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Odor and Odorous Chemical Emissions from Animal Buildings: Part 3. Chemical Emissions

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Abstract

The objective of this study was to measure the long-term odor emissions and corresponding concentrations and emissions of 20 odorous volatile organic compounds (VOCs). This study was an add-on study to the National Air Emission Monitoring Study (NAEMS). Odor and odorous gas measurements at four NAEMS sites, including dairy barns in Wisconsin (WISB) and Indiana (IN5B), a swine finisher barn in Indiana (IN3B), and swine gestation and farrowing barns in Iowa (IA4B), were conducted from November 2007 to May 2009. The odorous gas samples were collected every two weeks using sorbent tubes (samples were collected twice each season of the year, with the exception of spring 2009 when samples were collected three times) and analyzed by gas chromatography-mass spectrometry-olfactometry (GC-MS-O). In this article, we summarize the measured gas concentrations and emissions of the 20 target VOCs from each of the four sites. The average total odorous VOC concentrations for the entire sampling period were 276, 96.9, 1413 and 394 $\mu\text{g dsm}^{-3}$ for WISB, IN5B, IN3B, and IA4B, respectively. For the swine sites, the highest seasonal average total odorous VOC concentrations for each barn were observed during spring ($1890 \mu\text{g dsm}^{-3}$ for IN3B and $458 \mu\text{g dsm}^{-3}$ for IA4B). For the dairy sites, the highest seasonal average total odorous VOC concentrations were observed in winter at WISB ($446 \mu\text{g dsm}^{-3}$) and in summer at IN5B ($129 \mu\text{g dsm}^{-3}$). The average total emission rates for the 20 odorous VOCs were $290 \text{ mg h}^{-1} \text{ AU}^{-1}$ (WISB), $36.0 \text{ mg h}^{-1} \text{ AU}^{-1}$ (IN5B), $743 \text{ mg h}^{-1} \text{ AU}^{-1}$ (IN3B), $33.9 \text{ mg h}^{-1} \text{ AU}^{-1}$ (IA4B swine gestation barns), and $91.7 \text{ mg h}^{-1} \text{ AU}^{-1}$ (IA4B swine farrowing room). The average seasonal total odorous VOC emission rates were highest during summer at WISB ($805 \text{ mg h}^{-1} \text{ AU}^{-1}$), IN5B ($121 \text{ mg h}^{-1} \text{ AU}^{-1}$), and IN3B ($1250 \text{ mg h}^{-1} \text{ AU}^{-1}$) and during spring at IA4B ($95.8 \text{ mg h}^{-1} \text{ AU}^{-1}$). The emissions of specific VOCs varied between seasons, sites, and species. To date, this is the most comprehensive VOC measurement survey of odorous compound emission rates from commercial livestock buildings.

Keywords

Animal feeding operations, Gas chromatography-mass spectrometry, Volatile organic compounds

Disciplines

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Comments

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ODOR AND ODOROUS CHEMICAL EMISSIONS FROM ANIMAL BUILDINGS: PART 3. CHEMICAL EMISSIONS



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ABSTRACT. *The objective of this study was to measure the long-term odor emissions and corresponding concentrations and emissions of 20 odorous volatile organic compounds (VOCs). This study was an add-on study to the National Air Emission Monitoring Study (NAEMS). Odor and odorous gas measurements at four NAEMS sites, including dairy barns in Wisconsin (WI5B) and Indiana (IN5B), a swine finisher barn in Indiana (IN3B), and swine gestation and farrowing barns in Iowa (IA4B), were conducted from November 2007 to May 2009. The odorous gas samples were collected every two weeks using sorbent tubes (samples were collected twice each season of the year, with the exception of spring 2009 when samples were collected three times) and analyzed by gas chromatography-mass spectrometry-olfactometry (GC-MS-O). In this article, we summarize the measured gas concentrations and emissions of the 20 target VOCs from each of the four sites. The average total odorous VOC concentrations for the entire sampling period were 276, 96.9, 1413 and 394 $\mu\text{g dsm}^{-3}$ for WI5B, IN5B, IN3B, and IA4B, respectively. For the swine sites, the highest seasonal average total odorous VOC concentrations for each barn were observed during spring (1890 $\mu\text{g dsm}^{-3}$ for IN3B and 458 $\mu\text{g dsm}^{-3}$ for IA4B). For the dairy sites, the highest seasonal average total odorous VOC concentrations were observed in winter at WI5B (446 $\mu\text{g dsm}^{-3}$) and in summer at IN5B (129 $\mu\text{g dsm}^{-3}$). The average total emission rates for the 20 odorous VOCs were 290 $\text{mg h}^{-1} \text{AU}^{-1}$ (WI5B), 36.0 $\text{mg h}^{-1} \text{AU}^{-1}$ (IN5B), 743 $\text{mg h}^{-1} \text{AU}^{-1}$ (IN3B), 33.9 $\text{mg h}^{-1} \text{AU}^{-1}$ (IA4B swine gestation barns), and 91.7 $\text{mg h}^{-1} \text{AU}^{-1}$ (IA4B swine farrowing room). The average seasonal total odorous VOC emission rates were highest during summer at WI5B (805 $\text{mg h}^{-1} \text{AU}^{-1}$), IN5B (121 $\text{mg h}^{-1} \text{AU}^{-1}$), and IN3B (1250 $\text{mg h}^{-1} \text{AU}^{-1}$) and during spring at IA4B (95.8 $\text{mg h}^{-1} \text{AU}^{-1}$). The emissions of specific VOCs varied between seasons, sites, and species. To date, this is the most comprehensive VOC measurement survey of odorous compound emission rates from commercial livestock buildings.*

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Over the past decade, increasing numbers of large confined animal feeding operations (CAFOs) have been built in the U.S. and other parts of the world. The large number of animals raised in CAFOs can affect air quality with emissions of odor, volatile organic compounds (VOCs) and other gases, and particulate matter (PM) (NRC, 2003). Many studies have focused on monitoring gaseous emissions from CAFOs. However, most of them focused on ammonia (NH_3), hydrogen sulfide (H_2S), and PM measurements (Ni et al., 2002; Argo et al., 2003; Heber et al., 2006). The focus on comprehensive measurements of VOC emissions is relatively new. The National Air Emissions Monitoring Study (NAEMS) is the most recent large agricultural air quality monitoring study focused on CAFOs. Due to the possible health and environmental concerns, airborne emissions from CAFOs are under consideration for regulation by the U.S. EPA through the notification provisions of the Emergency Planning and Community Right-to-Know Act (EPCRA) and the Clean Air Act (CAA). However, the EPA has found it difficult to determine whether CAFOs are in violation of these regulations because of the lack of reli-

able emissions data. Thus, the NAEMS was initiated to improve a baseline emission database (Heber et al., 2008). The NAEMS was financially supported by the pork, dairy, egg, and broiler industries to monitor pollutant emission rates from 24 livestock and poultry production farms and manure storage areas for two years using consistent protocols to quantify aerial pollutant emissions. The NAEMS focused on monitoring emissions of gases including ammonia (NH₃), hydrogen sulfide (H₂S), carbon dioxide (CO₂), methane (CH₄), and other VOCs such as non-methane hydrocarbon compounds as well as total suspended particulates (TSP), PM smaller than 10 μm diameter (PM₁₀), and PM smaller than 2.5 μm diameter (PM_{2.5}) from 14 CAFOs in the egg, broiler, dairy, and swine production industries (Heber et al., 2008). The purpose of the NAEMS was to quantify aerial pollutant emissions and provide the EPA with a scientific basis for the application of existing air pollution regulations to livestock facilities. The NAEMS did not include odor and odorant emission measurements.

A 2003 National Research Council report identified odors as the most significant local air quality issue related to livestock and poultry production (NRC, 2003). Nuisance odors from CAFOs have been implicated as a cause of decreased quality of life (Thu et al., 1997) and reduced property values for surrounding communities (Palmquist et al., 1997). There are three primary sources of odor from livestock operations: (1) livestock housing, (2) manure storage structures, and (3) application of livestock manure to agricultural land (Parker et al., 2013). Odorous compounds emitted from livestock operations are mainly from manure and its decomposition during collection, handling, storage, and spreading (Edeogu et al., 2001; Lau et al., 2003). Decomposition and incomplete digestion of organic matter such as proteins and carbohydrates (Sunesson et al., 2001; Zhu, 2000) produce offensive odorous compounds. These compounds can be divided into four main chemical classes: volatile fatty acids (VFAs) (Mårtensson et al., 1999), aromatic compounds (indoles and phenols), nitrogen-containing compounds (NH₃ and volatile amines) (Hoeksma et al., 1992), and sulfur-containing compounds (mercaptans and sulfides) (Mackie et al., 1998; Zhu, 2000; Whitehead and Cotta, 2004; Lo et al., 2008).

Quantifying odorants emitted from CAFOs is one of the most challenging analytical tasks because of (1) the physical and chemical properties of the analytes, such as high polarity, reactivity and volatility, and ppb-level or lower concentrations; the (2) variability of the ambient air matrix (temperature, relative humidity, and PM); and (3) the difficulty in creating analytical standards for quantification (Wright et al., 2005; McConnell and Trabue, 2006). Some studies have identified and quantified the concentrations of gaseous compounds emitted from swine waste and swine operations (Lo et al., 2008; O'Neill and Phillips, 1992; Zahn et al., 1997; Schiffman et al., 2001; Zahn et al., 2001).

Trabue et al. (2008b) used sorbent tubes packed with Carbo-pack X and Carbo-pack C to collect air samples at approximately 1 m above the floor inside a tunnel-ventilated swine finishing building in Iowa. Using a gas chromatography-mass spectrometry (GC-MS) system to

analyze the samples, they observed that butanoic acid (28.8 μg m⁻³), 4-methylphenol (10.7 μg m⁻³), 4-ethylphenol (0.3 μg m⁻³), indole (0.2 μg m⁻³), and 3-methylindole (0.1 μg m⁻³) were the compounds detected most often above their odor detection threshold values. In another study, Trabue et al. (2008a) quantified volatile sulfur compounds (VSC) including H₂S, carbonyl sulfide, dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and dimethyl trisulfide (DMTS) from the same swine facility and from another swine building with natural ventilation. They used canisters to collect the samples and GC-MS to analyze the samples. Their results showed that H₂S was the only VSC above its odor threshold.

Kim et al. (2007) measured the concentrations of odorous sulfuric compounds in the gestation, farrowing, nursery, growing and fattening stages of pig production in Korea using Tedlar bags and a thermal desorption GC pulsed flame photometric detector (PFPD). Six samplings were taken during each of the moderate seasons in 2004 (spring and fall). The concentration ranges were 30 to 200 ppb for H₂S, 2.5 to 20 ppb for methyl mercaptan (CH₃SH), 1.5 to 12 ppb for DMS, and 0.5 to 7 ppb for DMDS. The researchers also estimated the emission rates of these four sulfur compounds by multiplying the average concentration measured near the air outlet by the mean ventilation rate. The floor area specific emission rates of H₂S, CH₃S, DMS, and DMDS from the pig production rooms were 14 to 64 mg m⁻² h⁻¹, 0.8 to 7.3 mg m⁻² h⁻¹, 0.4 to 3.4 mg m⁻² h⁻¹, and 0.2 to 1.9 mg m⁻² h⁻¹, respectively, and the live mass specific emission rates were 310 to 723 mg AU⁻¹ h⁻¹, 18 to 80 mg AU⁻¹ h⁻¹, 9 to 39 mg AU⁻¹ h⁻¹, and 5 to 22 mg AU⁻¹ h⁻¹, respectively.

