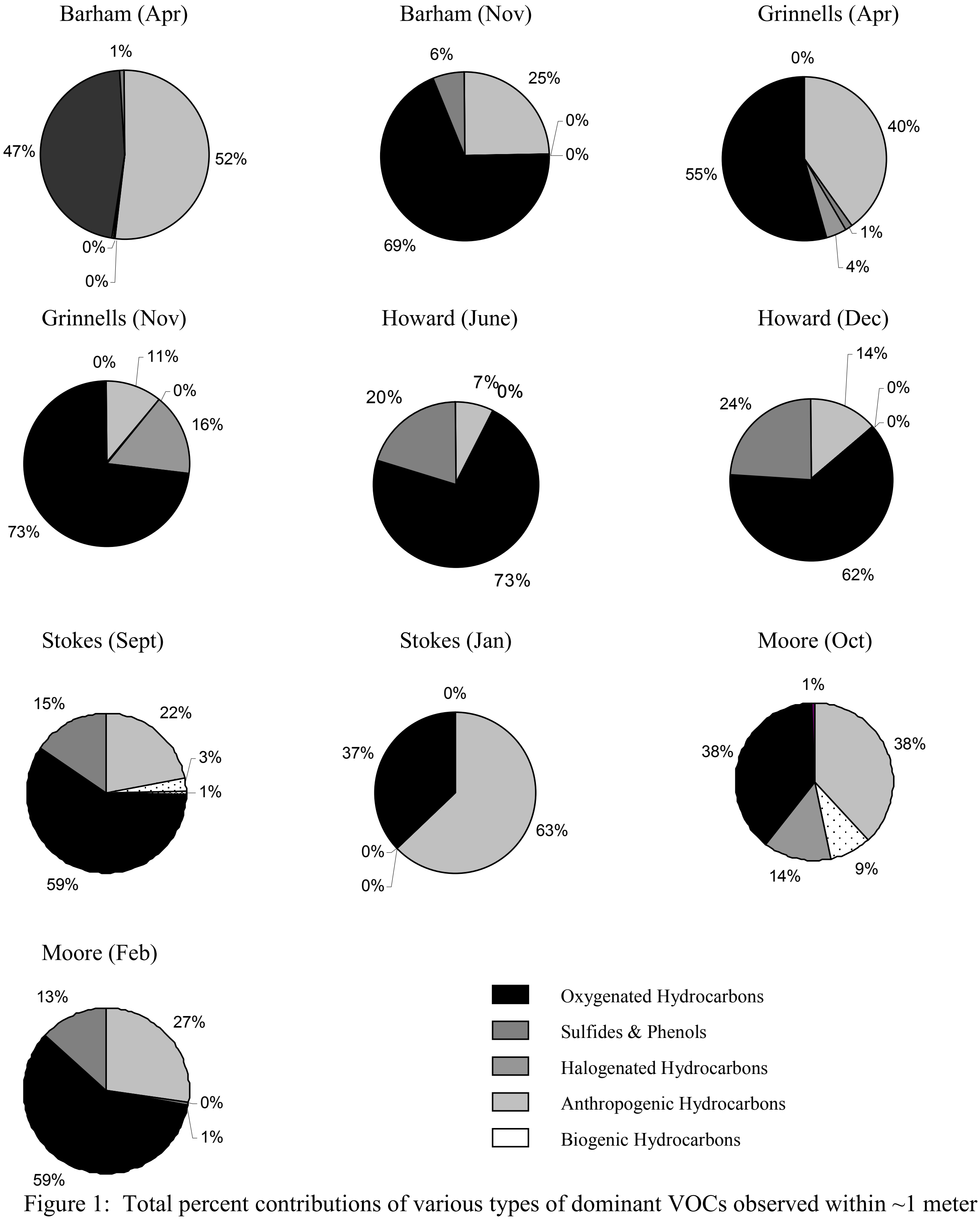

Figure 1: Total percent contributions of various types of dominant VOCs observed within ~1 meter of hog barn ventilation systems at each of the sampling sites. Sampling for each site was conducted during one warm and one cold season

observed near the barns. Similarities are observed in terms of specie composition near the various barns at the different sites; however, concentration levels tended to vary quite a bit, although all were within the same order of magnitude. Acetaldehyde, methanol, ethanol, and acetone were among the most dominant compounds measured near the barns. These four compounds, in addition to other oxygenated VOCs measured at the various sites, generally represented ~47-73% of net total measured VOCs that were emitted from the hog barns at ESTS facilities. Grinnells in November and Howard in June had the highest contribution of oxygenated VOCs, ~73%. At the conventional sites, oxygenated VOCs comprised ~37-59% of net total measured VOCs. Many of these samples were analyzed by GC/MS to confirm compound identification.

