RESEARCH REPORT
ENVIRONMENT

Title: Chemical Characterization of both particulates and gaseous emissions from impacted and non-impacted areas associated with swine feeding operations - **NPB #06-114** **REVISED**

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Industry Summary:

Odorants in the air include both volatile organic and volatile sulfur compounds. Movement of these compounds from swine feeding operations to surrounding community is thought to occur either through gas phase transport or through sorption onto particulate material (PM). This study was designed to measure both gaseous and PM sorbed odorants emitted from a swine facility and compare those compounds to background levels associated with rural environments. Volatile organic compounds (VOCs) were monitored using sorbent tubes and volatile sulfur compounds (VSC) were measured with both canisters and fluorescence detection. Samples were taken at an active swine facility (impacted) and at either a site 10 miles from any animal feeding operation (non-impacted) or upwind from the facility (control). PM filters were characterized by elemental analysis and odorant concentrations.

Key VOCs associated with odor included: volatile fatty acids (VFA), phenolic and indole compounds. Odorants in the swine housing areas had elevated levels of VFAs and phenol compounds, while pit fan areas had elevated levels of VFAs, phenol and indole compounds. In terms of concentration in air, total VFAs averaged 325 μg m^{-3}, total phenols 62.4 μg m^{-3} and total indoles 1.6 μg m^{-3}. However, if concentrations are adjusted to odor activity value (= conc. of odorant in air/odor threshold concentration) total VFAs, phenols, and indole compounds averaged 6.8, 6.5, and 5.0, respectively. Concentrations of odorants measured in the spring and fall were higher than summer which all were substantially higher than winter. Daily concentrations of odorants had a diurnal pattern with early morning and late evening being peaks. Odor profiles changed with distance with VFAs, phenols, and indole compounds all above their odor threshold at the facility, but indole and phenol compounds being detected up to 1 mile north offsite. Concentrations of the most odorous compounds were all below their odorous thresholds values for samples taken at the control/non-impacted site. Compounds typically above odor threshold concentrations included butanonic acid, 3-methylbutanoic acid, 4-methylphenol, 4-ethylphenol, indole, and 3-methylindole.

Volatile sulfur compounds, hydrogen sulfide (H_2S), methanethiol, and dimethyl sulfide were generally detected above their odor threshold values at the pit fan; however, during pumping of the deep pits levels of H_2S rose rapidly to over 1000 ppbv from the building and over 800 ppbv 46 m downwind (approximately 50 times odor threshold) from the facility, but rapidly declined when pumping ceased. There was little to no rise in levels of the other VSC during pumping.

Levels of PM_{10} between buildings and 46 m downwind averaged 60.5 and 49.7 $\mu g\ m^{-3}$, respectively, but levels were not significantly different. Control and non-impacted sites averaged 18.3 $\mu g\ m^{-3}$, which were significant lower ($p<0.05$) than PM_{10} measured near buildings. There was little difference between levels of PM_{10} collected in the spring, summer or fall, but winter PM_{10} was significantly lower ($p < 0.05$) than the other seasons. Levels of VFA were enriched compared to both phenol and indole compounds when comparing PM sorbed to vapor phase concentrations. Elemental analysis of PM showed significant higher levels ($p < 0.05$) of nitrogen compared to samples taken from non-impacted areas; however, carbon and sulfur levels were not significantly different.

Scientific Abstract:

The purpose of this study was to measure both gaseous and PM sorbed odorants emitted from a swine facility in central Iowa and compare those compounds to background levels associated with rural environments. Gaseous VOCs were captured in the field using sorbent tubes while gaseous VSCs were captured in the field using canisters (both glass and fused silica lined) and continuous monitoring of total reduced sulfur using pulsed fluorescence detection. Samples were taken at an active swine facility (impacted) and at either a site 10 miles from any animal feeding operation (non-impacted) or upwind from the facility (control). Sorbent tubes sampled in the field were analyzed by GC-MS using a thermal desorption (TDS) inlet system, and canisters samplers were also analyzed using a GC-MS system equipped with both a canister inlet system and pulsed flame photometric detector (PFPD, a highly sensitive sulfur detector). Particulate matter was sampled using HiVol particulate sampler (PM_{10} sampling head) equipped with quartz particulate filter paper. Filter samplers were analyzed for sorbed VOCs by extracting VOCs from filters in a heated tube apparatus purged with humidified nitrogen. VOCs extracted from the filters were captured on sorbent tubes for later TDS-GC-MS analysis. Filter samplers were analyzed for elemental C, N, and S using a tube combust instrument that quantifies gases by thermal conductivity detector.

Key VOCs associated with odor from the swine facility included: volatile fatty acids (VFA), phenol and indole compounds. Odorants in the swine housing areas had elevated levels of VFAs with some 4-methylphenol, while in pit fan areas levels of phenol and indole compounds were elevated. In terms of concentration in air, total VFAs averaged 325 $\mu g\ m^{-3}$, total phenols 62.4 $\mu g\ m^{-3}$ and total indoles 1.6 $\mu g\ m^{-3}$. However, if concentrations are adjusted to odor activity value (= conc. of odorant in air/odor threshold concentration) total VFAs, phenols, and indole compounds averaged 6.8, 6.5, and 5.0, respectively. Daily concentrations of odorants had a diurnal pattern with early morning and late evening having the highest levels. Odor profiles changed with distance with VFAs, phenols, and indole compounds all above their odor threshold at the facility, but indole and phenol compounds being detected up to 1 mile north offsite. Concentrations of the most odorous compounds were all below their odorous thresholds values for samples taken at the control/non-impacted site. Compounds typically above odor threshold concentrations included butanonic acid, 3-methylbutanoic acid, 4-methylphenol, 4-ethylphenol, indole, and 3-methylindole.

