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TECHNICAL PAPER

Comparison of seasonal phenol and *p*-cresol emissions from ground-level area sources in a dairy operation in central Texas

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Although there are more than 200 odor-causing volatile organic compounds (VOCs), phenol and p-*cresol are two prominent odor-causing VOCs found downwind from concentrated animal feeding operations (CAFOs). The VOC emissions from cattle and dairy production are difficult to quantify accurately because of their low concentrations, spatial variability, and limitations of available instruments. To quantify VOCs, a protocol following U.S. Environmental Protection Agency (EPA) Method TO-14A has been established based on the isolation flux chamber method and a portable gas chromatograph (GC) coupled with a purge-and-trap system. The general objective of this research was to quantify phenol and* p-*cresol emission rates (ERs) from different ground-level area sources (GLASs) in a free-stall dairy during summer and winter seasons using this protocol. Two-week-long sampling campaigns were conducted in a dairy operation in central Texas. Twenty-nine air samples were collected during winter and 37 samples were collected during summer from six specifically delineated GLASs (barn, loafing pen, lagoon, settling basin, silage pile, and walkway) at the free-stall dairy. Thirteen VOCs were identified during the sampling period and the GC was calibrated for phenol and* p-*cresol, the primary odorous VOCs identified. The overall calculated ERs for phenol and* p-*cresol were 2656 ± 728 and 763 ± 212 mg hd*$^{-1}$ *day*$^{-1}$*, respectively, during winter. Overall phenol and* p-*cresol ERs were calculated to be 1183 ± 361 and 551 ± 214 mg hd*$^{-1}$ *day*$^{-1}$*, respectively, during summer. In general, overall phenol and* p-*cresol ERs during winter were about 2.3 and 1.4 times, respectively, higher than those during summer.*

Implications: Concentrated animal feeding operations contribute a considerable amount of VOCs to the atmosphere. The phenol and p-cresol are two VOCs recognized as potential odor-causing compounds emitted from livestock operation. To develop effective strategies for mitigating livestock odorous VOC emissions, relative emissions from different GLAS in a livestock operation under different climate conditions should be quantified. It is also important to obtain direct estimates of VOC emissions from different GLAS in CAFOs to compile emission inventories. This research determined phenol and p-cresol emissions from different GLAS in a free-stall dairy and also identified areas in a dairy operations that have the highest phenol and p-cresol emissions.

Introduction

Poultry, swine, dairy, and cattle feedyard operations are the major stationary sources of odorous volatile organic compound (VOC) emissions from the agricultural sector causing public odor complaints (Lu et al., 2008). Volatile organic compounds also play a major role in the formation of photochemical oxidants in the atmosphere. The reaction of VOCs with nitrogen oxides (NO_x) in the presence of ultraviolet light can produce ozone (O_3), a criteria pollutant regulated under the National Ambient Air Quality Standards (NAAQS) (CFR, 2008). All VOCs are precursors to ozone formation to some extent, depending on their photochemical reactivity. Phenol is a highly reactive volatile organic compound (HRVOC) and is identified as a potential reactive organic gas (ROG) emitted from dairies (Howard et al., 2010). The *p*-cresol is exempt from the ROG list due to its low reactivity, but it is recognized as a potential

odor-causing compound emitted from livestock operations. In addition to ozone formation, odors from dairies and cattle feed-yards are nuisances associated with VOC emissions (Rabaud et al., 2002). Volatile fatty acids, *p*-cresol, phenol, 4-ethylphenol, indole, skatole, and sulfur-containing compounds are identified as contributors of odors from animal feeding operations (Cai et al., 2006; Koziel et al., 2006; Wright et al., 2005). Biogenic sources of VOCs, such as those contained in grass, hay, silage, and grains, are a major part of bovine diets. Volatile organic compounds are emitted from these biogenic sources during fermentation of starches, lipids, and proteins in the digestive system of cattle (enteric fermentation) and later in the feces and urine, or they are accumulated in cow's milk if they are not completely metabolized (Ciccioli et al., 1993). Previous research reported that ambient temperature, soil moisture, and manure composition are the primary factors controlling anaerobic decomposition in feedyard soils and influence the release of

odorous compounds to the atmosphere (Miller and Varel, 2001). It was also reported that livestock odors were mostly due to VOCs and defined as a mixture of carbon-, sulfur-, and nitrogen-containing compounds produced during incomplete anaerobic fermentation of manure (Miller and Varel, 2001). Rabaud et al. (2002) observed 20 odorous and nonodorous compounds in emissions downwind of a dairy, with concentrations varying from 0.55 to 320.20 $\mu g\, m^{-3}$. Observed compounds were straight-chain and aromatic hydrocarbon, chlorinated compounds, alcohols, aldehydes, ketones, and aromatic acids. Some VOCs having strong odor intensity indicated the presence of odor-causing VOCs in high concentrations (Rabaud et al., 2003). Thirty-five reactive volatile organic compounds (RVOCs) were also measured in a dairy with concentrations varying from 0.08 to 747.76 $\mu g\, m^{-3}$. Measured compounds included acids, esters, alcohols, aldehydes, ketones, halogenates, amines, and hydrocarbons (Rabaud et al., 2003). The authors concluded that this dairy emitted a wide variety of VOCs at significant concentrations.