Net acetaldehyde concentration, at Barham, during both sampling periods in April and November, were 16.23 ppbC and 40.12 ppbC, respectively. At Grinnells in November the net acetaldehyde concentration was determined to be 9.57 ppbC; however, acetaldehyde was not observed at a higher concentration level at the ventilation exhaust than the background sample in April. At the ESTs sites, ethanol was a dominant compound among all measured VOCs at all farms with the exception of Grinnells in April. Ethanol net concentration levels at Barham were 47.09 and 155.41 ppbC representing 16.6 and 40.1% of net total measured VOCs originating in the barn), in April and November, respectively. At Grinnells, ethanol net concentration was 110.74 ppbC in November (31.5% of net total measured VOCs), and 43.95 and 82.75 ppbC net concentrations at Howard in June and December, (58.8% and 38.5% of net totalmeasured VOCs), respectively. Ethanol concentrations at the two farms utilizing conventional waste treatment methods were comparable, e.g., at Stokes in September (67.65 ppbC net concentration and 28.7% of net total measured VOCs), and at Moore in February (18.7 ppbC net concentration and 22.8% of net total measured VOCs). Ethanol was not observed as a dominant compound at Moore in October. Considering the seasonal variability of these observations, temperature does not appear to be the primary or only determining factor in the concentration levels in these sample locations. High levels of methanol concentrations were observed at several sites. At Barham, during both April and November sampling episodes, the observed methanol concentration of 42.9 ppbC and 26.1 ppbC represented 15.1 and 6.8%, respectively, of net total measured was not observed as a dominant compound at Moore in October. Considering the seasonal variability of these observations, temperature does not appear to be the primary or only determining factor in the concentration levels in these sample locations. High levels of methanol concentrations were observed at several sites. At Barham, during both April and November sampling episodes, the observed methanol concentration of 42.9 ppbC and 26.1 ppbC represented 15.1 and 6.8%, respectively, of net total measured VOCs originating in the barn. At Grinnells in April, methanol concentrations were measured at 23.3 ppbC (20.2% of net total measured VOCs originating in the barn). Acetone was a dominant compound in the hog barns at all farms with the exceptions of the ESTs sites, Howard and Barham in June and November, respectively. At all sites where comparisons were made, acetone contributed ~3-12% of the net difference for total measured VOCs.

Detected Sulfur and Phenolic Compounds

Dimethyl sulfide and dimethyl disulfide were the two sulfur-type VOCs frequently observed at all of the site locations that were verified by GC/MS and quantified by