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Introduction:

There is a wealth of information on the odors emitted from swine production facilities. In fact, the US National Pork Producers Council (NPPC, 1995) cited over 1155 references concerning research evaluating 'odor' from swine operations. Today, over 400 compounds have been identified as odorous and originating from swine production (O'Neil and Phillips 1992, Spoelstra 1980, Yasuhara et al. 1984, Zahn et al. 1997, Schiffman et al. 2001). Much of the previous work has been focused on identifying all the components in the air that are associated with odor with the thought that odor is greater than the sum of its parts (i.e., individual compounds). However, if conclusions from the food industry are correct, less than 5% of the volatile compounds identified are actually responsible for odor (Grosch, 2000). In fact, most studies that claim to have identified the essence of odor from swine production typically have compounds mixtures of fewer than 10 compounds (Schaefer et al 1974, Yasuhara 1980, Hobbs et al. 2000, Zahn et al. 2001a), and recently, Wright et al. (2005) identified three compounds that were responsible for swine odor. There is considerable debate as to the compounds most responsible for swine odor but several compound classes stand out and these include: volatile fatty acids, phenol compounds, indole compounds, and reduced sulfur compounds.

Currently, there is much debate on the mechanistic transport of odor from animal feeding operations to the surrounding communities. Much of the thought is that odors are transported directly in the vapor phase or indirectly though attachment onto PM. While direct transport in the vapor phase is not debated, its importance is debated. Research has shown that compounds associated with odors are sorbed onto PM (Day et al., 1965, Hammond et al. 1979, Razote et al., 2004, Cai et al. 2006) and several have shown that those same compounds are concentrated on PM (Hammond et al. 1981, Bottcher 2001, Cai et al., 2006). Hammond et al. 1981 showed that dust filter could eliminate odor in a swine facility. However there is some evidence that both mechanisms are at play (Schiffman et al. 2001), but the contribution of each is difficult to determine. Consequently, the purpose of this study was to characterize gaseous and PM_{10} material emitted from a swine facility and compared impacted areas to non-impacted areas in terms of gases and PM.

Objectives:

The objectives of this study are to 1) monitor air quality from swine production facility and compare that to a site not impacted by animal agriculture; 2) monitor changes in both PM levels and gaseous emissions over a year and monitor fluxes in gaseous emissions over each sampling period; 3) characterize and quantify PM VOC profile and compare that to the gaseous VOC profile; 4) chemically characterize PM material elemental profile at various locations.

Materials and Methods:

Site Selection

The study was conducted at a commercial swine production facility located in central Iowa between fall 2006 and winter 2009. This site consists of three swine-finishing buildings naturally ventilated with total capacity of approx. 3000 head. Building dimensions are 12 m-wide, 60 m-long, 3.06 m-tall side walls, and peak height (H) of 4.8 with deep pit manure storage. Each building has 4 deep pit fans and 2 house fans. Prevailing wind directions from the facility are South-West in summers and North-West during winters. Manure is applied to the fields adjacent to the site, but air samples were not taken during manure application. The non-impacted site is located 15 miles northwest of the swine production facility and 10 miles to any existing animal production facility.

Air Sampling and Processing

Volatile Organic Compounds

All samples were collected on glass sorbent tubes (178 x 6 mm diameter) containing a multi-bed sorbent packing of Carbopack C and Carbopack X (1:2 ratio v/v) custom made by Supelco, Inc. (Bellafonte, PA). Prior to use, the sorbent tubes were conditioned on a Tube Conditioner (Gerstel, Inc. Baltimore, MD) at 300°C for a minimum of 2 hours with a nitrogen purge of 50-70 mL min-1. Conditioned tubes were either loaded into field gas samplers (GS 301 gas sampler, Gerstel, Inc.) or placed in-line with personal sampler (222-4 Series, SKC, Inc, Eighty Four, PA). Air samplers taken with GS1 samplers were placed at a minimum of three different locations around the facility with samples collected at 100 mL min^{-1} for 12 L (sampling time approximately 2 hours). Total volume of air sampled for each sorbent tube was recorded by the GS1 gas samplers. Personal samplers were placed at the facility in either the exit portions of the pit fan or the downwind side of the naturally ventilated swine buildings or samplers were placed one mile north of the facility with samples collected from samplers at approximately 10-15 mL min^{-1}. Total volume of air sampled was internally recorded on sampler counters. All surfaces exposed to the flow path prior to the sorbent tubes were constructed of either Teflon®, glass, or polypropylene material. Sampled sorbent tubes collected in the field were stored at ambient temperatures until transported back to the laboratory and stored at <-20°C until analyzed. All samples were analyzed within 60 days of the time they were sampled in the field. Prior to analysis, all samples were allowed to equilibrate to ambient temperatures. After analysis, the sorption tubes were conditioned as previously specified.

Volatile Sulfur Compounds

Initially, field samples were collected in 1.4 L fused silica lined (FSL) canisters purchased from Entech Instruments, Inc (Simi Valley, CA). Samples were collected by either filtered quick fill (grab samples) or time integrated samples (2 hours) using restriction samplers. All surfaces on quick connect's and restriction samplers were coated with sulfur inert fused silica. However, both hydrogen sulfide and methanethiol were lost in the initial sampling due to moisture effects in sampling. To lower the water content of field sampled air, a canister filter assembly containing a calcium chloride drying tube and Nafion dryer (Perma Pure LLC, Toms River, NJ) were inserted before restriction samplers. However, both hydrogen sulfide and methanethiol were still lost during sampling. Glass canisters were used subsequently with drying tubes containing restriction samplers. Due to loss of hydrogen sulfide during sampling, reduced sulfur compounds were monitored with API-101E (Teledyne Instruments, San Diego, CA) during pumping of swine pits and sulfur speciation was obtained with glass canisters using filtered grab samples.

Particulate Material (PM_{10})

Graseby-Andersen Hi Vol particulate samplers (Graseby Andersen, Smyrna, GA) were equipped with a 10-µm inlet and 10 x 8 inch filters. Particles in the air stream drawn through the inlet had aerodynamic diameters less than 10 µm and were deposited on a glass-fiber filter media. The mass of particulates was determined by the difference in filter weight before and after sampling. Samplers were designed to maintain a 10 +/- 0.5µm cut point over a flow rate range of 1.02 to 1.24 m^3 min^{-1}. The concentration of the particulate matter is calculated by dividing the weight gain of the filter by the volume of air sampled.

