Characterization of non-methane volatile organic compounds at swine facilities in eastern North Carolina

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Abstract

Samples were collected and analyzed in a field study to characterize C\textsubscript{2}–C\textsubscript{12} volatile organic compounds (VOCs) emitted at five swine facilities in Eastern North Carolina between April 2002 and February 2003. Two sites employed conventional lagoon and field spray technologies, while three 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 paraffins, olefins, aromatics, ethers, alcohols, aldehydes, ketones, halogenated hydrocarbons, 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. 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 (HCs), i.e., ethanol, methanol, acetaldehyde, and acetone. These compounds, in addition to other oxygenated VOCs measured at the various sites, generally represented $\approx$37–73\% of net total measured VOCs that were emitted from the hog barns at the various sites. Dimethyl sulfide and dimethyl disulfide, both recognized as malodorous compounds, were determined to have higher concentration levels at the barns than the background at every farm sampled with the exception of one farm during the warm sampling season.

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1. Introduction

A dramatic increase in swine production between 1987 and 1997 has made North Carolina the second largest producer of hogs in the United States, with a population of $\approx$10 million animals (NCDA, 2003). During this same timeframe, the number of hog farms declined by more than 60\% and today there are fewer than 5000 farms in the state. Consequently, more hogs are confined to smaller areas, thereby increasing amounts of odorous and potentially harmful compounds due to a higher amount of excretion.
In an effort to address environmental concerns, Project OPEN (Odors, Pathogens, and Emissions of Nitrogen) was established in December 2000 to evaluate various alternative waste treatment technologies (also referred to as “environmentally superior technologies” or ESTs) at hog production facilities for potentially hazardous air and water emissions as well as offensive odors. One aspect of this comprehensive study was to collect ambient volatile organic compounds (VOCs) samples at various suspect sources areas including upwind and downwind locations to characterize the compounds present in these environments.

Emissions of methane and ammonia from swine facilities have been well documented (McCulloch et al., 1998; Sharpe and Harper, 1999; Walker et al., 2000; Aneja et al., 2001; Childers et al., 2001). This study reports exclusively on the characterization of C2–C12 VOCs present in the ambient air at several swine facilities located in the eastern region of North Carolina, each during a warm and cool period. Because no swine facility was sampled multiple days during either study periods, the observations reported may be regarded as a survey to determine various gaseous compounds. Of particular interest are those VOCs associated with unpleasant odors from hog operations. VOCs have been reported from several swine farms in Eastern North Carolina to investigate odor complaints (Schiffman et al., 2001a). Sample collection strategy was designed to assess VOCs from suspected emission sources at the selected ESTs and conventional swine farm locations. Samples were collected at the housing areas and at the technologies (i.e., storage lagoons) at all sites. Additionally, samples were collected at upwind locations to these facilities.

The main objectives of this field study were to characterize C2–C12 VOCs that are present in the ambient atmosphere at swine confined animal feeding operations (CAFOs), identify the VOCs that may be classified as irritants and/or malodors in the atmosphere, compare concentrations from two conventional lagoon and spray technologies with three potential ESTs that have been implemented on different farms in this study, and address seasonal variations of VOC concentrations.

Due to the limited day-to-day sampling at each swine farm facility the results presented in this manuscript consist of the high C2–C12 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. 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 (Hammond et al., 1989; O’Neill and Phillips, 1992; Zahn et al., 1997).

2. Methods

2.1. Experimental research site descriptions

Samples were collected at four different farms and one laboratory site located in Eastern North Carolina. Three sites utilized various ESTs to treat animal waste while two sites maintained a conventional waste treatment technology. Individual site locations are shown in Fig. 1. Each site and its related waste treatment technology are briefly described below:

Barham Farm is a 4000 head farrow to wean operation located near Zebulon, NC (35.70°N, 78.32°W, 130 m 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 (4459 m²) 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 m²). Here, the liquid waste was treated via a de-nitrification/biofiltration process. The treated wastewater then used for two purposes: to flush fresh effluent from the hog barns and as a spray over agricultural crops for nutrient enrichment purposes (Cheng et al., 2000).