Previous studies reported that phenol and *p*-cresol were the most abundant odor-causing compounds found downwind from cattle feedyards and swine facilities (Parker et al., 2007; Wright et al., 2004). In contrast, McGinn et al. (2003) measured VOCs in three beef cattle feedyards in Canada (6000, 12,000, and 25,000 hd capacities) and found that acetic acid had the highest concentration downwind, followed by propionic acid and butyric acid. Although more than 200 VOCs contribute to odor from lagoons, Eniola et al. (2006) reported that *p*-cresol, *p*-ethyl phenol, and isovaleric acid have been recognized as the most persistent and significant odor contributors 1.6 km downwind from manure lagoons in concentrated animal feeding operations (CAFOs). Koziel et al. (2006) also reported that downwind odor is dominated by the relatively low volatility, high-molecular-weight, and polar compounds. The *p*-cresol alone appeared to carry much of the overall odor impact for swine and beef cattle operations (Koziel et al., 2006). Cai et al. (2010) reported that VFAs (acetic, propanoic, 2-methyl propanoic, butyric, and 3-methylbutanoic acid) and *p*-cresol showed seasonal variations in a Wisconsin dairy barn. Phenol and *p*-cresol are repeatedly used as indicators in odor studies (Auvermann et al., 2001). The compound *p*-cresol has a foul smell and phenol has a sweet and relatively pleasant odor (Bourque et al., 1987). The odor recognition thresholds of phenol and *p*-cresol are 0.059 ppmv ($226.8\,\mu g\, m^{-3}$) and 0.0019 ppmv ($8.4\,\mu g\, m^{-3}$), respectively (Yu et al., 1990). Odor threshold for phenol and *p*-cresol ranged from 0.0045 to 1.00 ppm (17.3 to $3845\,\mu g\, m^{-3}$) and 5×10^{-5} to 0.0079 ppm, respectively (0.24 to $38\,\mu g\, m^{-3}$) (The United State Library of Medicine, 1981). Parker et al. (2010) also reported geometric means of single-compound odor thresholds for phenol and *p*-cresol, which were 127 and $2.6\,\mu g\, m^{-3}$, respectively. The highest reported concentration of *p*-cresol measured at the property line downwind of a feedyard in the Texas Panhandle was 0.0681 ppbv compared to a commonly used published odor threshold 0.46 ppbv (Buser et al., 2007, National Oceanic and Atmospheric Administration).

Emission factors, usually expressed in kilograms VOC per head per year, are used to estimate the total production of VOCs from a given source. Currently, the U.S. Environmental

Protection Agency (EPA) has not published a standard VOC emission factor for cattle in AP-42 (U.S. Environmental Protection Agency), so different VOC emission factors are being implemented in various parts of the country. In Idaho, for instance, an emission factor of 7.3 kg VOC per dairy cow per year is used, based on research done by the South Coast Air Quality Management District (Idaho Department of Environmental Quality (IDEQ), 2003). The San Joaquin Valley Air Pollution Control District (SJVAPCD) in California has used an emission factor of 9.38 kg VOC per dairy cow per year (Air Resources Board (ARB), 2005). This emission factor (kg $hd^{-1}yr^{-1}$) represents the following group of compounds: VOC from cows breath and feed (1.23), ethylamines (0.01), miscellaneous dairy processes (0.55), lagoons and ponds (0.45), and VFAs (7.05) (Air Resources Board (ARB), 2005).

Limited information is available in the literature regarding emissions of phenol and *p*-cresol from dairies. To develop effective strategies for mitigating livestock odorous VOC emissions, relative emissions from different GLASs in a livestock operation under different climatic conditions should be quantified. Thus, measurements of odorous VOC emissions data from six specifically delineated GLASs (loafing pen, walkway, barn, silage pile, settling basin, and lagoon) were performed during summer and winter from the same free-stall dairy in Central Texas. However, VOC emissions from cattle and dairy production are difficult to quantify accurately because of their low concentrations, spatial variability in emissions, and the lack of a suite of instruments that is able to identify all VOCs. Characterizing VOC emissions from anthropogenic and biogenic sources involves a series of procedures to acquire accurate results. Although there are some standardized methods (e.g., EPA TO-14A and American Society for Testing and Materials [ASTM] D5466) for determining VOC concentrations in ambient air, specific methods are still needed for uncharacterized and complex sources such as dairies (Higashi and Cassel, 2004).