Quartz particulate filter paper was analyzed for both sorbed VOCs and total elemental carbon (C), nitrogen (N), and sulfur (S). Collected filters were placed in plastic bags and stored in a freezer (<-20°C) until processed. Samples used for VOC analysis were weighed and placed into an ATIS™ (Supleco, Bellefonte, PA) extraction glassware (13 mm id X 76 mm length) apparatus. The apparatus heated the extraction glassware to approximately 110°C, while purging the contents of the extraction cell with humidified nitrogen gas at 75 mL min^{-1} for a 1-2 hrs (total volume 4-9 L). Volatile organic compounds extracted were captured onto sorbent tubes (see description above) connected to the apparatus. Elemental C, N, and S from filters were analyzed using an Elementar VarioMAX CNS (Elementar Americas Inc., Mt. Laurel, NJ), which uses catalytic tube to combust and convert substances to target gases N_2, CO_2, and SO_2. Targeted gases were separated using adsorption columns and quantified using a thermal conductivity detector.

GC/MS Analysis

Volatile Organic Compounds

Sorbent tubes were analyzed by thermal desorption (TDS) using an Agilent 6890N GC (Agilent Technologies, Inc.). The 6980N GC was equipped with a 5975N Inert MSD (Agilent Technologies) with an odor port (Gerstel, Inc., Baltimore, MD) for GC-O analysis. The GC systems used a Gerstel TDSA (Gerstel, Inc.) as its TDS unit, a PTV (programmed temperature vaporizer) inlets (CIS 4, Gerstel, Inc.) and separated compounds on a 30m x 0.25mm x 0.25μm DB-FFAP column (J&W Scientific, Inc., Wilmington, DE) using a helium gas set at a maximum of 1.4 mL min^{-1} constant flow.

Thermal desorption (TDS) parameters were the following: splitless mode; initial temperature, 60^{o}C; final temperature, 300^{o}C; initial time 0.5 min; final hold time 3 min; ramp, 60^{o}C min^{-1}; with a transfer line temperature of 320^{o}C. The inlet was packed with glass bead/Carbopack C material with the following parameters: solvent vent mode; initial temperature, -30^{o}C(-160^{o}C when performing GC-O analysis), final temperature, 320^{o}C, initial time, 0.2 min, final time, 3 min; ramp, 12^{o}C sec^{-1}, vent flow 40 mL min^{-1}, and purge split flow 20 mL min^{-1} with 1 min delay. The GC instrument oven temperature program was the following: 1) initial temp, 80^{o}C hold 0.05 min; 2) ramp 10^{o}C min^{-1} to 220^{o}C; and 3) ramp 50^{o} C min^{-1} to 240^{o}C and hold 5 min. The MS transfer line and source temperatures were 240 and 150^{o}C, respectively, and MSD was operated in Scan mode (29-350 amu) at 4.4 scan s^{-1}.

Volatile Sulfur Compounds

Analysis of 1.4 L FSL-canisters was performed using an Entech Instrument, Inc. (Simi Valley, CA) canister system which was coupled to a Agilent 6890N GC system (Agilent Technologies, Inc.). Canisters were sampled using a robotic autosampler (7500, Entech Instruments, Inc.) interfaced with a three stage preconcentrator (7100, Entech Instruments, Inc.). The 7100 controls the amount of sample removed from each FSL-canister (i.e., 10-600 mL) and concentrates the sample using a three-stage trapping system. The 7100 used the cold trap dehydration technique for the concentration of VSCs. In this procedure, the VSCs in the air sample pass through the first stage (empty trap, temperature -20^{o}C) before being trapped in the second stage (Tenax, temperature -80^{o}C). Water in the air matrix is removed in the first stage. The second trap is heated and the VSCs are trapped again on cryofocusing trap (fused silica tube, temperature, -150^{o}C), which is rapidly heated and transfers the VSCs into an Agilent 6890N GC system. Transfer lines between the 7500, 7100 and GC system were coated with fused silica and set at 150^{o}C. The 6890N GC was equipped with GS-Gaspro column (30m x 0.32mm x 0.25um) (Agilent Technologies, Inc.) using helium gas at 0.7 mL min-1 constant flow, and equipped with both 5973 Inert MSD (Aglient Technologies) and PFPD (OI Analytical, College Station, TX) connected in parallel. The column effluent was split using an Agilent microfluidic plate (Agilent Technologies, Inc) prior to the MSD/PFPD detectors at an approximate 20:1 ratio.

The GC was set at a constant flow (0.7 mL^{-1}); oven temperature program was: initial temp, 40^{o}C; final temp., 260^{o}C; initial time, 1.0 min; final time, 17.0 min; and ramp 20^{o}C min^{-1}. Mass spectrometer was operated in scan mode with electron ionization (electron accelerating voltage: 70 V). The scan was set from m/z 24 to 300 in 0.7 s. For determination of the target compounds using MSD, selected ion chromatograms over molecular ions (hydrogen sulfide: 34 m/z; methanelthiol: 48 m/z, sulfur dioxide: 64 m/z , carbonyl sulfide: 60 m/z, carbon disulfide; 76 m/z; dimethyl sulfide: 62 m/z , dimethyl disulfide: 94 m/z, and dimethyl trisulfide: 126 m/z) were used. The PFPD detector was set at 200^{o}C, 2 mm combustor tube, detector voltage at 600 V, detector gate delay at 6 ms, gate width at 24 ms, and detector trigger at 400 mV.

Statistical Analysis

Comparisons of variance and mean separation (LSD) techniques were used to test for significant differences ($p < 0.05$) of the concentration individual compounds. All statistical analyses were performed using JMP version 5.1 (SAS Institute, 2003) statistical software.