Other than Kim et al. (2007), only a few publications have reported VOC emissions from swine barns or from manure storage and treatment. Zahn et al. (2001) measured the VOC emission rates at 29 swine manure management systems located in Iowa (24), Oklahoma (2), and North Carolina (3). Emission values were calculated with the theoretical profile shape micrometeorological method, and the estimated VOC emission rates varied from 0.9 to 23.2 kg VOC site⁻¹ d⁻¹ among different types of swine manure management systems. Bicudo et al. (2004) measured VOC emissions using a floating wind tunnel over the surface of six manure storage ponds. Emissions of three odorants (acetic acid, phenol, and 4-methylphenol) were reported out of ten quantified VOCs. The mean total VOC emissions were 205 and 302 μg s⁻¹ m⁻² in 2000 and 2001, respectively. Amon et al. (2007) measured VOC concentrations in an Australian straw-bedded pig finisher building with three compartments, each with 10 to 12 hogs. They used a VOC analyzer equipped with a flame ionization detector. The concentrations ranged from 50.3 to 176.5 mg d⁻¹ of VOC as methane per kg of pig weight. Emission rates were lower during cold weather (0.3°C to 2.8°C) than warm weather (11.1°C to 20.7°C).

To date, few studies have reported VOC concentrations measured at dairy operations (Mårtensson et al., 1999; Rabaud et al., 2003; Sunesson et al., 2001; Trabue et al., 2008b). Rabaud et al. (2003) identified 35 compounds in

the air from a small dairy located in northern California. The highest concentrations were reported for 1-propanol, butylamine, acetic acid, DMSO, ethyl ether, and methyl isobutyrate (386 to 748 $\mu\text{g m}^{-3}$). Sunesson et al. (2001) identified 70 compounds in the indoor air of buildings at eight dairy farms in northern Sweden. The compounds with the highest concentrations were 4-methylphenol, 2-butanone, ethyl acetate, α -pinene, and Δ^3 -carene, which generally varied from 10 to 200 $\mu\text{g m}^{-3}$. Trabue et al. (2009) quantified eleven odorants including six VFAs, five phenols, and indoles at a cattle feedlot in central Kansas. Field air samples were collected every 4 h over a four-day period in July 2008. Measured concentrations ranged from 0.12 to 33.69 $\mu\text{g m}^{-3}$. Laor et al. (2008) reported initial work characterizing key odorous VOCs associated with dairy manure. To date, there are no published data on odorous VOC emissions from dairy operations.

Quantification of odor and odorous compound emissions from confined CAFOs is necessary in order to (1) determine setback distances to reduce exposure of neighbors to unpleasant odors and nuisance, (2) estimate the emission factors for regulators and air quality management, and (3) determine which sources emit odorous VOCs. Best management practices can then be developed for reducing emissions and odors (Parker et al., 2010). However, the limited data have prevented the scientific community from obtaining a more complete profile of VOC emissions at CAFOs, especially the diurnal and seasonal variations, for developing emission models that estimate and predict the emission rates.

This project was funded by the USDA National Research Initiative (USDA-NRI) and supplemented the NAEMS with comprehensive measurements of odor emissions and chemical analysis of odorous compounds from four selected NAEMS sites, including two swine sites and two dairy sites. The objectives of this project were to (1) determine odor emission factors from the livestock buildings using common protocols and standardized olfactometry, (2) develop a comprehensive chemical library that delineates the most significant odorants and correlate this library with olfactometry results for the selected sites, and (3) disseminate information to stakeholders.

This article is part 3 in a six-part series presenting results from this NRI-funded project. Part 1 presented the project overview and collection methods (Bereznicki et al., 2012). Part 2 reported odor emission factors from four NAEMS sites using dynamic triangular forced-choice olfactometry with human panelists (Akdeniz et al., 2012a). This article (part 3) focuses on measuring odorous VOC concentrations and chemical emission factors using the sorbent tube and thermal desorption GC-MS method. Part 4 addressed correlations between sensory and chemical emissions (Akdeniz et al., 2012b). Part 5 investigated correlations between odor intensities measured with gas chromatography-mass spectrometry-olfactometry (GC-MS-O) and chemical concentrations (Zhang et al., 2015). Part 6 investigated correlations between odor concentrations and odor activity values using multivariate regression methods (Parker et al., 2012). The specific objectives of this article are to (1) iden-

tify the characteristic odorous chemicals related to livestock operations and (2) estimate odorous chemical emission factors from four NAEMS sites. To date, this is the most comprehensive VOC measurement survey of odorous compound emission rates from commercial livestock buildings.

MATERIALS AND METHODS

SITE DESCRIPTIONS

Gaseous samples were collected from November 2007 to May 2009 at four selected NAEMS sites: WI5B (dairy), IN5B (dairy), IN3B (swine finishing), and IA4B (sow gestation and farrowing). Detailed farm descriptions and sample collection and analyses techniques are presented in Part 1 of this series of articles (Bereznicki et al., 2012). Brief descriptions of these four sites are as follows:

Site WI5B was a dairy farm in Wisconsin consisting of two freestall barns with pine shaving and sand bedding and, initially, a manure flushing system. Flushing was replaced by scraping in September 2008. The barns were ventilated with a crossflow system. The barn capacities were 275 and 375 cows for barns 1 and 2, respectively. Barn 1 had dimensions of 93 m \times 28 m, and barn 2 had dimensions of 107 m \times 30 m.

Site IN5B was a dairy farm in Indiana consisting of two freestall barns with digested manure solids as bedding and a scrape manure removal system. The 472 m \times 29 m barns were tunnel-ventilated. Each barn had a capacity of 1500 to 1700 cows.

Site IN3B was a swine finishing farm in Indiana consisting of two quad barns with deep pits. Barns 1 and 2 at IN3B corresponded to two of the four rooms in one of the quad barns. Total capacity per quad barn was 4000 head, with 1000 head per room. The barns were tunnel-ventilated with room dimensions 61 m \times 12 m. The barns had concrete slatted floors. Air samples were collected at the pit fans rather than the wall fans, as was the case at IA4B (Bereznicki et al., 2012). The pit fans were always on, even in winter, whereas the wall fans cycled on and off.

Site IA4B was a sow gestation and farrowing farm in central Iowa consisting of two 1100-head gestation buildings (barns 1 and 2) with slatted concrete floors and deep pits and one 16-room farrowing room (barn 3) with 24 stalls, plastic-coated steel mesh flooring, and pull-plug shallow pits. All barns were tunnel-ventilated. The dimensions of barns 1 and 2 were 86 m \times 25 m, and the barn 3 farrowing room had dimensions of 21.3 m \times 6.5 m.

Barn areas of the sites were as follows: 2604 m² (barn 1) and 3210 m² (barn 2) at WI5B, 13,688 m² (barns 1 and 2) at IN5B, 732 m² (rooms 1 and 2) at IN3B, and 2150 m² (barns 1 and 2) and 138.5 m² (barn 3) at IA4B.

SAMPLE COLLECTION AND ANALYSES

Data collection began in November 2007 and was completed in May 2009, for a total duration of 17 months. Sampling times were divided into seasons of 4 to 13 weeks each, defined as follows:

- Winter 2008 (4 Dec. 2007 to 31 Jan. 2008)

- Spring 2008 (26 March to 29 May 2008)
- Summer 2008 (28 July to 9 Sept. 2008)
- Fall 2008 (22 Oct. to 9 Dec. 2008)
- Winter 2009 (20 Jan. to 24 Feb. 2009)
- Spring 2009 (10 March to 7 May 2009).

Gaseous samples were collected biweekly, with two sites sampled one week and the other two sites the next week. Samples were collected twice each season and each year, with the exception of spring 2009 when samples were collected three times. Each sample collection event included sampling from one inlet and one exhaust per barn (total of two barn samples) at sites W15B, IN5B, and IN3B. Additionally, one barn exhaust sample was collected from the farrowing room at IA4B, for a total of three barn samples and one inlet sample. Decisions about specific sample locations at each farm were consistent with the NAEMS project and were driven by the need to ensure that the sampling locations were representative of emissions. Specific criteria used for VOC sampling included: exhaust fan was always on (not cycling on/off), composite groups would be more representative of a specific location (e.g., pit fan group), and judicious use of limited resources. Detailed descriptions of each farm are presented by Bereznicki et al. (2012), including barn and management characteristics, site layout and sampling port locations, and characteristics of the three sampling regimes. All samples were collected between 7:00 a.m. and 4:00 p.m. local daylight time, (eastern daylight time for IN5B and IN3B, and central daylight time for W15B and IA4B) (Bereznicki et al., 2012). Diurnal variations were not within the scope of this study.

The field air samples were collected by sampling air through sorbent tubes (Zhang et al., 2010) from a manifold using a portable sampling pump (model 210-1002, SKC, Inc., Houston, Tex.) with a flow rate of 70 mL min⁻¹ for 60 min. The sample was delivered to the manifold by a multipoint gas sampling system (GSS) that drew air sequentially from representative locations in the barns, rooms, and outside. The sampling locations at each site were chosen to represent the background inlet (or ambient) air and the ventilation barn exhaust air at each site. Selection of all sampling locations for a GSS was controlled by a computerized data acquisition program (Ni et al., 2009).

Sorbent tubes (93 mm × 4 mm) were constructed of 304-grade stainless steel and double-passivated with a proprietary surface coating process (Zhang et al., 2010). The empty tubes were packed with 65 mg of Tenax TA (Supelco, Inc., Bellefonte, Pa.) and plugged at both ends with silanized glass wool and stainless steel screens to hold the sorbent material. Before the first use, the sorbent tubes were conditioned by thermal desorption (260°C for 5 h) with an N₂ flow rate of 100 mL min⁻¹. After conditioning and before each use, blank chromatograms of the sorbent tubes were investigated. For subsequent use, pre-conditioning at 260°C for 30 min was determined to be sufficient and was used for the entire study. Clean individual tubes were wrapped in aluminum foil. All tubes were placed in clean glass jars, sealed, and stored in a cooler during transit to and from the sampling sites.

For each sample collection event and each site, an addi-

tional tube was connected in series with the sampling tube. This was done to check for possible breakthroughs of compounds during sampling, which could compromise the results. A trip blank tube was also included for each sampling event for quality control and quality assurance. The sampling flow rates were checked with an NIST-traceable digital flowmeter (Bios International, Butler, N.J.). After sampling, the sorbent tubes were wrapped in aluminum foil and stored in a cooler for shipping to the Atmospheric Air Quality Laboratory at Iowa State University for analyses.

Twenty compounds were selected as the target odorants for quantification, including sulfur-containing compounds (DMDS, diethyl disulfide, DMTS, dimethyl sulfoxide, and dimethyl sulfone), VFAs (acetic, propanoic, isobutanoic, butanoic, isopentanoic, pentanoic, hexanoic, and heptanoic acids), phenolics (2-methoxyphenol, phenol, 4-methylphenol, 4-ethylphenol, and 1-(2-aminophenyl)ethanone), and indolics (indole and 3-methylindole). The selection of characteristic odorous compounds from CAFOs was based on previous studies (Mackie, 1998; Zhu, 2000; Whitehead and Cotta, 2004; Koziel et al., 2006; Bulliner et al., 2006). The measurements of 15 odorous compounds including VFAs, phenols, and indolics began in November 2007. Air sampling and analysis followed the method described by Zhang et al. (2010). The analysis of five sulfur-containing compounds was added in January 2009 using the same approach (Zhang et al., 2010). The standard solutions for gas standards were prepared by diluting stock solutions in methanol and stored at 4°C in the dark. The stock standard solutions of odorous compounds were prepared by adding known masses of pure target chemicals into a 40 mL pre-cleaned vial and then filling the vial with a known mass of methanol. Calibration of the sorbent tube method was performed as follows: 5 or 10 µL of the standard solution was spiked into a sorbent tube using an ATIS adsorbent tube injector system (Supelco, Inc.) and N₂ diluent flow of 50 mL min⁻¹. Validation of the thermal desorption-multidimensional gas chromatography-mass spectrometry (TD-MDGC-MS) method showed excellent sample recovery, selectivity, sensitivity, and precision. Gas standard sample recoveries from the sorbent material for ranged from 95.9% to 99.9%, from 95.4% to 99.5%, and from 97.7% to 102.5% for sulfur VOCs, VFAs, and phenolics, respectively. Average RSDs for seven-point calibrations for sulfur VOCs ranged from 1.4% to 7.1% with R² > 0.999, and limits of quantification ranged from 0.58 to 0.82 ng. Average RSDs for seven-point calibrations for VFAs ranged from 2.5% to 4.7% with R² > 0.998, and limits of quantification ranged from 0.01 to 0.04 ng. Average RSDs for seven-point calibrations for phenolics ranged from 2.2% to 4.2% with R² > 0.998, and limits of quantification ranged from 0.007 to 0.05 ng.