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 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 (Koger et al., 2000).

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 (7428 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. Similar to Barham Farm, the animal containment houses utilized a fan ventilation system (Humenic, 2000).

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.

### 2.2. Sample collection and sampling strategies

A total of 110 ambient air samples were collected in 6-L electropolished stainless steel SUMMAtm canisters, evacuated to a sub-ambient pressure of $<0.05$ mmHg. During sample collection, the valve on the canister was opened slowly over a timeframe of $\approx4$ min and then fully opened on the order of 1 min, thus allowing for a $\approx5$ min 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. The location of the sample collection depended on wind direction and sampling time was dependent on consistency of wind direction. Samples were not collected in instances where the wind direction was variable.

2.3. 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 pre-concentration approach. Repeat analysis of randomly selected samples was conducted in an effort to ensure the precision of the GC system concentration identification and quantitation. The GC column was 60 m x 0.32 mm ID fused silica column with a 1 μm 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 min⁻¹. After a 7.75 min hold period, the column temperature is programmed to 225 °C at 25 °C min⁻¹ rate and held at that temperature for 8 min. This temperature programming sequence provided separation of the C₂–C₁₂ compounds and conditioned the column for proceeding samples. Liquid nitrogen is used as the cryogen to obtain sub-ambient temperatures. An electronic pressure control device was used to maintain the helium carrier gas at 143 kPa throughout the analysis period. The pre-concentration system consisted of a 6-port gas sample valve configured to use a 25 cm x 3.2 mm stainless steel trap packed with 60–80 mesh glass beads as the sample loop. In operation, a measured sample aliquot was pulled through the glass bead trap while immersed in a Dewar of liquid argon. Liquid argon was used to prevent the condensation of oxygen and nitrogen for the sample air in the trap. The trapped VOCs were injected onto the column by a combination of valve switching, removing the liquid argon Dewar and replacing it with a Dewar of hot water (99 °C) (Harley et al., 2001).

The GC/FID system was calibrated using 0.25 ppm propane in air (±1.2%) National Institute of Standards and Technology Standard Reference Material (NIST SRM). The averaged area count per parts per billion carbon (ppbC) response factor determined with the propane standard was used to determine compound concentration in ppbC for all observed GC peaks (Dietz, 1967; Ackman, 1968; Apel, 1995). 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 column and column temperature programming operation used were identical to that used for the GC/FID systems. An electronic pressure control system was used to maintain a constant helium column flow rate at 1.4 cm³ min⁻¹ during the period of sample analysis. 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. Samples chosen for verification were typically based on the observed high peak concentration levels and/or the occurrence of unknown peaks.

As mentioned earlier all of the VOC results provided in this paper were determined with a uniform per-carbon response factor obtained with the NIST SRM propane calibration standard. All compounds reported here were determined using this uniform per carbon response obtained with the propane standard. It should be noted that, while propane calibration provides a quantitative per carbon response for all HC-type VOCs in the FID, the assumption is invalid for substituted HCs such as acetone and ethanol. Response adjustments referred to as effective carbon number (ECN) adjustments can be applied to the substituted VOCs to obtain reasonable concentrations for these compounds in terms of ppb (Jorgensen et al., 1990; Scalon and Willis, 1985; Sternberg et al., 1962). Most of the published ECN adjustment factors were obtained for the oxygenated HCs. Very limited information is available for the sulfur substituted VOCs. What limited information available for dimethyl sulfide suggests that the sulfur atom has no effect on the FID response, requiring no adjustment (Jorgensen et al., 1990).