Results:

Volatile Organic Compounds

Sampling Methodology

Two aspects of the sampling protocol were studied for sampling bias: 1)Do the surfaces on the samplers, and tubing going into the gas sampler's sorb odorants; and 2)Does PM sorbed on filters extract gas phase odorants in air during sampling. The first question was address by removing all tubing, filters, and sampler housing between sorbent tubes and pump head. Samplers with and without housing were placed side by side in the field, and the metric used to evaluate bias was recovery of odorants from sorbent tubes with pump head only to sorbent tubes placed in samplers. If samplers without sample housing or sampling tubes were higher than samplers with both housing and tubing, it would indicate that sampler housing or sampling line sorbed odorants from the air stream. Recovery of select odorants ranged from 63-162% averaging 126% (Table 1). The higher recovery shows that tubing and instrument housing did not negatively bias sampling for target compounds; however, the recovery of target compounds was on the high side of the expected 70-130%. Possible explanation for higher recovery is that sample housing had been previously used to sample pit fans. The higher recovery was not expected to affect results from pit fans, but it may affect control areas and other low concentration areas. The second question was address by placing a sampler at both the inlet and exhaust of the PM sampler. If gas samplers connected to the exhaust had lower values than samplers placed at the inlet of the PM samplers, it would indicate that PM sorbed to filters were extracting gaseous odorants from the air stream. Recovery of select odorants ranged from 70-172% averaging 93% (Table 1) showing that PM is considered in equilibrium with gaseous compounds of odorants.

Table 1. Validation of Sampling Equipment and Particulate Material Sampling

	Sampling Equipment			**Particulate Material Filter**		
Compound	**Closed^a ng**	**Open^b ng**	**Recovery %**	**Exhaust ng**	**Inlet ng**	**Recovery %**
Acetic acid	197.8	236.0	84	182.7	207.5	93
Propanoic acid	43.6	32.1	136	51.1	67.8	75
2-Methylpropanoic acid	9.2	5.7	162	10.3	11.8	87
Butanoic acid	14.8	24.1	162	35.6	51.9	70
3-Methylbutanoic acid	5.3	3.7	143	8.5	10.1	84
Pentanoic acid	6.6	4.3	156	8.1	8.0	100
Phenol	12.9	12.9	100	5.2	5.9	88
4-Methylphenol	6.0	7.6	126	10.0	13.4	75
4-Ethylphenol	1.5	1.5	63	4.1	2.4	172

^{a}Closed represents sampler with housing and tubing; ^{b}Open represents samplers without housing and tubing with sorbent tubes connected directly to pump.

Volatile Organic Compounds

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housing between sorbent tubes and pump head. Samplers with and without housing were placed side by side in the field, and the metric used to evaluate bias was recovery of odorants from sorbent tubes with pump head only to sorbent tubes placed in samplers. If samplers without sample housing or sampling tubes were higher than samplers with both housing and tubing, it would indicate that sampler housing or sampling line sorbed odorants from the air stream. Recovery of select odorants ranged from 63-162% averaging 126% (Table 1). The higher recovery shows that tubing and instrument housing did not negatively bias sampling for target compounds; however, the recovery of target compounds was on the high side of the expected 70-130%. Possible explanation for higher recovery is that sample housing had been previously used to sample pit fans. The higher recovery was not expected to affect results from pit fans, but it may affect control areas and other low concentration areas. The second question was address by placing a sampler at both the inlet and exhaust of the PM sampler. If gas samplers connected to the exhaust had lower values than samplers placed at the inlet of the PM samplers, it would indicate that PM sorbed to filters were extracting gaseous odorants from the air stream. Recovery of select odorants ranged from 70-172% averaging 93% (Table 1) showing that PM is considered in equilibrium with gaseous compounds of odorants.

Swine Facility

Monitoring of the swine facility occurred on eight separate occasions encompassing all four seasons of the year. Samplers were typically placed at the pit fans, 46 m downwind (north of building) and 20 m upwind (south of the buildings) in addition samplers were deployed on a tower (8 m high) during summer sampling and in between buildings. Key VOCs classes associated with odor measured from both the swine housing and pit fans included: volatile fatty acids (VFA), phenol and indole compounds (Figure 1). Samples taken from the pit fan show increased levels of VFAs, phenol and indole compounds; however, samples taken from the swine housing area showed high levels of VFAs with some phenol compounds (Tables 2-3). Volatile fatty acids were the most abundant odorants emitted. On average, total VFAs were approximately an order of magnitude higher than phenol compounds that were an order of magnitude higher than indole compounds (Tables 2-3).

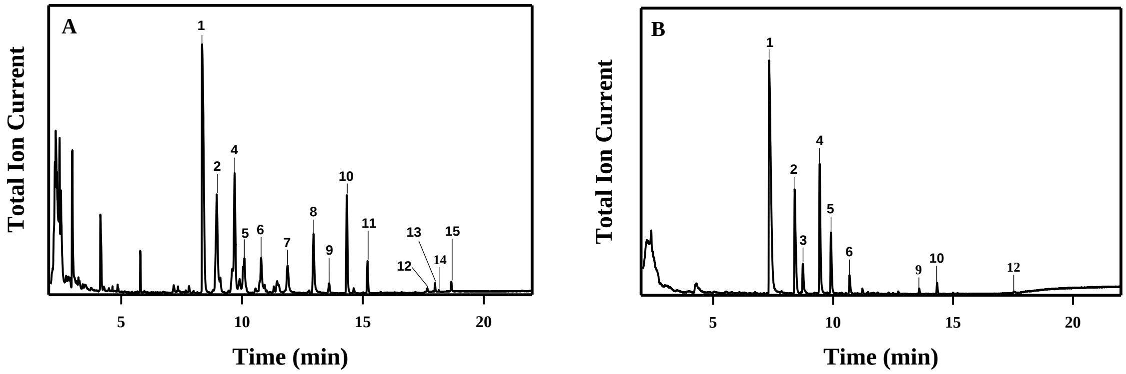

Figure 1. Thermal desorption analysis of air being emitted from a swine facility: A) Deep Pit; and B) Swine Housing. Compounds identified are as follows: 1) acetic acid; 2) propanoic acid; 3) 2-methylpropanoic acid; 4) butanoic acid; 5) 3-methylbutanoic acid; 6) pentanoic acid; 7) 4-methylpentanoic acid; 8) hexanoic acid; 9) phenol; 10) 4-methylphenol; 11) 4-ethylphenol; 12)benzoic acid; 13) indole; 14) 3-methylindole; and 15) 2-aminoacetophenone.