SAMPLE ANALYSES WITH TD-MDGC-MS OLFACTOMETRY

Simultaneous chemical and sensory analyses of live-stock odorants were conducted using a TD-MDGC-MS olfactometry (TD-MDGC-MS-O) system. The TD system consisted of a Model 3200 automated thermal desorption inlet for an Agilent 6890 GC developed by Microanalytics

(Round Rock, Tex.) based on a PAL autosampler (Zhang et al., 2010). The multidimensional GC-MS-O (Microanalytics) was equipped with two columns connected in series. The non-polar pre-column was 12 m, 0.53 mm i.d., and 1 µm film thickness, with 5% phenylmethylpolysiloxane stationary phase (BP5, SGE Analytical Science) and operated with constant pressure mode at 8.5 psi. The polar analytical column was a 25 m × 0.53 mm fused silica capillary column coated with polyethylene glycol (BP20 wax, SGE Analytical Science) at a film thickness of 1 µm. The column pressure was constant at 5.8 psi.

The system automation and data acquisition software included MultiTrax ver. 6.00, AromaTrax ver. 7.02 (Microanalytics) and ChemStation (Agilent Technologies, Santa Clara, Cal.). The general GC run parameters used were as follows: injector temperature of 260°C; flame ionization detector (FID) temperature of 280°C; column temperature of 40°C initial, 3 min hold, 7°C min⁻¹ ramp, 220°C final, and 10 min hold; and the carrier gas was GC-grade helium. The GC was operated in a constant pressure mode where the mid-point pressure, i.e., the pressure between pre-column and column, was always at 5.8 psi, and the heart-cut sweep pressure was 5.0 psi. The MS scan range was 33 to 280 m/z. Spectra were collected at 6 scans s⁻¹ using scan and selective ion monitoring (SIM) simultaneously. The electron multiplier voltage was set to 2700 V. MS tuning was performed daily using the default autotune setting and perfluorotributylamine (PFTBA).

Odor character, odor intensity, and hedonic tone of the target odorants were also analyzed simultaneously using the sniffing port on the GC-MS-O. The results are presented in Part 5 of this series (Zhang et al., 2015). A human panelist assessed the odor of each of the separated compounds (at the sniff port) simultaneously with chemical analyses. Odor caused by separated VOCs was evaluated with a 64-descriptor odor character panel, odor intensity scale, and odor hedonic tone scale with AromaTrax software (Microanalytics) summarizing this information in aromagrams.

EMISSION RATE ESTIMATION

The actual VOC concentration (µg m⁻³) was calculated using mass (ng) estimated with a calibrated MS detector divided by actual sampling volume (L) measured for each sample. The standard mass-based concentration was converted from the actual gas concentration according to equation 1:

$$C' = \frac{P'}{P_0} \times \frac{(273 + T_0)}{(273 + T')} \times C \quad (1)$$

where

C' = standard mass-based concentration, moist-air basis (µg sm⁻³)

P' = standard pressure (1 atm)

T' = standard temperature (20°C)

C = actual mass concentration (µg m⁻³)

P_0 = actual pressure (atm)

T_0 = temperature at sampling location (°C).

The dry standard concentration reported in this article was calculated according to equation 2:

$$C'' = \frac{C'}{(1 - W)} \quad (2)$$

where

C'' = dry standard mass concentration dry basis (µg dsm⁻³)

W = humidity ratio calculated with equation 3 (ASHRAE, 2013; Hoff et al., 2009):

$$W = 0.62198 \frac{e^{f(T)} \phi}{P_{act} - e^{f(T)} \phi} \quad (3)$$

where

W = humidity ratio (kg water kg⁻¹ dry air)

P_{act} = pressure at the sampling location (Pa)

ϕ = relative humidity (decimal).

For cases where $T < 273.15$ K:

$$f(T) = \frac{C_1}{T} + C_2 + C_3 T + C_4 T^2 + C_5 T^3 + C_6 T^4 + C_7 \ln T \quad (4)$$

For cases where $T > 273.16$ K:

$$f(T) = \frac{C_8}{T} + C_9 + C_{10} T + C_{11} T^2 + C_{12} T^3 + C_{13} \ln T \quad (5)$$

where

$C_1 = -5.565 \times 10^3$, $C_2 = 6.392$,

$C_3 = -9.678 \times 10^{-3}$, $C_4 = 6.222 \times 10^{-7}$,

$C_5 = 2.075 \times 10^{-9}$, $C_6 = -9.484 \times 10^{-13}$,

$C_7 = 4.163$, $C_8 = -5.800 \times 10^3$, $C_9 = 1.391$,

$C_{10} = -4.864 \times 10^{-2}$, $C_{11} = 4.176 \times 10^{-5}$,

$C_{12} = -1.445 \times 10^{-8}$, and $C_{13} = 6.545$

(ASHRAE, 2013; Hoff et al., 2009).

The emission rate for a barn was calculated as a product of ventilation rate (dsm³ h⁻¹, the volume of air exiting the barn per hour) and net VOC concentration (µg dsm⁻³, specifically, the concentration difference between exhaust and inlet air) on dry air basis:

$$E = Q \times (C'' - C''_0) / 1000 \quad (6)$$

where

E = barn emission rate (mg h⁻¹)

Q = barn outlet dry standard airflow (dsm³ h⁻¹) (calculated after Hoff et al., 2009)

C'' = exhaust air dry standard concentration (µg dsm⁻³)

C''_0 = air inlet dry standard concentration (µg dsm⁻³).

Barn ventilation rates were measured at each site using *in situ* calibrated fan curves from a Fan Assessment Numeration System (FANS, University of Kentucky, Lexington, Ky.) (Gates et al., 2004) with continuously measured differential static pressures. Emission rates are expressed as mass per hour per animal unit (mg h⁻¹ AU⁻¹, where AU is 500 kg of animal weight), mass per hour per head (mg h⁻¹ head⁻¹), and mass per hour per barn floor area (mg h⁻¹ m⁻²).

STATISTICAL ANALYSIS

The emissions of each VOC were analyzed for statistical significance of variations between sites, species, and season. The site variable was a main factor with two levels: (1) WI5B vs. IN5B or IA4B vs. IN3B for same species comparison and (2) WI5B + IN5B (dairy) vs. IA4B + IN3B (swine) for different species comparison. The emissions from the two barns at each site were considered in each block. SAS for Windows (ver. 8.02, SAS Institute Inc., Cary, N.C.) was used with split-block in time (season) analysis. The analysis was composed of two parts: the treatment part and the time part. The model developed by Sun et al. (2010) was used:

$$Y_{ijk} = u + (\rho_i + \alpha_j + \epsilon_{ij}) + \beta_k + (\alpha\beta)_{jk} + \epsilon_{ijk} \quad (7)$$

where Y_{ijk} is the compound emission rate, u is the overall mean, ρ_i is the block effect, α_j is the effect of main factor A (site), ϵ_{ij} is the random effect of the whole-plot units involving main factor A, β_k is the effect of the repeated measure (season), $(\alpha\beta)_{jk}$ is the interaction effect for site and season, and ϵ_{ijk} is the random effect of time.

It was assumed that there was equal variance for random effects among both subjects and across time intervals. Both PROC MIX and PROC GLM in SAS were used to evaluate significant differences (at the 5% level) between the sites for each VOC emission rate. Fifteen odorous VOCs including eight VFAs and seven phenolics and indolics were con-

sidered in the statistical analysis. Five sulfur-containing compounds were not included due to the lack of replicate data (i.e., quantification was added later in the study).

RESULTS AND DISCUSSION

ODOROUS VOC CONCENTRATIONS

The 20 odorous compounds were quantified including eight VFAs, seven phenolics and indolics, and five sulfur-containing compounds. Average measured concentrations at four sites from November 2007 to May 2009 are listed in table 1. The measured VFA concentrations were typically greater than the concentrations of phenolic and sulfur VOCs. The concentrations of VFAs were typically inversely proportional to their molecular weight. Significant seasonal variations in measured concentrations were observed at each site over the 17-month study (fig. 1). The seasonal variations for total odorous compound concentrations (TOCC) for each site over the 17-month period are shown in figure 1. Each data point for total odorant concentration is the sum of the concentrations of the 20 target odorants on each sampling date at each barn. The TOCC at the swine sites were typically higher than those at the dairy sites.

UNCERTAINTY RELATED TO DIMETHYL DISULFIDE AND DIMETHYL TRISULFIDE

Andersen et al. (2012) showed that methanethiol (MT) can convert to dimethyl disulfide (DMDS) and dimethyl

Table 1. Average dry standard mass concentrations ($\mu\text{g dsm}^{-3}$, standard deviations in parentheses) of 20 individual VOCs measured at the four sites (Amb = ambient, B1 = barn 1, B2 = barn 2, B3 = barn 3, and ND = not detected). Total sampling events were $n = 13$ for each sampling location at each site except IN5B, where $n = 12$.