EPA Compendium Method TO-14A specifies the use of initially evacuated canisters and pump-ventilated sample lines when collecting air samples from the field (U.S. Environmental Protection Agency (U.S. EPA), 1999). The gas canisters used for air sample storage must be specially treated, leak-free, stainless steel pressure vessels of desired volume, with a valve and passivated interior surfaces. After the samples have been collected, the canisters are properly labeled with a chain-of-custody (COC) form and transported to a laboratory for analysis. At the laboratory, the contents of each canister are analyzed using a high-resolution gas chromatograph (GC) coupled to one or more GC detectors. There are several problems associated with the current methods of measuring VOC concentrations. Adsorption of hydrocarbon molecules onto gas canister walls has been observed (Koziel et al., 2004; Scott Specialty Gases, 2004). Loss of gases from the canisters and reaction among gases during transport and storage is also a concern. The VOCs in ambient air of livestock operations have also been determined using sorbent tubes, referred to as EPA Method TO-17 (Cai et al., 2010; Parker, 2008; Trabue et al., 2011). In this method, air samples are pulled using a portable vacuum pump at a particular rate and time through stainless steel sorbent tubes filled with an

absorbent (commonly, Tenax TA) to trap analytes (VOCs). The tube is stored at less than 4 °C in the field and transferred to the laboratory for analysis with a GC/mass spectrometer (MS) equipped with an automatic thermal desorber (ATD).

Capareda et al. (2005) proposed a new protocol for quantifying VOC emissions from AFOs by introducing modifications to EPA Method TO-14A. This protocol (Capareda et al. 2005) included using a portable GC in the field where multiple flux measurements are made. All elements essential to Method TO-14A sample analysis (i.e., GC and GC detectors) are present except that the GC was taken to the field so that samples could be analyzed real time on site rather than storing them in gas canisters and analyzing them in a laboratory. The new protocol showed promising results for determining RVOCs fluxes from GLAS (Capareda et al., 2005a).

In this study, this protocol was used to determine odorous VOC emissions from a free-stall dairy with the following specific objectives: identify and quantify phenol and *p*-cresol concentrations from different GLAS in the dairy; estimate and compare the phenol and *p*-cresol emission rates (ERs) from different GLASs of the same dairy during summer and winter seasons; and identify areas in a dairy operations that have the greatest phenol and *p*-cresol emissions.

Materials and Methods

Air sampling and description of the dairy operation

The study was conducted in a free-stall dairy operation located in central Texas to determine emissions of the two odorous VOCs (phenol and *p*-cresol) from different GLASs (Figure 1). This facility had a naturally ventilated free-stall barn with open sides and ends. The barn was 140 m × 31 m (area about 4340 m^2) and housed about 460 and 330 milking cows during winter and summer, respectively. The barn was flushed once a day at 6:30 a.m. from a storage tank that recycled wastewater from the secondary lagoon. The flushed manure was channeled into a two-chambered gravitational settling basin for separating liquid and solids. The separated liquid was then piped into a primary anaerobic lagoon and the separated solids were

Figure 1. Aerial view of the free-stall dairy that was used in this study showing the ground-level sources (source: Google map).

applied to the pasture/crop field. During summer, the secondary lagoon was completely dry and the primary lagoon was nearly empty (the waterline surface area was 1/15 of the winter time). To excavate sludge from the primary lagoon, the wastewater was continuously pumped out to irrigate the adjacent crop field. In addition, approximately 50% reduction in silage area was noticed during the winter sampling compared to the summer as feeding progressed. The cows were kept in a loafing area for about 6 hours every day from around 12:30 to 6:30 a.m. until their first milking, and the barn was flushed. The loafing area was an unpaved, confined area with access to the barn and milking parlor including a paved walkway around the barn. Air samples were collected from six delineated GLASs, namely, the loafing pen, walkway (to and from parlor and loafing pen), barn, silage pile, settling basin, and lagoons within the dairy operation (Figure 1) during summer (August 2009) and winter (January 2010). The area of each GLAS is presented in Table 1 and its percent contribution to the total area is presented in Figure 2.