Levels of total odorants were highest in the fall and spring followed by summer and early winter levels significantly less (Tables 2-3). Volatile fatty acids were the dominant odorant for summer, fall and winter, while spring season had significant levels of both VFAs and phenolic compounds. Measuring odorants based on their odor activity value (OAV, = conc. of odorant in air/odor threshold concentration) rather than concentration levels is alternative technique to evaluate a compounds contribution to odor. In this method, the key odorants associated with

Table 2. Average Daily Air Concentrations of Odorants from Swine Pit Exhaust.

	Spring		Summer		Fall		Winter	
Compound	**$\mu g\ m^{-3}$**	**OAV[a]**	**$\mu g\ m^{-3}$**	**OAV**	**$\mu g\ m^{-3}$**	**OAV**	**$\mu g\ m^{-3}$**	**OAV**
Acetic acid	85.8	0.24	309.9	0.88	215.6	0.67	79.5	0.22
Propanoic acid	68.0	0.62	36.6	0.34	93.4	0.90	59.3	0.54
2-Methylpropanoic acid	18.3	0.26	3.6	0.05	14.7	0.22	8.2	0.11
Butanoic acid	70.3	4.93	16.6	1.19	59.2	4.02	51.4	3.60
3-Methylbutanoic acid	21.7	2.09	4.8	0.47	15.8	1.69	19.3	1.85
Pentanoic acid	33.5	1.54	1.4	0.07	11.1	0.55	1.0	0.04
Total VFA	299.5	9.67	370.7	3.00	411.6	8.06	219.5	6.38
Phenol	20.7	0.05	0.5	0.00	12.1	0.03	0.8	0.00
4-Methylphenol	116.9	13.97	2.5	0.29	55.0	9.13	4.1	0.49
4-Ethylphenol	6.0	0.84	1.1	0.15	4.5	0.85	1.1	0.15
Total Phenol	143.8	14.85	4.2	0.48	95.6	10.05	6.0	0.64
Indole	0.6	4.05	0.1	0.44	1.8	11.64	0.4	2.84
3-Methylindole	2.3	0.77	0.2	0.06	0.3	0.09	0.8	0.25
Total Indole	3.0	4.82	0.2	0.49	2.1	11.73	1.2	3.09
Total Odorants	446.8	29.38	375.1	3.97	509.3	29.84	225.7	10.11

[a] OAV, odor activity value: ratio of odorants concentration in air to its odor threshold value. Odor threshold values were taken from Devos et. al. 1990.

Table 3. Average Daily Air Concentrations of Odorants in Swine Building, Control Site, and Downwind (46 m).

	Building Air		**Control Spring**		**DW[q] Spring**		**Control Fall**		**DW Fall**	
Cpd[a]	**$\mu g\ m^{-3}$**	**OAV[p]**	**$\mu g\ m^{-3}$**	**OAV**	**$\mu g\ m^{-3}$**	**OAV**	**$\mu g\ m^{-3}$**	**OAV**	**$\mu g\ m^{-3}$**	**OAV**
AA[b]	21.98	0.06	1.89	0.01	44.13	0.12	3.64	0.01	27.72	0.08
PA[c]	39.31	0.36	0.33	0.00	17.43	0.16	0.35	0.00	75.23	0.69
2MPA[d]	5.00	0.07	0.16	0.00	1.89	0.03	0.14	0.00	1.02	0.01
BA[e]	13.87	0.98	0.11	0.01	11.69	0.83	0.25	0.02	4.47	0.32
3MBA[f]	3.08	0.30	0.13	0.01	9.55	0.93	0.04	0.00	0.95	0.09
PenA[g]	2.10	0.10	0.10	0.00	2.48	0.12	0.06	0.00	1.26	0.06
TVFA[h]	97.50	2.09	2.84	0.02	88.91	2.19	5.97	0.03	112.83	1.26
Phenol	1.91	0.00	0.15	0.00	1.31	0.00	0.11	0.00	0.83	0.00
4MP[i]	1.62	0.20	0.01	0.01	6.92	0.83	0.05	0.01	3.74	0.45
4EP[j]	0.19	0.03	0.04	0.00	0.31	0.05	0.04	0.01	0.84	0.13
TP[k]	3.73	0.23	0.04	0.01	7.59	0.88	0.09	0.02	4.58	0.58
Indole	0.012	0.08	0.00	0.03	0.06	0.41	0.17	1.08	3.42	22.12
3MI[l]	0.003	0.00	0.00	0.00	0.15	0.05	0.08	0.03	0.44	0.15
TI[m]	0.02	0.08	0.01	0.03	0.21	0.46	0.25	1.11	3.86	22.27
TO[n]		2.40		0.06		3.53		1.16		24.11

[a] Cpd, Compound; [b] AA, acetic acid; [c] PA, propanoic acid; [d] 2MPA, 2-methylpropanoic acid; [e] BA, butanoic acid; [f] 3MBA, 3-methylbutanoic acid; [g] PenA, pentanoic acid; [h] TVFA, total volatile fatty acids; [i] 4MP, 4-methylphenol; [j] 4EP, 4-ethylphenol; [k] TP, total phenols; [l] 3MI, 3-methylindole; [m] TI, total indole; [n] TO, total odorants; [o] OAV, odor activity value: ratio of odorants concentration in air to its odor threshold value. Odor threshold values were taken from Devos et. al. 1990; [p] DW, downwind (46 m).

swine pits are both VFAs and phenolic compounds. Key odorants based on high OAVs included butanoic acid, 3-methylbutanoic acid, 4-methylphenol, and indole. Based on total OAV of the swine pits both spring and fall season would have significant more odor events than either summer or early winter.

The swine facility was monitored at several locations for all four season with each sampling lasting approximately one week. Figures 2-5 show average daily concentration levels of both total VFA and total phenolic compounds during each sampling period. These figures show that levels of odorants at the source (pit fan) were approximately an order of magnitude higher than levels measured 46 m downwind from the swine finishing units (Figures 2-4). Compounds measured at control sites of the swine facility (typically south west of the swine buildings) had significantly lower levels of odorants, yet these locations still had higher levels of odorants than non-impacted areas (Figures 2 and 4). These figures show that emission of odors from swine facilities have a diurnal cycles with peak levels occurring in the early morning and late evening hours (Figures 2-4). This is not surprising since stable air patterns are typically associated with early evening, which is typically associated with odor events. This indicates that odor events will predominately occur in the evening hours as has been shown by Wing et al., 2008.