Compound	WI5B Dairy Site			IN5B Dairy Site			IN3B Swine Finisher Site			IA4B Swine Sow Site			
	Amb	B1	B2	Amb	B1	B2	Amb	B1	B2	Amb	B1	B2	B3
Acetic acid	50.4 (± 31.5)	178 (± 185)	186 (± 294)	27.8 (± 19.9)	48.9 (± 29.8)	47.6 (± 24.9)	32.6 (± 34.5)	264 (± 353)	203 (± 116)	20.4 (± 14.5)	64.5 (± 40.9)	76.9 (± 56.8)	74.2 (± 65.8)
Propanoic acid	4.13 (± 2.88)	42.9 (± 31.8)	49.5 (± 63.3)	3.14 (± 1.60)	19.0 (± 18.0)	32.6 (± 32.8)	15.2 (± 12.1)	392 (± 438)	403 (± 303)	4.85 (± 5.70)	49.7 (± 33.0)	75.9 (± 49.8)	97.2 (± 100)
2-methyl propanoic acid	1.29 (± 1.78)	7.24 (± 7.88)	3.60 (± 4.26)	0.890 (± 1.60)	1.23 (± 1.52)	1.03 (± 1.55)	2.84 (± 3.48)	56.4 (± 54.1)	54.8 (± 34.8)	1.38 (± 1.87)	10.6 (± 4.64)	15.4 (± 18.7)	22.2 (± 19.1)
Butyric acid	3.06 (± 3.18)	17.5 (± 13.8)	12.7 (± 10.4)	1.99 (± 2.58)	4.45 (± 4.22)	7.59 (± 7.79)	16.9 (± 16.7)	394 (± 428)	403 (± 249)	3.01 (± 3.29)	31.9 (± 17.1)	50.4 (± 44.3)	172 (± 173)
3-methyl butanoic acid	1.25 (± 2.03)	5.46 (± 5.49)	2.72 (± 3.45)	1.10 (± 2.05)	1.34 (± 1.93)	1.86 (± 2.79)	3.81 (± 5.05)	56.0 (± 55.7)	56.6 (± 33.2)	1.40 (± 2.08)	13.5 (± 9.33)	21.2 (± 30.7)	24.4 (± 19.3)
Pentanoic acid	1.70 (± 2.60)	6.87 (± 9.97)	2.10 (± 2.83)	1.51 (± 2.98)	1.55 (± 2.67)	1.83 (± 3.11)	4.55 (± 5.65)	84.6 (± 101)	85.5 (± 67.8)	1.59 (± 2.45)	6.31 (± 4.81)	9.06 (± 8.91)	40.9 (± 42.7)
Hexanoic acid	1.90 (± 2.55)	6.44 (± 8.79)	2.27 (± 3.01)	1.81 (± 4.77)	1.63 (± 3.19)	2.12 (± 3.79)	3.09 (± 5.97)	17.6 (± 18.9)	19.1 (± 14.8)	1.15 (± 1.85)	3.02 (± 3.74)	3.84 (± 4.52)	91.9 (± 113)
Heptanoic acid	0.060 (± 0.22)	0.109 (± 0.206)	0.089 (± 0.174)	0.020 (± 0.028)	0.067 (± 0.132)	0.076 (± 0.113)	0.321 (± 0.347)	6.06 (± 8.32)	6.38 (± 7.24)	0.057 (± 0.138)	0.564 (± 0.521)	0.371 (± 0.398)	0.353 (± 0.367)
2-methoxyphenol	0.851 (± 2.73)	5.43 (± 11.1)	0.789 (± 2.66)	1.42 (± 3.26)	0.767 (± 2.60)	0.761 (± 2.59)	0.777 (± 2.48)	6.45 (± 11.5)	4.64 (± 9.21)	1.52 (± 3.57)	1.79 (± 4.09)	1.55 (± 3.61)	3.95 (± 9.70)
Phenol	1.06 (± 0.694)	4.84 (± 5.19)	2.13 (± 1.81)	1.25 (± 0.833)	2.20 (± 2.32)	3.18 (± 2.57)	2.01 (± 1.45)	14.1 (± 13.0)	17.0 (± 15.2)	1.26 (± 0.904)	7.45 (± 4.75)	6.09 (± 5.50)	8.36 (± 4.77)
4-methylphenol	0.407 (± 0.420)	4.48 (± 3.36)	2.82 (± 2.98)	0.597 (± 0.412)	3.83 (± 3.57)	6.66 (± 6.95)	4.51 (± 4.82)	86.3 (± 89.1)	135 (± 119)	0.469 (± 0.329)	73.3 (± 59.1)	59.5 (± 80.0)	28.8 (± 13.7)
4-ethylphenol	0.0220 (± 0.0263)	1.11 (± 2.26)	0.280 (± 0.525)	0.384 (± 0.652)	0.895 (± 0.821)	1.15 (± 1.42)	0.491 (± 0.754)	6.55 (± 8.02)	7.42 (± 8.96)	0.305 (± 0.650)	4.88 (± 3.86)	5.11 (± 5.11)	3.60 (± 1.98)
1-(2-aminophenyl)-ethanone	0.00366 (± 0.00650)	0.937 (± 2.27)	0.00634 (± 0.0106)	0.551 (± 1.90)	0.00423 (± 0.00751)	0.00220 (± 0.0111)	0.00931 (± 2.43)	1.07 (± 3.15)	2.23 (± 3.08)	1.87 (± 1.82)	0.534 (± 2.79)	1.39 (± 2.60)	1.39 (± 2.36)
Indole	0.00478 (± 0.00602)	0.631 (± 1.52)	0.00591 (± 0.00949)	0.00221 (± 0.00359)	0.0119 (± 0.0136)	0.0248 (± 0.0337)	0.0717 (± 0.156)	2.95 (± 3.37)	3.16 (± 3.94)	0.0473 (± 0.156)	0.924 (± 0.716)	0.757 (± 1.03)	1.26 (± 1.22)
3-methylindole	0.00356 (± 0.00990)	0.518 (± 1.26)	0.00232 (± 0.00335)	0.00203 (± 0.00390)	0.00220 (± 0.00390)	0.00698 (± 0.0137)	3.45 (± 5.11)	3.45 (± 5.01)	5.47 (± 8.87)	1.46 (± 0.521)	3.27 (± 2.91)	3.06 (± 5.70)	1.28 (± 1.36)
Dimethyl disulfide ^[a]	0.182 (± 0.330)	0.657 (± 0.236)	0.391 (± 0.090)	0.116 (± 0.0655)	0.399 (± 0.407)	0.427 (± 0.205)	0.847 (± 0.863)	4.10 (± 2.81)	2.90 (± 1.79)	0.0290 (± 0.0648)	0.612 (± 0.353)	0.533 (± 0.215)	2.60 (± 0.766)
Diethyl disulfide	1.47 (± 2.86)	0.910 (± 1.61)	0.641 (± 1.04)	0.0720 (± 0.140)	0.00402 (± 0.00805)	0.0482 (± 0.0963)	2.56 (± 4.15)	2.23 (± 3.89)	2.38 (± 4.09)	0.357 (± 0.793)	0.444 (± 1.07)	0.558 (± 1.21)	0.311 (± 0.549)
Dimethyl trisulfide ^[a]	ND	0.0274 (± 0.0215)	0.0195 (± 0.0145)	0.00532 (± 0.0106)	ND	0.00668 (± 0.00855)	0.00563 (± 0.0138)	0.0719 (± 0.0528)	0.0530 (± 0.0558)	ND	0.0121 (± 0.0108)	0.0106 (± 0.00330)	0.0134 (± 0.0217)
Dimethyl sulfoxide	0.0363 (± 0.0726)	0.379 (± 0.251)	0.142 (± 0.118)	0.0264 (± 0.0203)	0.0107 (± 0.0120)	0.212 (± 0.350)	0.306 (± 0.528)	0.190 (± 0.118)	0.450 (± 0.607)	0.019 (± 0.043)	0.0215 (± 0.0245)	0.0368 (± 0.0299)	0.0324 (± 0.0170)
Dimethyl sulfone	0.108 (± 0.083)	0.356 (± 0.102)	0.300 (± 0.090)	0.0496 (± 0.0367)	0.0374 (± 0.0503)	0.0855 (± 0.0689)	0.458 (± 0.365)	8.56 (± 9.36)	6.03 (± 5.09)	0.0483 (± 0.156)	1.24 (± 0.712)	1.64 (± 1.02)	0.733 (± 1.21)

^[a] Measured DMDS and DMTS concentrations and emissions could be confounded by conversion of methanethiol into DMDS and DMTS.

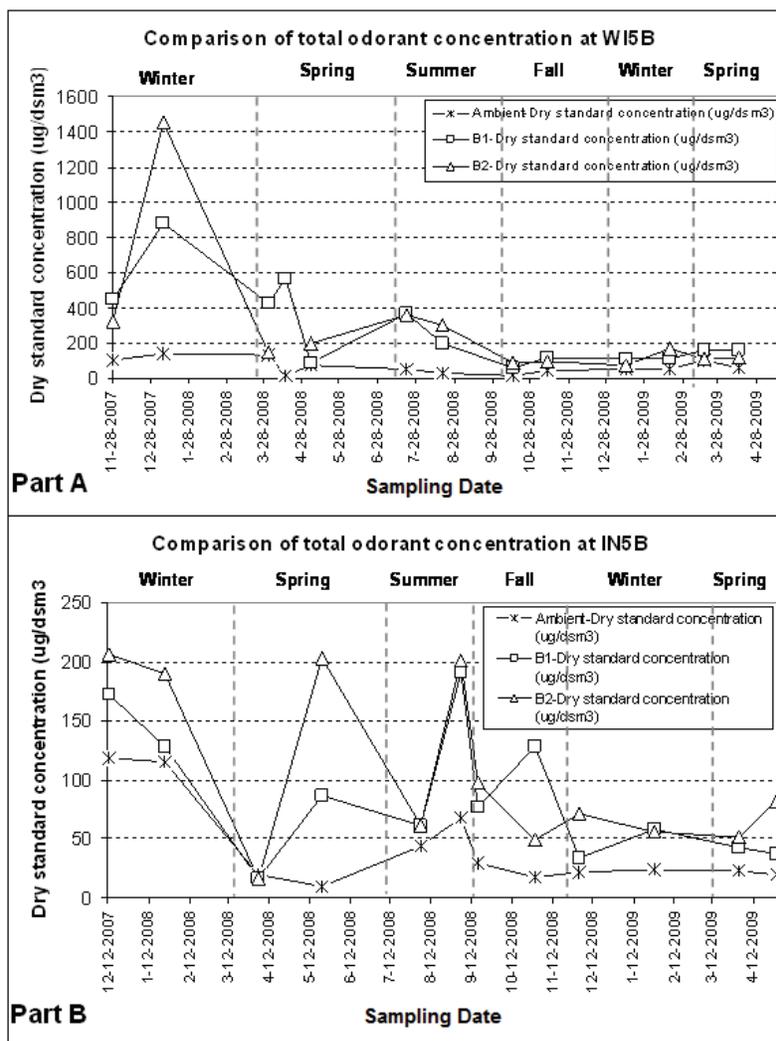


Figure 1. Seasonal variations of total odorous compound concentrations (TOCC) over a 17-month period at four sites: Part A = Wisconsin dairy site WI5B, and Part B = Indiana dairy site IN5B (B1 = barn 1, B2 = barn 2, and B3 = barn 3).

trisulfide (DMTS) using sorbent tubes and thermal desorption. An additional experiment was conducted after this project to determine the extent of MT conversion to DMDS or DMTS using moist air and dry air. It was determined that complete conversion of MT to DMDS (97.5% to 99.5%) and DMTS (0.5% to 2.5%) is possible for moist standard gas stored on sorbent tubes for 1 to 3 days. Conversion of MT in dry air was slower. It is not possible to determine the extent of the MT conversion with field air samples nor to determine the exact fraction of DMDS or DMTS that resulted from MT conversion. Liu et al. (2011) and Feilberg et al. (2010) measured MT at 2 to 4 ppb (~7.8 to 15.6 $\mu\text{g m}^{-3}$) in the exhaust air of swine research farms using a PTR-MS approach that is not affected by this conversion. Assuming that a similar range of MT concentrations was present at the swine barn exhaust in this research and that storage of MT on sorbent tubes was affected by dimerization, the resulting DMDS and DMTS concentrations were greater than those reported in table 1. Thus, caution should be exercised in interpreting the measured DMDS and DMTS concentrations as emissions, as they are likely confounded by conversion of MT.