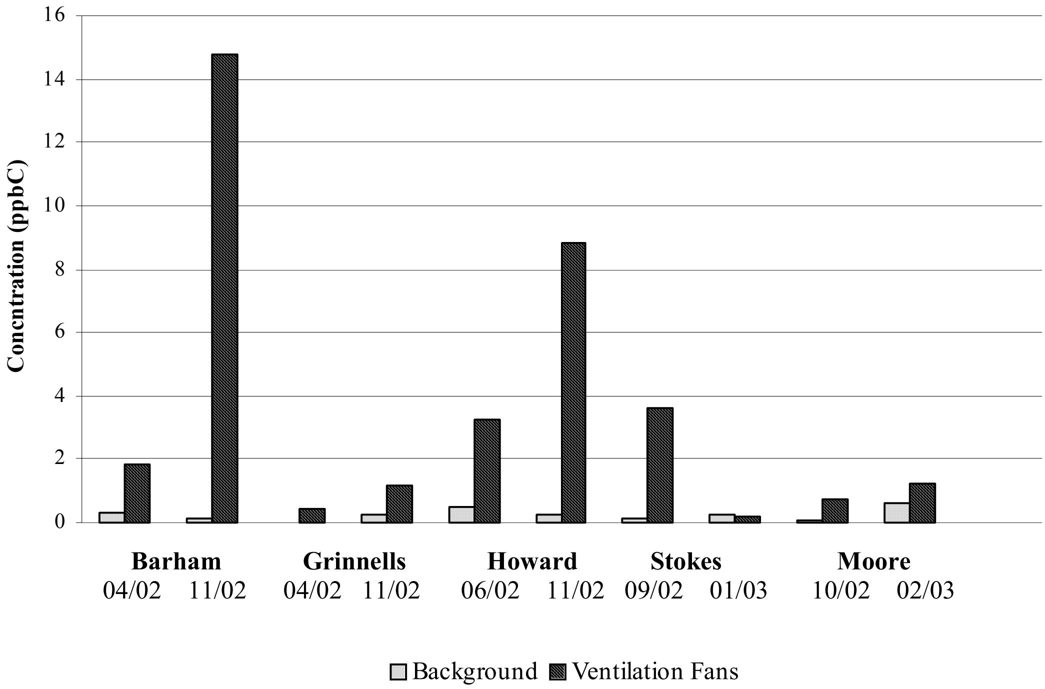

Figure 2: Total reduced organic sulfur (dimethyl sulfide and dimethyl disulfide) concentrations (ppbC) at various swine facilities in Eastern North Carolina

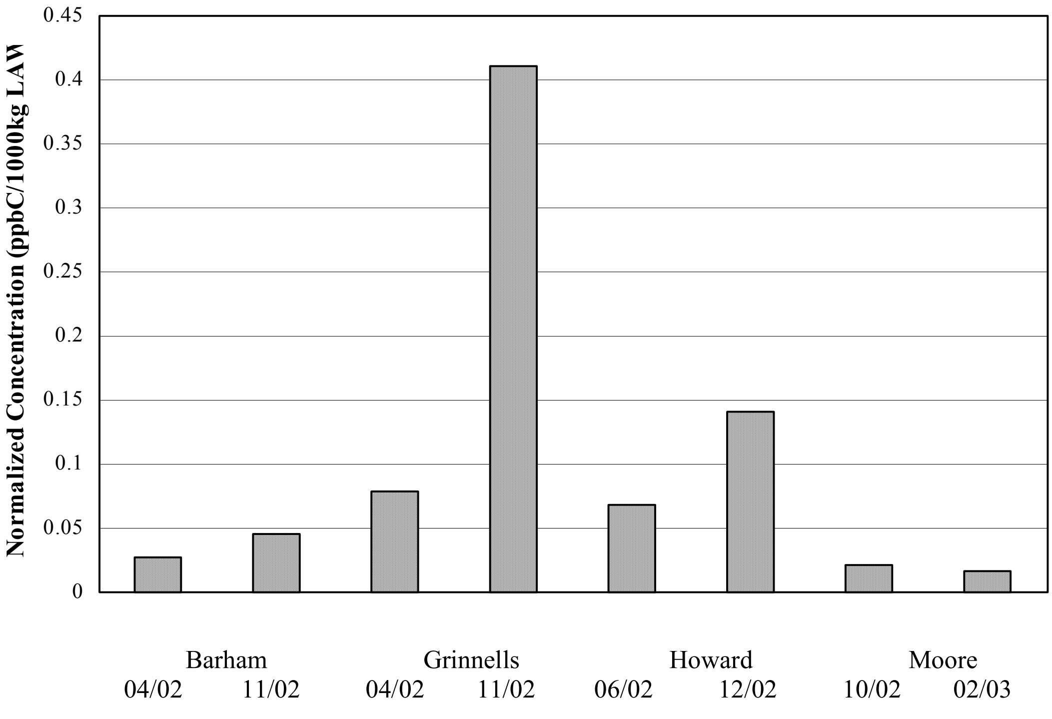

Figure 3: Total reduced organic sulfur concentrations (dimethyl sulfide and dimethyl disulfide) (ppbC) detected at ventilation fans, normalized by live animal weight (LAW)

GC/FID. These compounds are recognized as malodorous VOCs with odor thresholds, defined as the concentration at which odor is first detected, of 2.24 and 12.3 ppb, respectively[9]. Dimethyl sulfide was measured at levels above its odor threshold at Barham in November, (14.4 ppbC net total concentration) and at Howard in December (6.6 ppbC net total concentration). At the barn ventilation systems for all sites, dimethyl detectable limits. It is unlikely that the percent compositions of the detected compounds remained the same after emission into the ambient air. This is due to dispersion, vertical mixing, and/or photochemical reactions that occur in the atmosphere near ground level.