Surprisingly levels of both VFAs and phenolic compounds at the downwind sampling location were a fraction of those measured in either spring or fall, which is different than what occurred in the summer. One potential reason is vertical lift occurring due to heating of the buildings that was strongest in the summer compared to either spring or fall seasons with average

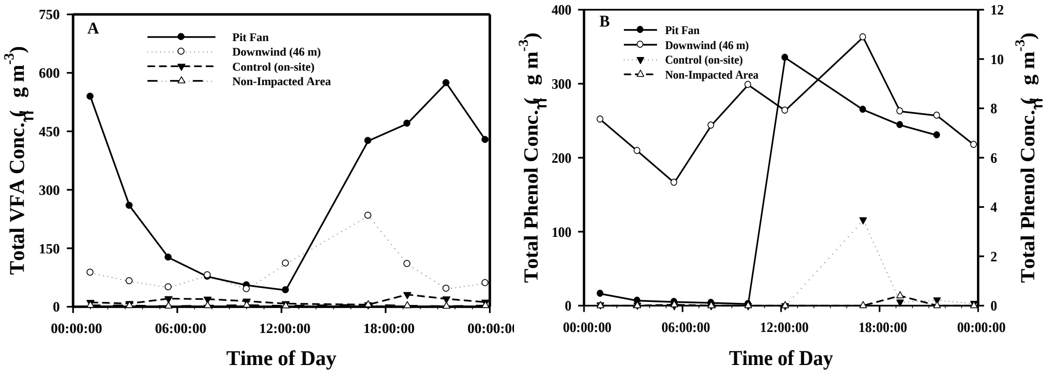

Figure 2. Average daily concentration of total volatile fatty acids and phenols in late Spring 2007: A) Total Fatty acids; B) Total Phenols (pit fan data on left Y axis and all others on right Y axis).

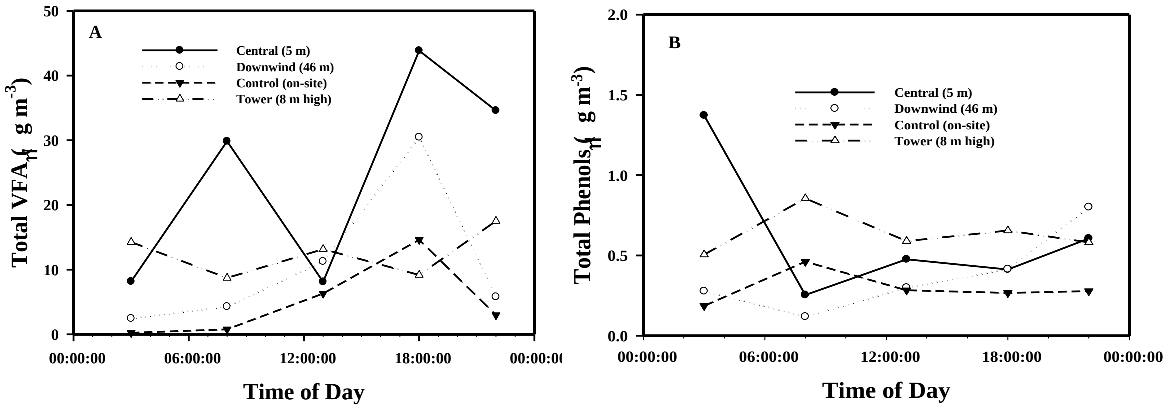

Figure 3. Average daily concentration of total volatile fatty acids and phenols in Summer 2008: A) Total Fatty acids; B) Total Phenols.

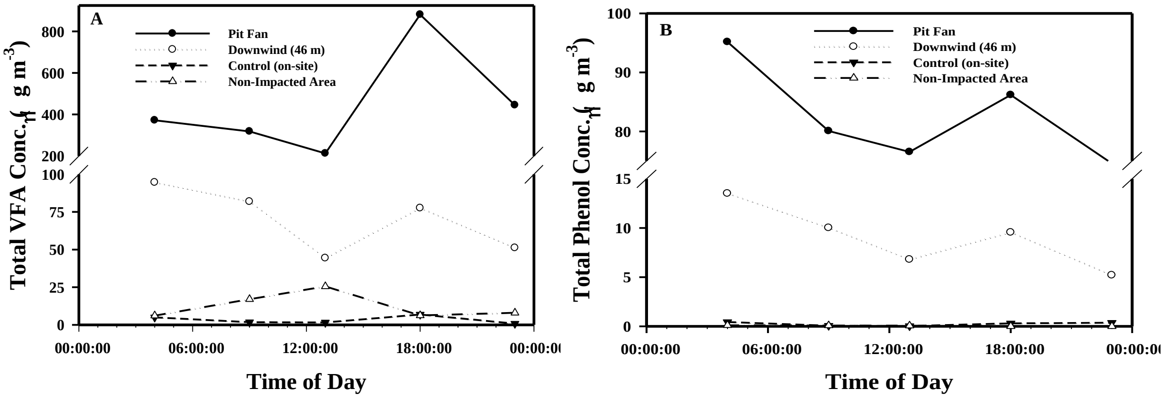

Figure 4. Average daily concentration of total volatile fatty acids and phenols in Fall 2007: A) Total Fatty acids; B) Total Phenols.