For the swine sites, the TOCC at each barn for each season were highest during spring, with average concentrations of 1890 and 458 $\mu\text{g dsm}^{-3}$ at IN3B and IA4B, respectively. For the dairy sites, the total concentration at WI5B was highest during winter (446 $\mu\text{g dsm}^{-3}$), whereas the highest concentration at IN5B was in summer (129 $\mu\text{g dsm}^{-3}$). Higher concentrations during spring at the swine sites could potentially be attributed to the manure accumulation in the deep pit and to the age and weight of the animals housed in the barn at IN3B. The average TOCC for WI5B, IN5B, IN3B, and IA4B were 276, 96.9, 1413, and 394 $\mu\text{g dsm}^{-3}$, respectively. For the dairy sites, the total odorous VOC concentration at WI5B was approximately three times higher than at IN5B. For the swine sites, the total odorous VOC concentration at IN3B was more than three times higher than at IA4B. This was likely because the air samples at IN3B were collected from pit exhaust fans, whereas the air samples at IA4B were collected from wall exhaust fans. The VFA concentrations were predominant among all other odorous VOC groups (i.e., phenolics, indolics, VSCs) measured in this study for all four sites. For the swine sites (IN3B and IA4B), the average total VFA concentrations from the barn exhaust

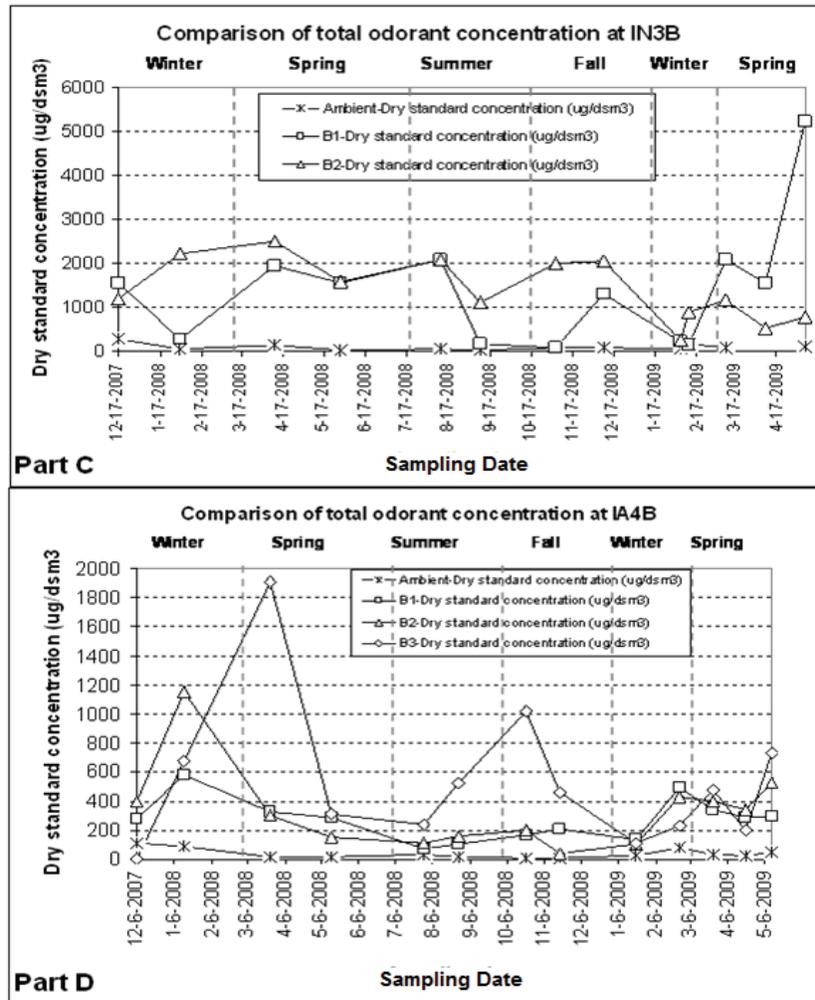


Figure 1 (continued). Seasonal variations of total odorous compound concentrations (TOCC) over a 17-month period at four sites: Part C = Indiana swine finisher site IN3B, and Part D = Iowa sow gestation and farrowing site IA4B (B1 = barn 1, B2 = barn 2, and B3 = barn 3).

fans were 1250 and 321 $\mu\text{g dsm}^{-3}$, respectively. For the dairy sites (WI5B and IN5B), the average total VFA concentration were 265 and 87 $\mu\text{g dsm}^{-3}$, respectively. The total VFA concentrations at the inlet air (ambient) for all four sites ranged between 35 and 80 $\mu\text{g dsm}^{-3}$. A comparison of total VFA concentrations between the different barns for the four sites is shown in figure 2.

The total VFA concentrations were significantly higher at the swine sites (especially at IN3B, the swine finisher site) than at the dairy sites. The total indolics and phenolics concentrations and the total VSC concentrations followed the same trends as the VFA concentrations between four sites. Among seven phenolic and indolic compounds, 4-methylphenol was the most abundant compound in the exhaust air at the swine and dairy sites, and its concentrations were well above its odor detection threshold (Devos et al., 1990; Parker et al., 2012). The compound 4-methylphenol has been identified as a key priority odorant inside swine facilities, downwind of beef cattle feedyards, and from land-applied swine manure (Wright et al., 2005; Koziel et al., 2006; Bulliner et al., 2006; Trabue et al., 2008b; Parker et al., 2012). Compared with VFAs and phenolic and indolic compounds, five VSCs were

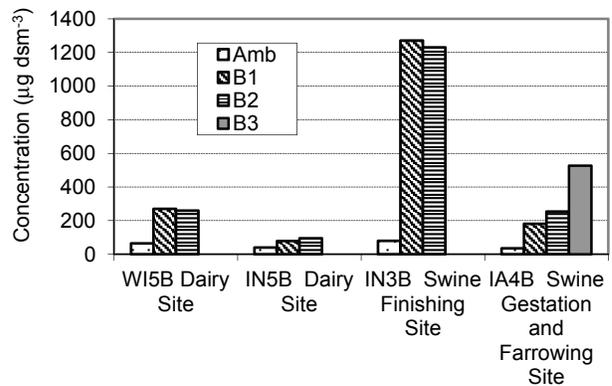


Figure 2. Comparison of average total VFA concentrations between four sites (Amb = ambient, B1 = barn 1, B2 = barn 2, and B3 = barn 3).

measured at relatively lower concentrations. Only DMDS was often above its odor detection threshold (Parker et al., 2012).

Among the eight VFAs, the short-chain VFAs (acetic, propanoic, 2-methyl propanoic, and butanoic acids) were measured at higher concentrations. This result is consistent

with the findings for VFA concentrations in swine odor (Mackie et al., 1998). Trabue et al. (2008b) also reported that acetic, propanoic, and butanoic acids were often the most abundant compounds on a mass basis inside swine facilities. VFAs originate in part from amino acid deamination by anaerobic bacteria in the gastrointestinal tract and feces (Mackie et al., 1998). Production of certain VFAs also results from anaerobic microbial fermentation of soluble carbohydrates (Mackie et al., 1998). Previous research (Imoto and Namioka, 1978) found the proportion of VFAs in pig feces to be about 50:40:10 for acetate, propionate, and butyrate, respectively, for pigs fed both low- and high-carbohydrate diets. In this study, the mean percentage proportion of VFAs in the exhaust air for site IA4B and in the pit fan air for site IN3B was 21:29:30 for acetic, propanoic and butyric acids. The difference between this study and the previous study could be due to different analytical methods, different diets, ma-

nure age, or different sample sources, i.e., fresh manure in the previous study versus air from the exhaust fans (IA4B) and pit fans (IN3B) in this study.

Similar patterns for VFAs are also associated with dairy operations. Patni et al. (1985) reported changes in the VFA content of dairy cattle liquid manure slurry during storage in covered concrete tanks. On the average, acetic acid constituted 65% to 70% of the total VFAs in manure slurry, while isobutyric, valeric, and isovaleric acids together accounted for only 6% to 8%. In this study, the average acetic acid concentration for the two dairy sites was about 67% of the total VFAs, and propanoic and butyric acids were about 29% and 6% of the total VFAs, respectively.

ODOROUS VOC EMISSION RATES

The average emission rates of 20 odorous VOCs at four sites for four seasons over 17 months are listed in tables 2 through 6. Emission rates are expressed as mass per hour per

Table 2. Average emission rates for 20 odorous VOCs at dairy site W15B. Emission rates are averages for two dairy barns: four samples per barn collected in winter, two samples per barn collected in summer, five samples from barn 1 and four samples from barn 2 collected in spring, and two samples per barn collected in fall (ND = not detected, and NA = not available).

Compound	Winter			Summer			Spring			Fall		
	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)
Acetic acid	1.27E+01	1.34E+02	9.52E+01	5.50E+01	5.75E+02	4.09E+02	1.05E+01	1.21E+02	7.42E+01	4.98E+00	5.30E+01	3.77E+01
Propanoic acid	2.73E+00	2.81E+01	2.00E+01	3.44E+01	3.57E+02	2.54E+02	4.17E+00	4.77E+01	2.94E+01	2.04E+00	2.14E+01	1.52E+01
2-methyl propanoic acid	2.64E-01	2.89E+00	2.06E+00	1.74E+00	1.89E+01	1.35E+01	6.74E-01	8.17E+00	4.89E+00	1.93E-01	2.04E+00	1.45E+00
Butyric acid	4.75E-01	5.08E+00	3.62E+00	1.24E+01	1.36E+02	9.70E+01	1.69E+00	1.89E+01	1.18E+01	9.70E-01	1.03E+01	7.33E+00
3-methyl butanoic acid	1.75E-01	1.91E+00	1.36E+00	1.30E+00	1.43E+01	1.02E+01	5.05E-01	6.04E+00	3.64E+00	1.99E-01	2.13E+00	1.52E+00
Pentanoic acid	7.13E-02	7.91E-01	5.62E-01	7.70E-01	8.49E+00	6.04E+00	8.91E-01	1.09E+01	6.49E+00	9.24E-02	9.74E-01	6.93E-01
Hexanoic acid	6.79E-02	7.46E-01	5.31E-01	4.37E-01	4.70E+00	3.34E+00	7.82E-01	9.59E+00	5.70E+00	7.38E-02	7.66E-01	5.45E-01
Heptanoic acid	1.32E-03	1.40E-02	9.94E-03	1.01E-02	1.18E-01	8.42E-02	8.99E-01	1.11E+01	6.58E+00	5.95E-05	7.20E-04	5.12E-04
2-methoxyphenol	1.38E-02	1.46E-01	1.04E-01	9.23E-03	1.06E-01	7.56E-02	1.19E-03	1.25E-02	8.12E-03	0.00E+00	0.00E+00	0.00E+00
Phenol	1.25E-01	1.30E+00	9.26E-01	5.00E-01	5.38E+00	3.82E+00	6.56E-01	8.04E+00	4.78E+00	5.93E-02	6.19E-01	4.40E-01
4-methylphenol	1.92E-01	1.96E+00	1.40E+00	1.02E+00	1.13E+01	8.03E+00	8.43E-01	9.71E+00	5.97E+00	1.99E-01	2.13E+00	1.51E+00
4-ethylphenol	1.92E-02	1.86E-01	1.32E-01	5.70E-02	6.24E-01	4.43E-01	2.12E-01	2.58E+00	1.54E+00	1.34E-02	1.47E-01	1.04E-01
1-(2-aminophenyl)-ethanone	ND	ND	ND	6.02E-03	6.68E-02	4.75E-02	1.82E-01	2.24E+00	1.33E+00	5.40E-05	5.16E-04	3.67E-04
Indole	9.05E-04	9.83E-03	6.99E-03	1.34E-03	1.59E-02	1.13E-02	1.21E-01	1.50E+00	8.86E-01	5.99E-04	6.27E-03	4.46E-03
3-methylindole	2.69E-05	3.00E-04	2.14E-04	1.99E-03	2.01E-02	1.43E-02	1.01E-01	1.24E+00	7.36E-01	1.64E-04	1.76E-03	1.25E-03
Dimethyl disulfide ^[a]	1.77E-02	1.96E-01	1.39E-01	NA	NA	NA	1.03E-01	1.13E+00	8.06E-01	NA	NA	NA
Diethyl disulfide	9.11E-03	9.63E-02	6.85E-02	NA	NA	NA	3.77E-03	4.06E-02	2.89E-02	NA	NA	NA
Dimethyl trisulfide ^[a]	1.57E-03	1.67E-02	1.19E-02	NA	NA	NA	5.92E-03	6.57E-02	4.68E-02	NA	NA	NA
Dimethyl sulfoxide	1.79E-02	2.00E-01	1.42E-01	NA	NA	NA	3.69E-02	4.12E-01	2.93E-01	NA	NA	NA
Dimethyl sulfone	1.77E-02	1.92E-01	1.37E-01	NA	NA	NA	3.94E-02	4.30E-01	3.06E-01	NA	NA	NA
Total VOC emission rate	1.68E+01	1.78E+02	1.26E+02	1.08E+02	1.13E+03	8.05E+02	2.24E+01	2.61E+02	1.60E+02	8.82E+00	9.35E+01	6.65E+01

^[a] Measured DMDS and DMTS concentrations and emissions could be confounded by conversion of methanethiol into DMDS and DMTS.