Sampling was conducted for 5 consecutive days during daylight hours (9:00 a.m. to 7:00 p.m.). Size of each GLAS and accessibility of the measuring instrument to it were considered to determine the number of samples (3–10) to be taken from each GLAS (Table 1). Before sampling was initiated, an imaginary 36-cell (6 × 6) grid for each GLAS was assigned a number from 1 to 36. Randomly generated cell numbers were selected to place a flux chamber for sampling in that GLAS. Twenty-nine and 37 chromatograms of air samples were acquired from different GLASs of the dairy during a week-long sampling campaign each in the summer and winter, respectively. The ambient air temperatures were measured and recorded using HOBO sensors and data loggers (model U23-001; Onset Computer Corporation, Pocasset, MA).

Sampling protocol

Isolation flux chamber and flux generation

The protocol proposed by Capareda et al. (2005a; 1995b) for VOCs was used for quantifying phenol and *p*-cresol emissions from this dairy. A schematic of sampling system used to determine odorous VOC emissions is shown in Figure 3. This protocol consisted of a flux chamber (Figure 4) and a portable GC. The flux chamber was used to generate and collect air samples from each GLAS. The upper (hemispherical dome) portion of the flux chamber used in the field was made of Plexiglas, whereas the bottom (cylindrical skirt) was made of stainless steel. The two portions were flanged together by 6.35-mm (1/4-inch) steel bolts. The footprint area and volume of the flux chamber were 0.192 m^2 and 54.5 L, respectively. To keep sampling bias and measurement error to a minimum, recommended flux chamber operating parameters were adopted and measurements were made based on the flux chamber user guide (Gholson et al. 1989; Kienbusch, 1986). Those include gas sealing around the flux chamber bottom and placing flux chamber gently on the source to minimize soil disturbance. A sweep air flow rate of 5 L min^{-1} was maintained using a mass-flow controller to alleviate the issues associated with the creation of a
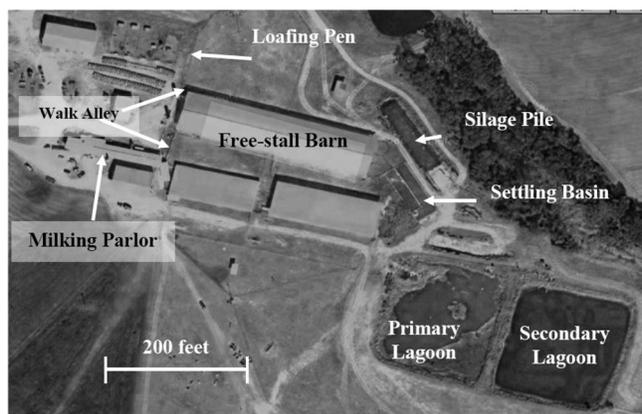
Table 1. Number of samples, GLAS area, ambient temperature (average ± standard deviation), volumetric concentrations (average ± standard deviation) during summer and winter

GLAS	Number of Samples		GLAS Area (m^2)		Ambient Temperature (°C)		Phenol (ppbv)		*p*-Cresol (ppbv)	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
Barn	3	9	1980	1980	0.6 ± 0.4	23.8 ± 2.1	151 ± 114[yz]*	38 ± 12[d]*	29 ± 29 yz	15 ± 5 cd
Manure lane Bedding	3	3	1524	1524	8.3 ± 1.1	26.6 ± 2.2	58 ± 1.4[z]*	18 ± 7[d]*	14 ± 5.8 z	8.4 ± 5.5 d
Loafing pen	6	10	22638	22638	9.4 ± 1.6	36.1 ± 2.8	209 ± 59 yz*	99 ± 29 bc*	52 ± 18 xy	42 ± 17 b
Lagoon	4	3	7525	506	7.39 ± 1.2	34.4 ± 1.9	284 ± 77 y*	74 ± 26 cd*	74 ± 13x*	30 ± 10 bc*
Primary Secondary	3	—	7027	—	8.4 ± 0.9	—	128 ± 11 yz	—	38 ± 4 yz	—
Settling basin	3	6	892	892	15.8 ± 1.9	31.2 ± 1.9	55 ± 9 z	127 ± 67 ab	15 ± 2 z*	24 ± 5 cd*
Silage	4	3	480	942	8.9 ± 1.3	31.3 ± 1.4	569 ± 227 x*	177 ± 54 a*	72 ± 35 x	57 ± 13 a
Walkway	3	3	739	739	12.7 ± 1.0	36.1 ± 3.1	110 ± 14 yz*	65 ± 23 cd*	19 ± 5 yz*	31 ± 6 bc*
Total	29	37	42805	29221						