CONCLUSIONS

A total of 110 samples were collected by means of SUMMA electropolished stainless steel canisters to characterize volatile organic compounds (VOCs) detected at six swine facilities in Eastern North Carolina between April 2002 and March 2003. Two sites employed traditional lagoon and field spray technologies; while four sites utilized various potential ESTs in an effort to reduce ammonia and VOCs emissions, odor and odorants, and pathogens at swine farms. More than 100 compounds, including various paraffins, aromatics, olefins, ethers, monoterpenes, alcohols, aldehydes, ketones, halogenated hydrocarbons, phenols, and sulfides were identified and quantified by GC/FID analysis. Many of these compounds have been determined to play an important role as precursors to tropospheric ozone, fine particulate matter (PM_{fine}), and other atmospheric photochemical oxidation formation such as peroxyacetal nitrate (PAN)[19]. Other compounds observed (e.g., reduced organic sulfur compounds) are related to odor and irritation senses [9,20].

One complex sample collected at Barham Farm helped to characterize several sulfur-type VOCs, including dimethyl sulfide and dimethyl disulfide. Carbonyl sulfide and carbon disulfide were positively identified by GC/MS analysis but could not be quantitatively determined by GC/FID. Another compound commonly associated with malodors at swine facilities as well as general air toxicity, 4-methylphenol, was also identified in many of the GC/FID sample results and verified by GC/MS analysis. The GC/MS analysis of selected samples also served to verify and/or identify many VOCs reported here.

Overall, the highest VOC concentration levels measured at each of the sites were in close proximity to the hog barns. The dominant compounds observed near the hog barns from each sampling period were compared with background samples (i.e., upwind of lagoons and houses) collected in the same timeframe, with the difference referred to as the net concentration. The total measured VOCs at the hog barns were typically dominated by ethanol, methanol, acetaldehyde, and acetone. These compounds, in addition to other oxygenated VOCs measured at the various sites, generally represented ~47-73% of net total measured VOCs that were emitted from the hog barns at ESTs facilities. Grinnells in November and Howard in June had the highest contribution of oxygenated VOCs, ~73%. At the conventional sites, oxygenated VOCs comprised ~37-59% of net total measured VOCs. Several of these compounds, most particularly acetaldehyde, may participate in the photooxidant process to produce downwind photochemical ozone.

Dimethyl sulfide and dimethyl disulfide, both recognized as malodorous compounds, had concentration levels at the barns above the background concentration at every farm sampled with the only exception of Stokes in September. Dimethyl sulfide was measured at levels above its odor threshold (2.24 ppb) at Barham in November (7.2 ppbC net total concentration) and Howard in Decmeber (3.3 ppbC net total concentration). Grinnells had the overall highest normalized concentration of dimethyl sulfide and dimethyl disulfide during the November sampling period (0.411 ppbC/1000kg) while the lowest normalized levels were observed at Moore where concentrations were 0.007 ppbC/1000kg in both October and February. Normalized concentration levels for these sulfur-type VOCs were consistently higher during the colder season than the warmer season at each of the farms with the exception of Moore, where the normalized concentration levels were the same. 4-methylphenol, another odorous compound associated with swine waste was also measured at higher levels near the barns than the background levels at Barham and Grinnells in April, Howard and Stokes during each sampling campaign, and at Moore in February. The largest net concentrations of 4-methylphenol were measured at Howard Farm in June and December, at 12.47 ppbC and 43.41 ppbC (16.7 and 20.2% of net total measured VOCs), respectively, and at Stokes Farm in September (32.7 ppbC net concentration, 13.9% of net total measured VOCs).

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