Table 3. Average emission rates for 20 odorous VOCs at dairy site IN5B. Emission rates are averages for two dairy barns: four samples from each barn collected in winter, two samples from each barn collected in summer, four samples from each barn collected in spring, and two samples from each barn collected in fall (ND = not detected, and NA = not available).

Compound	Winter			Summer			Spring			Fall		
	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)
Acetic acid	7.56E-01	6.18E+00	4.87E+00	5.25E+00	4.18E+01	3.29E+01	1.07E+00	8.56E+00	6.74E+00	1.30E+00	1.08E+01	8.47E+00
Propanoic acid	6.71E-01	5.39E+00	4.24E+00	6.87E+00	5.41E+01	4.26E+01	1.39E+00	1.09E+01	8.60E+00	1.39E+00	1.14E+01	8.94E+00
2-methyl propanoic acid	4.98E-03	4.01E-02	3.16E-02	6.96E-02	5.51E-01	4.34E-01	4.08E-02	3.23E-01	2.54E-01	4.24E-02	3.48E-01	2.74E-01
Butyric acid	1.94E-01	1.55E+00	1.22E+00	4.23E-01	3.33E+00	2.62E+00	2.26E-01	1.77E+00	1.39E+00	3.02E-01	2.49E+00	1.96E+00
3-methyl butanoic acid	2.49E-02	1.97E-01	1.55E-01	5.30E-02	4.15E-01	3.27E-01	1.78E-02	1.40E-01	1.10E-01	5.28E-02	4.35E-01	3.43E-01
Pentanoic acid	1.12E-02	8.83E-02	6.95E-02	2.31E-04	1.79E-03	1.41E-03	1.42E-02	1.11E-01	8.75E-02	4.01E-02	3.29E-01	2.59E-01
Hexanoic acid	8.05E-02	6.54E-01	5.15E-01	ND	ND	ND	5.59E-03	4.37E-02	3.44E-02	6.89E-03	5.66E-02	4.46E-02
Heptanoic acid	4.73E-04	3.86E-03	3.04E-03	ND	ND	ND	5.05E-04	4.12E-03	3.25E-03	ND	ND	ND
2-methoxyphenol	7.26E-04	5.86E-03	4.61E-03	3.17E-02	2.53E-01	1.99E-01	8.92E-04	7.00E-03	5.51E-03	6.30E-03	5.07E-02	3.99E-02
Phenol	1.60E-02	1.27E-01	9.99E-02	5.34E-01	4.24E+00	3.34E+00	1.26E-01	9.94E-01	7.82E-01	1.22E-01	9.85E-01	7.76E-01
4-methylphenol	1.47E-01	1.18E+00	9.29E-01	4.37E-01	3.07E+00	2.41E+00	3.62E-01	2.86E+00	2.25E+00	4.99E-01	4.01E+00	3.16E+00
4-ethylphenol	1.78E-02	1.43E-01	1.13E-01	1.59E-01	1.25E+00	9.83E-01	5.18E-02	4.11E-01	3.24E-01	8.93E-02	7.17E-01	5.65E-01
1-(2-aminophenyl)-ethanone	2.96E-05	2.37E-04	1.87E-04	2.17E-03	1.70E-02	1.34E-02	2.86E-04	2.24E-03	1.76E-03	2.26E-04	1.77E-03	1.40E-03
Indole	1.31E-04	1.07E-03	8.39E-04	3.32E-03	2.61E-02	2.06E-02	1.57E-03	1.24E-02	9.78E-03	1.82E-03	1.47E-02	1.15E-02
3-methylindole	1.48E-05	1.22E-04	9.58E-05	1.68E-03	1.33E-02	1.04E-02	4.36E-04	3.43E-03	2.70E-03	1.85E-04	1.49E-03	1.18E-03
Dimethyl disulfide ^[a]	4.39E-03	3.57E-02	2.81E-02	NA	NA	NA	3.03E-02	2.45E-01	1.93E-01	NA	NA	NA
Diethyl disulfide	0.00E+00	0.00E+00	0.00E+00	NA	NA	NA	1.36E-04	1.13E-03	8.87E-04	NA	NA	NA
Dimethyl trisulfide ^[a]	0.00E+00	0.00E+00	0.00E+00	NA	NA	NA	4.67E-04	3.66E-03	2.88E-03	NA	NA	NA
Dimethyl sulfoxide	5.94E-03	4.77E-02	3.75E-02	NA	NA	NA	9.99E-05	7.83E-04	6.17E-04	NA	NA	NA
Dimethyl sulfone	1.35E-03	1.09E-02	8.59E-03	NA	NA	NA	2.31E-03	1.87E-02	1.47E-02	NA	NA	NA
Total VOC emission rate	1.94	15.7	12.3	13.8	109	85.9	3.34	26.4	20.8	3.85	31.6	24.9

^[a] Measured DMDS and DMTS concentrations and emissions could be confounded by conversion of methanethiol into DMDS and DMTS.

Table 4. Average emission rates for 20 odorous VOCs at swine finisher site IN3B. Emission rates are averages for two swine finisher barns: four samples from each barn collected in winter, two samples from each barn collected in summer, three samples from barn 1 and four samples from barn 2 collected in spring, and two samples from each barn collected in fall (NA = not available).

Compound	Winter			Summer			Spring			Fall		
	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)
Acetic acid	2.55E+00	4.69E+00	2.49E+01	1.38E+01	1.83E+01	1.33E+02	2.62E+01	1.62E+01	1.86E+02	1.27E+01	8.93E+00	6.83E+01
Propanoic acid	4.58E+00	7.14E+00	3.74E+01	9.11E+01	1.25E+02	6.60E+02	3.79E+01	2.44E+01	2.42E+02	2.22E+01	1.55E+01	1.31E+02
2-methyl propanoic acid	7.02E-01	1.17E+00	6.09E+00	4.52E+00	6.09E+00	3.72E+01	7.12E+00	4.62E+00	4.34E+01	4.26E+00	2.98E+00	2.34E+01
Butyric acid	4.49E+00	6.67E+00	3.50E+01	3.22E+01	4.31E+01	2.82E+02	6.30E+01	4.11E+01	3.72E+02	3.00E+01	2.09E+01	1.81E+02
3-methyl butanoic acid	8.70E-01	1.37E+00	7.20E+00	4.56E+00	6.13E+00	3.89E+01	6.28E+00	4.01E+00	4.05E+01	3.95E+00	2.77E+00	2.13E+01
Pentanoic acid	8.10E-01	1.20E+00	6.40E+00	4.70E+00	6.18E+00	4.64E+01	1.21E+01	7.84E+00	7.42E+01	5.50E+00	3.84E+00	3.22E+01
Hexanoic acid	1.94E-01	3.41E-01	1.84E+00	1.11E+00	1.48E+00	9.36E+00	2.36E+00	1.56E+00	1.36E+01	1.34E+00	9.30E-01	8.42E+00
Heptanoic acid	6.78E-02	9.51E-02	4.74E-01	1.60E-02	1.83E-02	2.91E-01	1.02E+00	7.07E-01	4.69E+00	2.66E-02	1.84E-02	1.65E-01
2-methoxyphenol	5.51E-02	1.20E-01	6.35E-01	4.21E-01	5.70E-01	3.42E+00	3.99E-01	2.17E-01	3.66E+00	9.28E-01	6.50E-01	5.04E+00
Phenol	2.14E-01	2.62E-01	1.43E+00	7.69E-01	1.05E+00	5.52E+00	1.02E+00	6.48E-01	6.54E+00	1.11E+00	7.84E-01	4.99E+00
4-methylphenol	3.28E+00	3.95E+00	2.17E+01	4.77E+00	6.49E+00	3.52E+01	6.68E+00	4.15E+00	4.60E+01	7.70E+00	5.40E+00	4.03E+01
4-ethylphenol	1.18E-01	1.40E-01	7.72E-01	7.75E-02	1.03E-01	7.39E-01	5.29E-01	3.35E-01	3.58E+00	3.51E-01	2.46E-01	1.90E+00
1-(2-aminophenyl)-ethanone	8.05E-03	9.54E-03	4.98E-02	1.97E-02	2.67E-02	1.53E-01	2.19E-01	1.53E-01	1.02E+00	2.03E-02	1.41E-02	1.28E-01
Indole	7.74E-02	7.87E-02	4.25E-01	2.73E-02	3.71E-02	2.21E-01	2.30E-01	1.41E-01	1.65E+00	1.60E-01	1.13E-01	7.38E-01
3-methylindole	1.99E-01	2.09E-01	1.13E+00	2.22E-02	3.00E-02	1.84E-01	1.68E-01	1.07E-01	1.11E+00	2.35E-01	1.67E-01	9.47E-01
Dimethyl disulfide ^[a]	7.76E-03	1.90E-02	7.87E-02	NA	NA	NA	1.77E-01	9.68E-02	1.67E+00	9.25E-02	6.60E-02	3.69E-01
Diethyl disulfide	0.00E+00	0.00E+00	0.00E+00	NA	NA	NA	0.00E+00	0.00E+00	0.00E+00	1.08E-01	7.52E-02	4.29E-01
Dimethyl trisulfide ^[a]	8.83E-04	2.48E-03	9.00E-03	NA	NA	NA	2.46E-03	1.32E-03	2.30E-02	6.03E-03	4.28E-03	2.40E-02
Dimethyl sulfoxide	4.52E-03	1.02E-02	6.21E-02	NA	NA	NA	3.83E-03	1.24E-03	5.94E-02	4.08E-03	2.87E-03	1.62E-02
Dimethyl sulfone	9.91E-02	2.44E-01	1.33E+00	NA	NA	NA	6.45E-01	4.04E-01	4.75E+00	6.19E-01	4.39E-01	2.46E+00
Total VOC emission rate	18.3	27.7	147	158	214	1252	166	107	1046	91.3	63.7	523

^[a] Measured DMDS and DMTS concentrations and emissions could be confounded by conversion of methanethiol into DMDS and DMTS.

Table 5. Average emission rates for 20 odorous VOCs at the IA4B swine gestation barns (B1 and B2). Emission rates are averages for two swine gestation barns: four samples from each barn collected in winter, two samples from each barn collected in summer, three samples from barn 1 and four samples from barn 2 collected in spring, and two samples from each barn collected in fall (NA = not available).