Notes: The values in a column, representing average concentration for different GLAS in a particular season, followed by common letter(s) do not differ significantly at $P \leq 0.05$. The values in a row, representing average concentration for two seasons in a particular GLAS, followed by * do not differ significantly at $P \leq 0.05$.
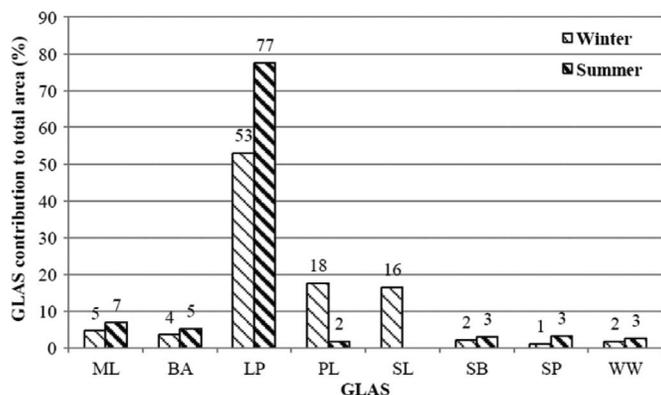
Figure 2. Seasonal contribution of the GLAS area to the total area at the free-stall dairy. ML = manure lane; BA = bedding area; LP = loafing pen; PL = primary lagoon; SL = secondary lagoon; SB = settling basin; SP = silage pile; WW = walkway.

microenvironment thereby avoiding negative bias associated with stagnant air or insufficient airflow in the chamber (Gholson et al., 1989; Kienbusch, 1986)

Before the sampling was initiated, the flux chamber was purged with zero-grade air at a flow rate of 5 L min⁻¹ for about 30 min. Also, at the end of air sampling at each location in a GLAS, the air sampling tube and the flux chamber were purged when relocated. The compressed zero-grade air used for sampling had O_2 content between 19.5% and 23.5% and total hydrocarbon (THC) concentrations below 0.2 ppbv. Teflon tubing (0.635 cm inner diameter [i.d.]) was used to convey 5 L min⁻¹ zero-grade air ("sweep air") to the flux chamber. Three holes on top of the chamber allowed air to escape while a fourth hole at the apex of the dome was used to convey sample air (2 L min⁻¹) back into the GC though another 45-m-long Teflon tube identical to that used to convey sweep air. The volume of air samples drawn from the flux chamber was regulated by a mass-flow controller connected to the pump. The incoming air from the flux chamber was connected to a splitter that diverts incoming air either to a greenhouse gas (GHG) GC or a VOC GC or both GCs concurrently. Of the 2 L min⁻¹ of air drawn from the flux chamber, 360 mL min⁻¹ was directed to the purge-and-trap system of the VOC GC for 10 min. Thus, VOCs were concentrated using two adsorbent traps (described below) connected to the GC before being injected into the GC column. Excess air was purged out of the GC while injected samples (desorbed gas from the traps after being heated) were analyzed in the system. Any moisture in air samples was filtered during sampling by a Nafion dryer placed immediately before the gas input manifolds of GCs (Figure 3).