3. Results

Due to the nature of Project OPEN, the farms were available for sampling for about 2-week increments in each warm and cold season, resulting in some limitations of our sampling strategies. Among the suspected VOC source areas including storage lagoons, confinement houses, and on-site crop soils, highest VOC concentrations were typically observed at the hog barn ventilation locations for all sites. These specific results from the barns provide the most suitable database to compare both composition and concentration differences between sites and for both seasons and so will be the basis of discussion for this study. The data results presented here consist of 1-day sampling from the barns at each swine farm facility for both warm and cold seasons.
3.1. Identification of the VOCs with the GC systems

Using a GC/FID approach, individual VOCs were 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 during the April sampling period at the outlet of a pipe leading from the covered lagoon to the electric generator system at the Barham Farm discussed earlier greatly assisted in the identification of many of these sulfur compounds. The 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. Methane was clearly the most abundant VOC observed by the FID; however, quantitative determination of this compound could not be made with the analytical column and pre-concentration procedures used with the GC/FID system. The sample served to demonstrate the complex VOC mixture produced by the treatment of hog waste that may be released to the ambient air. The GC/FID chromatogram of this complex sample, as well as a sample collected

Fig. 2. Chromatograms for two samples collected at Barham Farm. The top chromatogram represents a complex sample collected from the impermeable covered lagoon and the lower chromatogram represents a sample collected in front of the hog barn ventilation fan.
in the ambient air in front of a hog barn, is provided in Fig. 2. Analysis of this sample by GC/MS provided identification to many of the unidentified compounds observed with the GC/FID analysis. The most abundant C2–C12 VOCs consisted of dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide (representing 21.1%, 17.7%, and 24.4%, respectively, of the total concentration of all the GC compound peaks eluting from isobutane to the last compound peak).

Sulfides were of particular interest because many produce distinct malodors. Fourteen other sulfur-type VOCs were identified, including thiophene, 2-methylthiophene, 3-methylthiophene, methylacetyldisulfide, 2-ethylthiophene, 2,5-dimethylthiophene, 3-ethylthiophene, 2,3-dimethylthiophene, methylisopropyl disulfide, methyl-propyl disulfide, methyl-sec-butyldisulfide, and dimethyl tetrasulfide. Since GC/MS confirmed peak identification, these compounds were added to the GC/FID CALTABLE to use for the other canister samples collected at the swine farm sites. Many of these compounds have previously been identified at swine facilities (Hammond et al., 1989; O’Neill and Phillips, 1992; Schifman et al., 2001a). Two other sulfur-containing VOCs also observed in the GC/MS results included carbonyl sulfide, which eluted early from the GC column at the retention time between the C2 and C3 hydrocarbons, and carbon disulfide, which eluted from the GC column at about 14.7 min, near 2-methyl-2-butene. Neither compound is expected to respond in the FID. Hydrogen sulfide is expected to be unresponsive in the FID and is expected to elute from the GC column prior to the C2 hydrocarbons. Due to its retention time location, this compound could not be positively identified with this GC/MS system. Other VOCs identified in the sample by GC/MS included alkanes, alkenes, ketones, and aldehydes. The last compound peak observed on the GC/FID system typically occurs at approximately 37 min, since compound peaks beyond this retention time have vapor pressures <0.01 mm and are considered to be non-existent in the vapor phase.

### 3.2. VOCs observed at hog barns

Highest VOC concentrations generally observed at each of the five 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.

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 similar. Since these farms are corporate owned, it is anticipated that they adhere to the same operational routine. It is expected that the feed provided to the animals at the facilities is the same type, as should the cleaning agents used to sanitize the barns each time the animals are removed. With these expectations in mind, comparisons were made to determine the types as well as the concentration levels of detected compounds being emitted from these different houses. 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.

Table 1 provides a list of net concentration levels for select VOCs from samples that were collected simultaneously in front of the hog barn fan ventilation systems as well as upwind of the site. A supplemental table also included with the manuscript for these samples provides a comprehensive list of all compounds that were identified and quantified by the GC/FID system as well as their respective RTINDEX values. Many of the VOCs identified have been determined to play an important role as precursors to tropospheric ozone, fine particulate matter (PM\textsubscript{fine}), and other atmospheric photochemical oxidation formation such as peroxyacetal nitrate (PAN) (Kang et al., 2001). The total VOCs detected by the FID as well as the percent sum of identified VOC peaks are also listed in the supplemental table. Generally, about 59–84% of the total VOC peaks determined by the FID have been identified by the updated CALTABLE that included the sulfur-type VOCs.