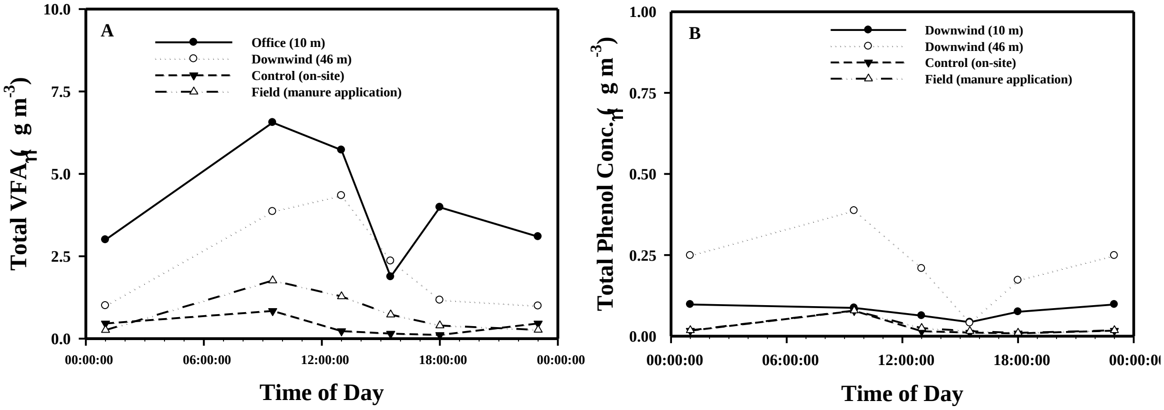

Figure 5. Average daily concentration of total volatile fatty acids and phenols in Winter 2009: A) Total Fatty acids; B) Total Phenols.

temperature differences of 9-12°F. The low levels of odorants measured during the winter pumping of the swine pits was not unexpected given average temperatures between winter and any other season was greater than 50°F. It should also be noted that manure applied to field resulted in little emission due again to low temperatures during its application.

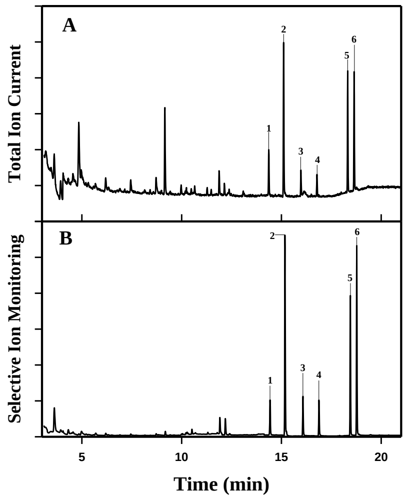

Figure 6. Thermal desorption analysis of evening air one mile downwind of a swine facility in central Iowa: A) Total Ion Current; and B) Selective Ion Monitoring. Compounds identified are as follows: 1) phenol; 2) 4-methylphenol; 3) 4-ethylphenol; 4) 4-propylphenol; 5)indole; and 6) 3-methylindole.

Field samples taken 1 mile north of the facility showed elevated levels of phenol and indole compounds compared to other odorants (Figure 6). While VFAs compounds are typically the highest concentration at the swine facility they are diluted out downwind. Based on OAV both indole and phenol compounds are the most abundant odorants.

Particulate Material

Table 4 is list of concentrations for PM_{10} determined during the different seasons. Particulate matter samplers were taken eight separate times during all four seasons. Samples taken in the spring and summer seasons were estimates since initial mass were not recorded for individual filters prior to deployment in the field, but all filters came from same lot and several remaining filters in the lot were weighed and initial mass were assumed similar. No control samples were taken in either the summer or winter seasons due to loss of access to the non-impacted site. It was surprising that in the summer season downwind concentrations of PM_{10} were higher than those taken between buildings; however, this pattern of downwind location being higher than central location in the summer season was similar to patterns for odorants (Figure 3). This again may be a result of vertical lift occurring due to heating of the buildings that was strongest in the summer compared to either spring or fall seasons.

Elemental analysis of PM_{10} for C, N, and S showed that neither C nor S were significant different between samples taken from either impacted or non-impacted sites. However, N content of PM_{10} showed that impacted areas had a significantly higher amount than non-impacted areas. It is thought that ammonia sorbed to PM_{10} was reason for higher N content.

Table 5 is a compilation of the speciation of major odorants sorbed onto PM_{10}. This table shows that concentration levels of odorants on PM_{10} decrease with distance from a facility and VFAs are the single biggest odorant sorbed to PM_{10}. The patterns of odorants is also similar to patterns of odorants from swine housing area (Figure 1). This pattern suggests that the main source of PM_{10} from a swine facility is swine housing and not the deep pits. Based on OAVs the VFAs are approximately 10 times levels of indole compounds and indole compounds are approximately three fold larger than phenols OAV. This again is in contrast to levels of OAV from deep pits in which each chemical class were similar in terms of total summation of OAVs (Table 2).

Table 4. Average Daily Concentrations of PM_{10} from Swine Facility and Control sites.

	Central[a]	Downwind[b]	Control[c]
	μg m^{-3}		
Spring	74.3	45.9	
Summer	52.7	64.3	
Fall	54.4	38.9	18.3
Winter	9.0	2.8	
Average[d]	60.5	49.7	18.3

[a]Central, PM sampler placed between swine housing units; [b]Downwind, includes PM samplers place both north (46 m) and south (30 m) from the facility; [c]Control, includes PM sampler placed at both south west area of the swine facility or non-impacted area; and [d]Aver age, average concentration of PM_{10} for summer, spring and fall.

Table 5. Average Concentration of Odorants on PM_{10} from swine facility and control sites.

Compound	**Central[a]**	**Downwind[b]**	**Control[c]**
		ng g PM_{10}^{-1}	
Acetic acid	8141.8	5326.7	259.2
Propanoic acid	4524.3	1564.2	49.6
2-Methylpropanoic acid	1314.1	539.5	52.9
Butanoic acid	2776.4	908.2	71.4
3-Methylbutanoic acid	1218.6	474.3	99.3
Pentanoic acid	1484.5	635.5	80.3
Total VFA	22774.7	10945.9	830.9
Phenol	43.8	34.8	5.6
4-Methylphenol	90.2	75.4	2.2
4-Ethylphenol	17.9	9.4	0.2
Total Phenol	152.8	120.1	8.1
Indole	5.1	8.7	0.6
3-Methylindole	5.6	3.0	0.5
Total Indole	10.8	11.7	1.0

[a]Central, PM sampler placed between swine housing units; [b]Downwind, includes PM samplers place both north (46 m) and south (30 m) from the facility, [c]Control, includes PM sampler placed at both south west area of the swine facility or non-impacted area.