Descriptions of VOC GC

The GC was a portable unit manufactured by SRI Instruments (model 8610C; Torrance, CA) with event (sampling duration, sample injection into GC column, temperature of the column, etc.) programming capability. Two traps satisfying EPA Method TO-14A purge-and-trap preconcentration requirements were installed in the system to concentrate VOCs in the sample air to detectable levels: a Carbosieve trap (Restek Corporation, Bellefonte, PA), which concentrated highly volatile compounds with low boiling points more readily and with higher chromatogram peaks and a chemically inert Tenax-GR trap (Restek Corporation, Bellefonte, PA), which concentrated most other hydrocarbons. After 10 min of concentrating on the traps, the VOCs were desorbed by heating to 200 °C for 5 min and then automatically injected into the GC column. No attempt was made to differentiate the compounds adsorbed onto each trap. The effect of the mass-flow controller and Teflon-coated diaphragm of the vacuum pump on gas concentrations was checked in the laboratory using calibration gases. Negligible differences in the GC responses (gas concentrations) were noted (~1.5%) between direct flow of the calibration gas to sorbent tubes and
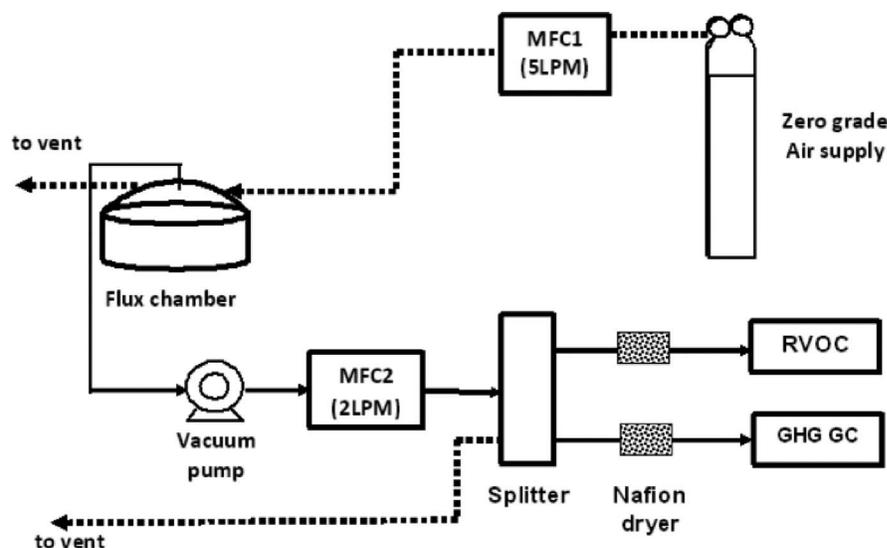
Figure 3. Schematic setup for VOC field sampling protocol (not to scale).
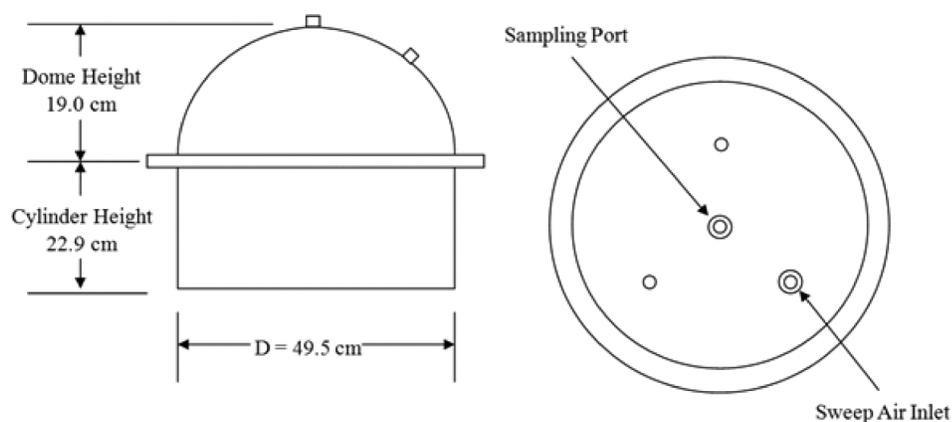

Figure 4. Flux chamber used for air sampling.

passing the gas through a pump and flow controller before it entered the sorbent traps.

The GC was equipped with two nonspecific detectors: a photo-ionization detector (PID), which "responds to all molecules whose potential is below 10.6 eV, including aromatics and molecules with carbon double bonds" (SRI Instruments, 2008), and a flame-ionization detector (FID), which is a mass-sensitive hydrocarbon detector with a nearly universal response to organic compounds (compounds containing CH groups). Typical sample detection limits for the FID are 10^{-14} g carbon sec^{-1}, with a linear response range of 10^6 to 10^7 orders of magnitude (Karger et al., 1973). The GC column was a nonpolar, 100% dimethylpolysiloxane phase, stainless-steel-treated capillary column (MXT-1; Restek Corporation, Bellefonte, PA) that was 60 m long with a 0.53 mm inner diameter and 5.0 μm film diameter. The carrier gas used was helium (He) at a flow rate of 100 mL min^{-1}. The compounds were detected by the FID and PID detectors with temperatures set at 150 °C. The GC column temperature was programmed to maintain an initial temperature of 40 °C for 10 min (sampling or concentrating time). The column was then programmed to heat at 10 °C min^{-1} to 210 °C, and was maintained at 210 °C for another 15 min. Compound peaks were recorded and analyzed with PeakSimple Chromatography Data System Software (Ver. 3.72; SRI Instruments). This GC measurement system was housed inside an air-conditioned trailer. Blank field samples were run before air sampling began at each location (ground-level area sources [GLAS]) to ensure the column was clean and functioning properly. At the beginning of each day field blanks were obtained by running the GC with the same method (temperature and event program) except the air mixture was not flowing through the GC systems. In this study, 1–2 blanks were found to be sufficient to produce a peak less chromatogram (showed no detectable peak).