Fig. 3 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. Net compound concentrations, i.e., fan ventilation minus background values, listed in Table 1 and the supplemental table was used for the determination. Oxygenated VOCs appear to be the most abundant compounds 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 EST 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.

Referring to the data in Table 1, net acetaldehyde concentration, at Barham, during both sampling periods in April and November, were 16.23 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 EST 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 total measured 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 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.

At Barham in April, propane comprised ~40% (114.0 ppbC) of the net difference in concentration of measured VOCs. The reason for this unusually high concentration level is unclear. The most likely source of propane is from heating systems that use liquid propane. The use of such heating systems at Barham was not determined. Elevated propane was not observed at this facility when sampled in November.

<table>
<thead>
<tr>
<th>Farm site</th>
<th>sampling date</th>
<th>Farm type</th>
<th>Compound</th>
<th>Net concentration levels (ppbC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stokes 09/02</td>
<td>Conv.</td>
<td>Acetaldehyde</td>
<td>2.35</td>
<td>12.9</td>
</tr>
<tr>
<td>Stokes 01/03</td>
<td>Conv.</td>
<td>Methanol</td>
<td>10.78</td>
<td>0.61</td>
</tr>
<tr>
<td>Moore 10/02</td>
<td>Conv.</td>
<td>Ethanol</td>
<td>67.65</td>
<td>0.21</td>
</tr>
<tr>
<td>Moore 02</td>
<td>Conv.</td>
<td>Acetone</td>
<td>27.40</td>
<td>0.21</td>
</tr>
<tr>
<td>Grinnells 04/02</td>
<td>Conv.</td>
<td>Dimethylether</td>
<td>0.39</td>
<td>0.54</td>
</tr>
<tr>
<td>Grinnells 11/02</td>
<td>EST</td>
<td>4-methylphenol</td>
<td>32.65</td>
<td>10.56</td>
</tr>
<tr>
<td>Howard 06/02</td>
<td>EST</td>
<td>n/d</td>
<td>n/d</td>
<td>n/d</td>
</tr>
<tr>
<td>Barham 04/02</td>
<td>EST</td>
<td>n/d</td>
<td>n/d</td>
<td>n/d</td>
</tr>
</tbody>
</table>
| n/d: net concentrations were either below detectable limits or background concentration levels were higher than barn concentration levels measured simultaneously.
3.3. 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 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 (Schiffman et al., 2001a). 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). For comparison, the ppbC concentration at these two sites were converted to ppb by dividing the number of carbon atoms, i.e., 14.4/2 and 6.6/2, to obtain 7.2 and 3.3 ppb concentrations. No adjustments for ECN were made since it is assumed that sulfur had no effect on the FID response (Jorgensen et al., 1990). At the barn ventilation systems for all sites, dimethyl sulfide was measured above the respective background levels with the exception of Stokes Farm in January. In this instance, the levels were comparable, 0.21 ppbC measured at the barns and 0.25 ppbC upwind. For all sites, dimethyl sulfide was detected in the background ambient air with the exceptions of Grinnells in April. At the barn ventilation systems, dimethyl disulfide was detected at the ESTs sites Barham, Grinnells, and Howard, during both sampling episodes. For the conventional sites, dimethyl disulfide was detected at Moore during both sampling episodes and at Stokes in September. Highest concentration levels were measured at Howard Farm, 0.77 and 2.15 ppbC, in June and December, respectively. Dimethyl disulfide was not measured (i.e., below detectable limits) in the upwind samples during any of the sampling episodes at the conventional sites. Dimethyl disulfide was measured at ≤0.12 ppbC at Barham in April, Grinnells in November, and Howard in June, and was below detectable limits for the other sampling episodes at the ESTs sites. Observed concentration levels for dimethyl disulfide at all sites never approached the 12.3 ppb odor threshold level. Fig. 4 provides a comparison of the concentrations of these reduced organic sulfur compounds emitted from houses with their average concentrations in the ambient air around swine facilities.