Compound	Winter			Summer			Spring			Fall		
	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)
Acetic acid	1.29E+00	2.65E+00	5.31E+00	3.36E+00	5.38E+00	1.08E+01	2.09E+00	4.26E+00	8.54E+00	6.49E-01	1.34E+00	2.69E+00
Propanoic acid	1.60E+00	3.24E+00	6.49E+00	3.52E+00	4.95E+00	9.91E+00	2.37E+00	4.90E+00	9.82E+00	1.24E+00	2.57E+00	5.15E+00
2-methyl propanoic acid	4.50E-01	9.22E-01	1.85E+00	5.21E-01	8.79E-01	1.76E+00	3.43E-01	7.13E-01	1.43E+00	2.98E-01	6.20E-01	1.24E+00
Butyric acid	1.16E+00	2.38E+00	4.76E+00	1.71E+00	2.60E+00	5.20E+00	1.67E+00	3.46E+00	6.93E+00	9.28E-01	1.93E+00	3.86E+00
3-methyl butanoic acid	7.23E-01	1.49E+00	2.98E+00	6.39E-01	1.00E+00	2.00E+00	4.51E-01	9.32E-01	1.87E+00	2.78E-01	5.76E-01	1.15E+00
Pentanoic acid	2.11E-01	4.34E-01	8.70E-01	3.93E-01	5.42E-01	1.09E+00	2.39E-01	4.93E-01	9.89E-01	1.06E-01	2.18E-01	4.37E-01
Hexanoic acid	1.18E-01	2.44E-01	4.89E-01	8.04E-02	9.70E-02	1.94E-01	4.98E-02	1.02E-01	2.05E-01	3.25E-02	6.70E-02	1.34E-01
Heptanoic acid	8.60E-03	1.85E-02	3.71E-02	1.84E-02	4.33E-02	8.68E-02	1.48E-02	3.05E-02	6.11E-02	2.03E-02	4.29E-02	8.60E-02
2-methoxyphenol	7.86E-03	1.65E-02	3.31E-02	9.81E-04	1.20E-03	2.40E-03	2.31E-03	4.98E-03	1.00E-02	0.00E+00	0.00E+00	0.00E+00
Phenol	1.72E-01	3.60E-01	7.22E-01	1.12E-01	1.80E-01	3.60E-01	2.26E-01	4.69E-01	9.40E-01	1.33E-01	2.80E-01	5.61E-01
4-methylphenol	2.69E+00	5.61E+00	1.12E+01	1.39E+00	2.29E+00	4.59E+00	2.13E+00	4.44E+00	8.91E+00	1.11E+00	2.34E+00	4.69E+00
4-ethylphenol	1.34E-01	2.77E-01	5.56E-01	6.85E-02	1.16E-01	2.32E-01	1.98E-01	4.12E-01	8.25E-01	5.62E-02	1.18E-01	2.37E-01
1-(2-aminophenyl)-ethanone	4.85E-02	1.03E-01	2.06E-01	3.45E-02	6.02E-02	1.21E-01	7.46E-03	1.56E-02	3.13E-02	3.19E-03	6.75E-03	1.35E-02
Indole	3.12E-02	6.47E-02	1.30E-01	2.09E-02	5.04E-02	1.01E-01	2.52E-02	5.27E-02	1.06E-01	1.67E-02	3.54E-02	7.09E-02
3-methylindole	1.11E-01	2.29E-01	4.59E-01	3.14E-02	1.34E-01	2.68E-01	1.27E-01	2.66E-01	5.33E-01	6.69E-02	1.42E-01	2.85E-01
Dimethyl disulfide ^[a]	1.03E-02	2.15E-02	4.30E-02	NA	NA	NA	2.40E-02	4.99E-02	9.99E-02	NA	NA	NA
Diethyl disulfide	6.75E-03	1.44E-02	2.88E-02	NA	NA	NA	1.51E-04	3.05E-04	6.10E-04	NA	NA	NA
Dimethyl trisulfide ^[a]	2.14E-04	4.47E-04	8.96E-04	NA	NA	NA	4.77E-04	9.92E-04	1.99E-03	NA	NA	NA
Dimethyl sulfoxide	3.56E-04	7.32E-04	1.47E-03	NA	NA	NA	5.22E-04	1.05E-03	2.10E-03	NA	NA	NA
Dimethyl sulfone	2.99E-02	6.17E-02	1.24E-01	NA	NA	NA	5.61E-02	1.15E-01	2.31E-01	NA	NA	NA
Total VOC emission rate	8.80	18.1	36.3	11.9	18.3	36.7	10.0	20.7	41.5	4.94	10.3	20.6

^[a] Measured DMDS and DMTS concentrations and emissions could be confounded by conversion of methanethiol into DMDS and DMTS.

animal unit (mg h⁻¹ AU⁻¹), mass per hour per head (mg h⁻¹ head⁻¹), and mass per hour per barn floor area (mg h⁻¹ m⁻²). The total VOC emission rates for 20 odorants were estimated by summing the overall mean emission rates of the individual odorants. The total VOC emissions were 290 and 36.0 mg h⁻¹ AU⁻¹, respectively, for dairy sites WI5B and IN5B, 743 and 33.9 mg h⁻¹ AU⁻¹, respectively for swine finisher site IN3B and the IA4B swine gestation barns, and 91.7 mg h⁻¹ AU⁻¹ for the IA4B swine farrowing room. Site IN3B had the highest apparent odorous VOC emission rate. This is probably due to (1) greater manure production per AU at finishing sites because of the ad lib feeding vs. limited feeding in sow gestation, (2) deeper manure in the pits of finishing barns as compared with farrowing barns, which are emptied every farrowing cycle, and (3) possibly warmer manure temperature in finishing barns due to greater live mass density and higher temperatures as compared with gestation stalls.

Comparing the VOC emission rates from the animal buildings in this study with the emission rates from manure storages reported by Zahn et al. (2001), Bicudo et al. (2004), and Amon et al. (2007) is challenging due to the different units used and the different sources measured. Similarly, there are no published data on VOC emissions from confined dairy barns. Filipy et al. (2006) reported emission rates of DMS (13.8 µg cow⁻¹ s⁻¹) from the lactating stall area at the Washington State University Knott Dairy Farm using an atmospheric tracer method.

The seasonal variations of total odorous compound emission rates normalized by animal weight (AU = 500 kg) and ventilation rates for the four sites are shown in figure 3. Several factors may affect VOC concentrations inside the barn as well as the emission rates, including animal age and weight, feed type, waste storage and/or flushing frequency,

Table 6. Average emission rates for 20 odorous VOCs at the IA4B swine farrowing room (B3). Emission rates are averages: four samples collected in winter, two samples collected in summer, four samples collected in spring, and two samples in fall (NA = not available).

Compound	Winter			Summer			Spring			Fall		
	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)	(mg h ⁻¹ m ⁻²)	(mg h ⁻¹ head ⁻¹)	(mg h ⁻¹ AU ⁻¹)
Acetic acid	3.64E-01	2.10E+00	3.70E+00	1.14E+00	6.59E+00	1.19E+01	3.81E+00	2.20E+01	3.99E+01	2.44E-01	1.41E+00	2.54E+00
Propanoic acid	5.84E-01	3.37E+00	5.88E+00	1.56E+00	8.98E+00	1.62E+01	2.99E+00	1.72E+01	3.16E+01	6.88E-01	3.97E+00	7.17E+00
2-methyl propanoic acid	2.03E-01	1.17E+00	2.03E+00	3.41E-01	1.97E+00	3.56E+00	4.62E-01	2.67E+00	4.88E+00	1.94E-01	1.12E+00	2.03E+00
Butyric acid	1.65E+00	9.52E+00	1.64E+01	3.05E+00	1.76E+01	3.17E+01	4.05E+00	2.34E+01	4.32E+01	1.19E+00	6.85E+00	1.25E+01
3-methyl butanoic acid	4.03E-01	2.33E+00	4.01E+00	3.95E-01	2.28E+00	4.12E+00	5.55E-01	3.20E+00	5.77E+00	1.70E-01	9.80E-01	1.78E+00
Pentanoic acid	3.04E-01	1.75E+00	3.02E+00	5.32E-01	3.07E+00	5.55E+00	1.10E+00	6.34E+00	1.17E+01	2.95E-01	1.70E+00	3.12E+00
Hexanoic acid	3.80E-01	2.19E+00	3.79E+00	1.17E+00	6.76E+00	1.22E+01	2.81E+00	1.62E+01	3.01E+01	7.76E-01	4.48E+00	8.25E+00
Heptanoic acid	2.81E-03	1.62E-02	2.88E-02	3.86E-04	2.23E-03	4.19E-03	1.30E-02	7.52E-02	1.33E-01	3.99E-03	2.30E-02	4.11E-02
2-methoxyphenol	2.93E-03	1.69E-02	2.89E-02	8.23E-03	4.75E-02	8.56E-02	1.14E-01	6.56E-01	1.25E+00	1.48E-03	8.52E-03	1.58E-02
Phenol	7.27E-02	4.19E-01	7.40E-01	1.79E-01	1.03E+00	1.86E+00	2.32E-01	1.34E+00	2.43E+00	6.48E-02	3.74E-01	6.77E-01
4-methylphenol	3.67E-01	2.12E+00	3.72E+00	4.75E-01	2.74E+00	4.94E+00	1.05E+00	6.04E+00	1.08E+01	2.19E-01	1.26E+00	2.30E+00
4-ethylphenol	4.20E-02	2.43E-01	4.32E-01	5.35E-02	3.09E-01	5.56E-01	1.38E-01	7.98E-01	1.44E+00	2.02E-02	1.16E-01	2.11E-01
1-(2-aminophenyl)-ethanone	3.77E-02	2.18E-01	3.73E-01	1.84E-02	1.06E-01	1.91E-01	3.26E-02	1.88E-01	3.52E-01	1.04E-03	5.97E-03	1.08E-02
Indole	1.15E-02	6.62E-02	1.15E-01	7.75E-03	4.47E-02	8.08E-02	5.30E-02	3.06E-01	5.54E-01	9.27E-03	5.35E-02	9.67E-02
3-methylindole	1.39E-02	7.99E-02	1.37E-01	2.13E-03	1.23E-02	2.22E-02	6.36E-02	3.67E-01	6.63E-01	9.00E-03	5.20E-02	9.46E-02
Dimethyl disulfide ^[a]	4.13E-02	2.38E-01	4.30E-01	NA	NA	NA	1.01E-01	5.80E-01	1.03E+00	NA	NA	NA
Diethyl disulfide	1.94E-03	1.12E-02	1.98E-02	NA	NA	NA	1.63E-03	9.43E-03	1.70E-02	NA	NA	NA
Dimethyl trisulfide ^[a]	1.17E-04	6.75E-04	1.19E-03	NA	NA	NA	1.15E-03	6.64E-03	1.20E-02	NA	NA	NA
Dimethyl sulfoxide	6.06E-04	3.50E-03	6.17E-03	NA	NA	NA	6.29E-04	3.63E-03	6.29E-03	NA	NA	NA
Dimethyl sulfone	1.05E-02	6.07E-02	1.09E-01	NA	NA	NA	2.28E-02	1.32E-01	2.30E-01	NA	NA	NA
Total VOC emission rate	4.49	25.9	45.0	8.93	51.5	93.0	17.6	101	186	3.88	22.4	40.8

^[a] Measured DMDS and DMTS concentrations and emissions could be confounded by conversion of methanethiol into DMDS and DMTS.