Identification of compounds

Concurrent to in-field chromatography, air samples were also collected in cleaned and evacuated gas canisters. To fill the 6-L canisters (TO-Can Canister; Restek Corporation, Bellefonte,

PA), air from the flux chamber was drawn in using a vacuum pump (model UN035TT; KNF Neuberger, Trenton, NJ) at the rate of 2 L min^{-1} until the canister pressure reached 30 psi. The air samples collected in gas canisters were sent to the Air Quality Laboratory of West Texas A&M University in Canyon, TX, for analysis. The GC/MS (Varian 3800/Saturn 2000 GC/MS; Varian, Walnut Creek, CA) equipped with an automatic thermal desorber (Perkin-Elmer, Shelton, CT) system at West Texas A&M University was set up for identifying 13 target compounds including phenol and *p*-cresol. Air samples collected in canisters were analyzed with GC/MS to identify which compounds were contained in the sampled air chromatograms using our GC measurement systems. A total of 13 odorous VOCs (acetic acid, propionic acid, isobutyric acid, phenol, *p*-cresol, 4-ethylphenol, butyric acid, isovaleric acid, hexanoic acid, 2-aminoacetophenone, indole, and skatole) were identified using a GC/MS system. Because of the high cost of calibration gas, our initial attempt was to calibrate the GC with two VFAs (acetic and propionic acid) and two phenolic compounds (phenol and *p*-cresol). The acetic and propionic acid calibration gas was found unstable at 1 ppm concentration level. Therefore, we only proceeded with phenol and *p*-cresol. Of the 13 compounds identified by GC/MS, the identity of the two odor-causing VOCs (phenol and *p*-cresol) was confirmed by matching retention times to those of standard gases. In this study, phenol and *p*-cresol standards were used to calibrate the GC for estimating ERs of these two odorous VOCs.

Calibration, method detection limits, and percent recovery

To ensure accurate calculation of concentrations from the chromatograms acquired during field sampling, gas standards were introduced into the portable GC following the field sampling protocol. Standard gases (phenol and *p*-cresol) were procured from Scott Specialty Gases (Air Liquide America Specialty Gases, Plumsteadville, PA). Both FID and PID detectors responded well for phenol and *p*-cresol. In this study, responses from the FID were used for identification and quantification. To generate calibration equations, 1 ppmv of each standard gas balanced in nitrogen was passed through the traps at a rate of 360 mL min^{-1} for 2.5, 5, 10, 15, and 20 min to concentrate the respective analyte on the traps. For phenol and *p*-cresol, standard curves were developed from five known volumes of each standard with three to seven replicates at each volume. For field sample analysis, a linear regression (forced through the origin) was fit between the peak areas and compound

weights (μg) to interpolate the total concentration of compounds in the field samples. The molecular mass and density of respective compounds used in the calculations at standard atmospheric conditions (25 °C and 1 atm.). Method detection limits (MDLs) were calculated per U.S. EPA guidelines (U.S. Environmental Protection Agency, 1995) as the product of the standard deviation of seven replicates and the Student's *t* value at the 99% confidence level. The percent recovery was calculated using the ratio of the mass of a particular compound (μg) concentrated in the trap to the mass of analyte (μg) derived from the corresponding regression equation of the compound and expressed in percent. The regression coefficients (R^2) of the standard equations, MDL, and percent recovery reflect the accuracy and reliability of the phenol and *p*-cresol measurements using the portable GC (Table 2).

Determination of breakthrough volume

The term breakthrough volume (BTV) is defined as the volume of carrier gas that will purge an analyte through 1.0 g of adsorbent resin in a desorption tube at a specific temperature (ATAS GL Science Company, 2001). The BTV of each target gas was determined by passing a range of sample volume of standard gas through desorption tubes over which the GC response was linear (Air Resources Board (ARB), 2005). For a fixed flow rate of 350–360 mL min^{-1} used during field sampling, a range of sample volumes was created by increasing sample collection times (2.5, 5, 10, 15, and 20 min) to concentrate the phenol and *p*-cresol in the adsorbent resin. As presented in Figure 5, these research data showed that after 10 min of trapping phenol and *p*-cresol (3.6 L volume), no breakthrough was observed (i.e., the plot between area counts under a peak and a range of volume up to 3.6 L was linear). To eliminate the affect of moisture on the BTV, a Nafion dryer was used downstream of the purge-and-trap system (Figure 3). The trap temperature was set at 35 °C to concentrate low-boiling-point highly volatile compounds in the Carbosieve trap.

Emission rate estimation

To compare the estimated emission rates (ER) between the summer and winter the measured volumetric concentrations of phenol and *p*-cresol were converted to a mass concentrations (μg m^{-3}) using the ideal gas law at standard temperature and pressure (25 °C and 1 atm) (eq 1). Equations 2 and 3 were used to calculate emission flux (EFlux), and emission rate (ER), respectively.