Volatile Sulfur Compounds (VSCs)

Monitoring of the swine facility for occurred on three separate occasions two occurring during the fall and one other during the pumping of deep pits. Canister samples were typically placed at the pit fans and unlike VOC samplers canisters always had field personnel present during sampling. During sampling while deep pits were pumped, a field sampler for total reduced sulfur compounds (API-101E, Teledyne Instruments) was used for continuously monitoring purposes.

Initial laboratory studies demonstrated that the canister sampling procedure for VSCs would work; however, in the field moisture severally affected our sampling and analysis technique (Trabue et al., 2008). Additional water scrubs were added, Nafion dryer, for lowering moisture levels to increase VSC stability. It was later realized that ammonia emitted from the swine operations, not to mention other animal feeding operations, negatively impacted the sampling technique: 1) ammonia irreversibly sorbs on the sulfonic acid groups within the Nafion dryer which in turns makes the Nafion dryers useless; and 2) ammonia reacted with the fused silica lining stripping the protective coating from canister surface and dramatically reducing the stability of reactive sulfur compounds with each successive sampling.

Table 6 is a speciation of VSCs at the various sampling dates. Hydrogen sulfide was by far the most abundant VSC during pumping of deep pits and Figure 6 demonstrates the high levels of hydrogen sulfide measured 46 m downwind from the swine building facilities. However, when deep pits were not being pumped methanethiol and carbon disulfide was measured at near or higher OAV levels than hydrogen sulfide (Table 6). Both Tables 2, 3, and 5 show that odor from swine operations is a mixture of both VOCs and VSC.

Table 6. Concentration and Speciation of Volatile Sulfur Compounds from Swine Facility.

	Fall 2006		Fall 2007		Winter 2009 Deep Pit Pumping					
Compound	Deep Pit Fan		Deep Pit Fan		Before Pumping[f]		During Pumping[g]		Deep Pit Fan	
	µg m^{-3}	**OAV**[e]	**µg m^{-3}**	**OAV**	**µg m^{-3}**	**OAV**	**µg m^{-3}**	**OAV**	**µg m^{-3}**	**OAV**
H_2S[a]	44.2	1.8	42.9	1.7	35.8	1.4	6326.0	254.1	1117.8	44.9
Methanethiol	13.4	6.1	1.8	0.8	1.9	0.9	21.1	9.6	4.2	1.9
CS_2[b]	1.3	0.0	0.2	0.0	2.3	0.0	1.6	0.0	0.6	0.0
COS[c]	4.3	0.0	1.8	0.0	7.1	0.1	17.4	0.1	5.0	0.0
DMS[d]	13.5	2.4	0.0	0.0	9.3	1.7	5.5	1.0	1.0	0.2
Total OAV		10.3		2.5		4.1		264.8		47.0

[a]H_2S, hydrogen sulfide; [b]CS_2, carbon disulfide; [c]COS, carbonyl sulfide; [d]DMS, dimethyl sulfide, [e]OAV, odor activity value ; [f]Before pumping, samples taken in animal housing unit before the pumping of the deep pits; [g]During pumping, samples taken in animal housing unit during the pumping of the deep pits.

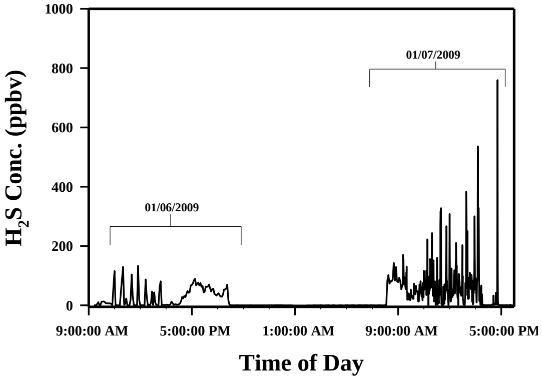

Figure 7. Downwind (46 m) concentration of hydrogen sulfide during pumping of deep pit in Winter 2009.

Discussion:

This study shows that odor from swine feeding operations has both a VOC and VSC component (Tables 2, 3 and 5). Key chemical classes at the swine facility included: VFAs; phenols; indoles; mercaptans; and sulfide compounds. Compounds with OAVs greater than one at the swine facility included: butanoic acid, 3-methylbutanoic acid, 4-methylphenol, indole, hydrogen sulfide, methanethiol, and carbon disulfide, while compounds with OAVs close to one included propanoic acid; 4-ethylphenol; and 3-methylindole. However, at the downwind location, the odor profile changes with the less volatile compounds, phenols and indoles, emerging as the key odorants, while the more volatile compounds (VFAs, mercaptans, and sulfide) were not detected at all. These results compliments the work of both Wright et al. (2005) and Trabue et al. (2009) who showed that both phenol and indole compounds are key odorants from animal feeding operations. In addition our results challenge, the idea that VFA compounds can be used as surrogates for odor (Zahn et al., 2001a,b and Zhu et al., 2002) since these compounds dilute rapidly in the environment after being emitted into the environment. It should be noted that pumping of the deep pits changes everything and that only hydrogen sulfide stands out as the key odorant with OAVs. In addition, our results also show that there is higher odorants concentrations emitted from a swine facility compared to the rural landscape.

Analysis of PM_{10} showed that VFAs concentrations were enriched on PM compared to either phenol or indole compounds compared to concentrations in air. The preference for VFAs over aromatic compounds on PM indicates the surface of PM is potentially lipophilic in nature similar to leaf surfaces (Reischl et al., 1987). The VFAs were by far the most abundant compounds in terms of both concentration levels and OAV. Both Cai et al. (2006) and Razote et al. (2004) showed similar trends in the importance of VFAs on PM; however, Cai et al. (2006) showed that phenol and indole compounds were significant contributors to odor as well. However, based on odorous compound profiles on the PM_{10} material and the concentration of PM_{10} at 46 m downwind location vapor phase concentration of total VFAs would be about 100 times greater than VFAs sorbed to PM_{10} and total phenols would be approximately five orders of magnitude larger in the vapor phase than sorbed onto PM_{10}. All of this suggests that odor is carried mainly in the vapor phase and not sorbed to PM_{10}.

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