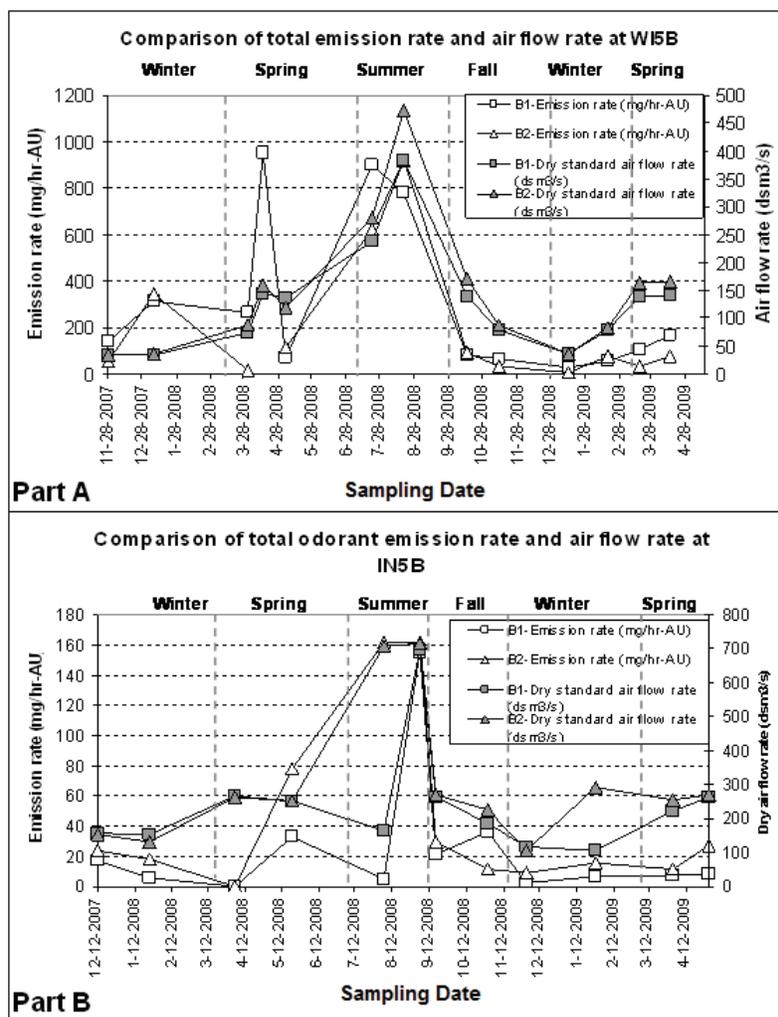


Figure 3. Seasonal variations of total odorous VOC emission rates and airflow rates over a 17-month period at four sites: Part A = Wisconsin dairy site W15B, and Part B = Indiana dairy site IN5B.

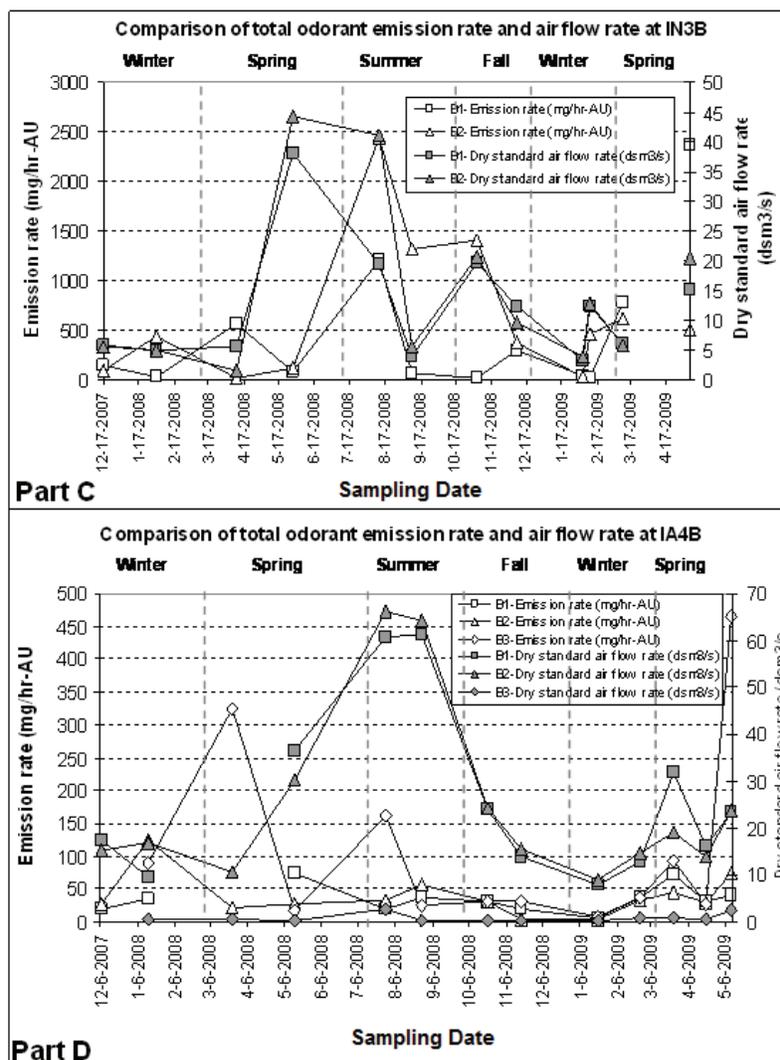


Figure 3 (continued). Seasonal variations of total odorous VOC emission rates and airflow rates over a 17-month period at four sites: Part C = Indiana swine finisher site IN3B, and Part D = Iowa sow gestation and farrowing site IA4B.

length of time since the barn has been cleaned and/or waste removed, barn ventilation rate, barn temperature (which influences ventilation rate as well as gas volatilization), and meteorological parameters (i.e., ambient temperature and relative humidity), all of which may play a role in emissions (Blunden et al., 2008). In this study, for all four sites except IA4B, the total odorous VOC emission rates were highest during summer at 805 mg h⁻¹ AU⁻¹ for WI5B, 121 mg h⁻¹ AU⁻¹ for IN5B, and 1250 mg h⁻¹ AU⁻¹ for IN3B, respectively. Amon et al. (2007) also observed that VOC emissions were 40% to 60% lower in cold conditions. The total odorous VOC emission rate at IA4B was highest during spring at 95.8 mg h⁻¹ AU⁻¹, which is about two times higher than the summer emission rate. One important factor was that the manure depth in the deep pit reached the highest level during spring. Site IA4B usually removed the manure twice a year during early May and late fall. This indicates that animal waste stored inside the confined structure may play a large role in the gas emission rates from the barns, especially for barns with deep pits as the manure

may be stored underneath the floor for months, which may significantly affect the rate of gaseous emissions.

The relationships between the total odorous VOC emission rates and ventilation rates for all sites are also shown in figure 3. Most of the time during the sampling period, the emission rates seemed to follow similar trends as the ventilation rates, especially for the two dairy sites. This suggests that the VOC emissions were driven primarily by increased air temperature and correlated with increased ventilation. Both high ventilation rates and high odorous VOC emission rates were observed during summer, except for the emission rates at IA4B. The average ventilation rates for all sites were highest during summer at 572 dsm³ s⁻¹ for IN5B, 343 dsm³ s⁻¹ for WI5B, 17.5 dsm³ s⁻¹ for IN3B, and 42.5 dsm³ s⁻¹ for IA4B. The emission rates for IN5B, WI5B, and IN3B were highest during summer as well. It indicates that increased ventilation rates may lead to increased odorous VOC emission rates, although the other factors mentioned above could also affect the gaseous emission rates.

STATISTICAL ANALYSIS OF ODOROUS VOC EMISSION RATES

Statistical analysis aimed at testing of significant differences between the four seasons for each compound emission rate at each site. For the swine gestation barns at site IA4B, only acetic acid ($p < 0.05$) and propanoic acid ($p < 0.05$) had a weak seasonal significant difference. For swine finisher site IN3B, 4-ethylphenol, indole, and most of the VFAs (except for hexanoic and heptanoic acids) exhibited seasonal significant differences. For dairy site WI5B, five VFAs (acetic, propanoic, 2-methyl propanoic, butyric, and 3-methyl butanoic acid) and one phenolic (4-methylphenol) had seasonal significant differences. Only three compounds (2-methoxyphenol, 1-(2-aminophenyl)-ethanone, and indole) had seasonal significant differences at dairy site IN5B.

Statistical analysis was also conducted for differences between two sites within the same species and between different species. For the dairy sites, five acids (acetic, propanoic, 2-methyl propanoic, butyric, and 3-methyl butanoic) were significantly different. For the swine sites, most of these odorants were significantly different between sites with the exception of heptanoic acid, 1-(2-aminophenyl)-ethanone, and 3-methylindole. For different species, ten odorants were significantly different between swine and dairy sites; however, acetic acid, heptanoic acid, phenol, 4-ethylphenol, and 1-(2-aminophenyl)-ethanone were not significantly different.

CONCLUSIONS

This study was the most comprehensive field survey of emissions of odorous compounds from Midwestern swine and dairy production sites to date. It is also the first report that characterizes the odorous VOC emissions from dairy operations. The following specific conclusions were drawn from this study:

- Based on 13 distributed sampling events over a 17-month period during which samples were collected over 1 h intervals, the overall average total of 20 odorous VOC concentrations for sites WI5B, IN5B, IN3B, and IA4B were 276, 96.9, 1410, and 394 $\mu\text{g dsm}^{-3}$, respectively.
- Seasonal patterns of VOC emissions at the swine and dairy sites were observed. For the swine sites, the total odorous compound concentration for each barn was highest during spring, with values of 1890 $\mu\text{g dsm}^{-3}$ for IN3B and 458 $\mu\text{g dsm}^{-3}$ for IA4B. For the dairy sites, the total concentration was highest in winter for WI5B (446 $\mu\text{g dsm}^{-3}$) and in summer for IN5B (129 $\mu\text{g dsm}^{-3}$).
- The total odorant emission rates for 20 odorous VOCs were 290 $\text{mg h}^{-1} \text{AU}^{-1}$ for dairy site WI5B, 36.0 $\text{mg h}^{-1} \text{AU}^{-1}$ for dairy site IN5B, 743 $\text{mg h}^{-1} \text{AU}^{-1}$ for swine finisher site IN3B, 33.9 $\text{mg h}^{-1} \text{AU}^{-1}$ for the swine gestation barns at IA4B, and 91.7 $\text{mg h}^{-1} \text{AU}^{-1}$ for the swine farrowing room at IA4B.
- Seasonal variations in VOC emissions were observed. At all sites except IA4B, the total odorous

VOC emission rates were highest during summer, with values of 805 $\text{mg h}^{-1} \text{AU}^{-1}$ for WI5B, 121 $\text{mg h}^{-1} \text{AU}^{-1}$ for IN5B, and 1250 $\text{mg h}^{-1} \text{AU}^{-1}$ for IN3B. The total odorous VOC emission rate at IA4B was highest during spring (95.8 $\text{mg h}^{-1} \text{AU}^{-1}$), perhaps due to significant manure depths.

- The average ventilation rates for all sites were highest during summer, with values of 572 $\text{dsm}^3 \text{s}^{-1}$ for IN5B, 343 $\text{dsm}^3 \text{s}^{-1}$ for WI5B, 17.5 $\text{dsm}^3 \text{s}^{-1}$ for IN3B, and 42.5 $\text{dsm}^3 \text{s}^{-1}$ for IA4B. The emission rates for IN5B, WI5B, and IN3B were highest during summer as well. This indicates that increased temperature, resulting in increased ventilation rates, leads to increased odorous VOC emission rates.
- Only acetic acid ($p < 0.05$) and propanoic acid ($p < 0.05$) showed a weak seasonal significant difference for IA4B. For IN3B, 4-ethylphenol and indole and most of the VFAs except hexanoic and heptanoic acid had seasonal significant differences. At WI5B, five VFAs (acetic, propanoic, 2-methyl propanoic, butyric, and 3-methyl butanoic acid) and one phenolic (4-methylphenol) had seasonal significant differences. Only three compounds (2-methoxyphenol, 1-(2-aminophenyl)-ethanone, and indole) had seasonal significant differences for IN5B.
- Considering differences in VOC emissions between the two dairy sites, acetic, propanoic, 2-methyl propanoic, butanoic, and 3-methyl butanoic acid were significantly different. Most odorants were significantly different (except heptanoic acid, 1-(2-aminophenyl)-ethanone, and 3-methylindole) between the two swine sites. Ten odorants (except acetic acid, heptanoic acid, phenol, 4-ethylphenol, and 1-(2-aminophenyl)-ethanone) were significantly different between the dairy and swine sites.

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