Another malodorous compound associated with swine farms, 4-methylphenol, which has an odor threshold of 5.3 ppb (van Gemert and Nettenbreijer, 1978), was measured at the barns at the ESTs sites, Barham, Grinnells, and Howard during each sampling campaign. Previously, Zahn et al. (2001) reported levels of ~0.9 ppbV at a mechanically ventilated hog barn exhaust and Schiffman et al. (2001a) reported average concentrations of 9 ppbV inside swine buildings. In this study, highest concentrations of 4-methylphenol were measured at Howard in June and December, 12.5 ppbC net concentration (16.7% of net total VOCs) and 43.3 ppbC net concentration (20.1% of net total VOCs), respectively, at Stokes in September (32.7 ppbC net concentration, 13.9% of net total VOCs) and at Moore in February (10.50 ppbC and 12.8% of net total VOCs). 4-methylphenol was not detected at Stokes at all during the January sampling period or at Moore in October. To convert the measured ppbC concentrations of 4-methylphenol to ppb, an ECN value of 6.38 (Jorgensen et al., 1990) was used. Only the December measurement at Howard, i.e., 43.3 ppbC/6.38 or 6.78 ppb, exceeded the compound odor threshold of 5.3 ppb.

We note that carbonyl sulfide and carbon disulfide were detected through GC/MS analyses but could not be determined by the GC/FID. Known standards of these compounds were not available to obtain quantitative results with the GC/MS system. Carbon disulfide has an odor threshold of ~16 ppb and there is no known odor
threshold established for carbonyl sulfide (US Department of Health and Human Services (USDHHS), 1993). Schiffman et al. (2001b) determined that intensity of the odorous emissions from swine facilities resulted from the combined effect of odorous compounds present at sub-threshold concentrations in addition to individual compounds observed above their respective odor threshold levels.

The reduced organic sulfur compounds observed at the exhaust ventilation fans of each farm were normalized by live animal weight (LAW) in the barn (ppbC1000 kg−1). These results are presented in Fig. 5. It is important to keep in mind that the age and type of animal, in addition to LAW, varied from farm to farm. At Barham, concentration levels were 0.021 ppbC 1000 kg−1 and 0.046 ppbC 1000 kg−1 in April and November, respectively. At Grinnells total levels were 0.079 ppbC 1000 kg−1 in April and 0.411 ppbC 1000 kg−1 in November. At Howard sulfur concentrations were 0.068 ppbC 1000 kg−1 in June and 0.141 ppbC 1000 kg−1 in December. Grinnells had the overall highest normalized concentration during the November sampling period. The lowest normalized levels of dimethyl sulfide and dimethyl disulfide were observed at Moore where concentrations were 0.007 ppbC 1000 kg−1 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 (Fig. 5) with the exception of Moore, where the normalized concentration levels were the same. Barns that utilize fan ventilation systems generally have multiple fans at each house. The number of fans running at a given time is dependent on the temperature inside the house. In the cooler months it is expected that fewer fans are operating, thereby allowing a buildup of VOCs to occur within the houses, as there tends to be less airflow. Samples collection for this study was conducted in front of operational fans outside of the houses and so this may explain the higher observed concentrations for these compounds.

Many of the other sulfur-type VOCs were observed to have very small percent concentrations. These compounds may be present but concentration levels are below 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.

4. Conclusions

A total of 110 samples were collected by means of SUMMATM electropolished stainless steel canisters to characterize volatile organic compounds (VOCs) detected at five swine facilities in Eastern North Carolina between April 2002 and February 2003. Two sites, Stokes Farm and Moore Farm, employed traditional lagoon and field spray technologies; while three sites, Barham Farm, Grinnells Laboratories, and Howard Farm, 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) (Kang et al., 2001). Other compounds observed (e.g., reduced organic sulfur compounds) are related to odor and irritation senses (Schiffman et al., 2001a; Kuroda et al., 1996).

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.

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. The largest VOC concentration levels were the same. 4-methylphenol 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 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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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2005.03.053

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