Table 2. Physical characteristics and analytical method performance

Compounds	CAS No.	MW (g mol^{-1})	MP (°C)	BP (°C)	Retention Time (min)	Standard Equations	R^2	MDL (ppbv)	Percent Recovery
Phenol (C$_6$H$_5$OH)	108-95-2	94.11	40–42	182	22.13	$y = 0.164(x)$	0.98	9.08	96.7
p-Cresol (CH$_3$C$_6$H$_4$OH)	106-44-5	108.14	34	202	24.28	$y = 0.140(x)$	0.96	8.13	95.2

Notes: CAS No. = Chemical Abstracts Service Number; MW = molecular weight; BP = boiling point; MP = melting point; MDL = method detection limit.
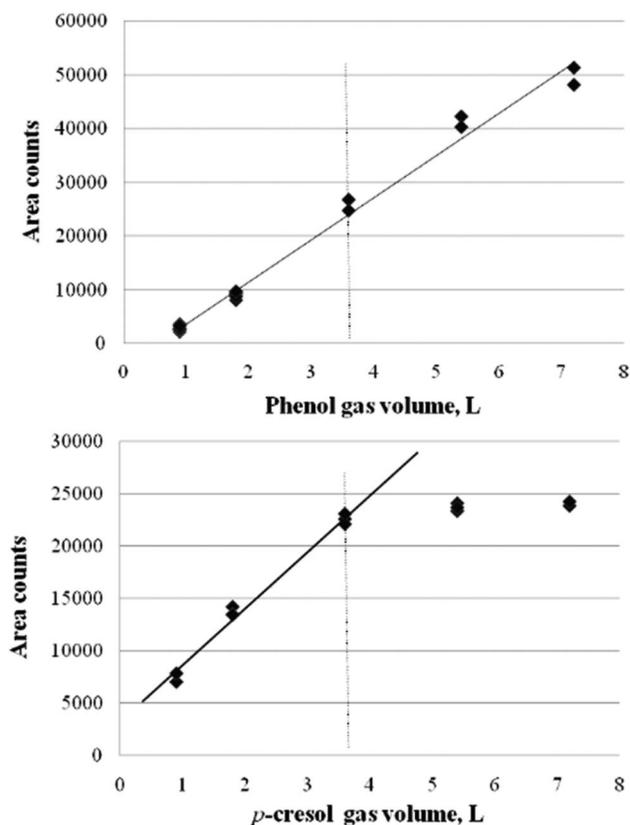
Figure 5. Breakthrough curves for phenol (top) and *p*-cresol (bottom).

$$C_{\text{mass}} = \frac{1000 \times (C_{\text{ppm}}) \times \text{MW}_p}{24.45} \qquad (1)$$

$$\text{EFlux} = \frac{C_{\text{mass}} \times V_{\text{fc}}}{A_{\text{fc}}} \qquad (2)$$

$$\text{ER} = \frac{\text{EFlux} \times 1.44}{\text{TNA}} \times A_{\text{sc}} \qquad (3)$$

where C_{mass} is the concentration of a compound on a mass basis (μg m^{-3}), C_{ppmv} is the volumetric concentration of compound (ppmv), MW$_p$ is the molecular weight (g mol^{-1}) of compound at standard pressure and temperature, 24.45 is the volume per mole of an ideal gas at standard temperature and pressure (L gmol^{-1}), EFlux is the gas emission flux (μg m^{-2} min^{-1}), V_{fc} is the flow rate of air supplied to the flux chamber (m^3 min^{-1}), A_{fc} is the foot print area of flux chamber (m^2), ER is the emission rate (mg hd^{-1} day^{-1}), A_{sc} is the area of source (GLAS; m^2), and TNA is the total number of animals.

Statistical analysis

The arithmetic means as measure of central tendencies were used to compare concentrations and ERs among the GLAS between seasons, and standard deviations were used to indicate the dispersion of concentrations and ERs in each GLAS. Measured gas concentrations and estimated emission rates

from each GLAS in the dairy were compared. The null hypothesis tested states that mean VOCs concentrations and ERs among different GLASs and between seasons for a particular GLAS were equal. Statistical analyses of the measured VOC concentrations and estimated emission rates were carried out through analysis of variance (ANOVA) using General Linear Model function in SAS (SAS, 1999). Significance of the observed difference between any pair of GLAS VOC means (among different GLASs in a particular season, and between summer and winter for a particular GLAS) was determined by Duncan's multiple range test (Steel et al., 1997) at 5% level of significance ($P \leq 0.05$) if the main effect (GLAS/season) was significant using F test at $P \leq 0.05$.

Results and Discussion

Phenol and *p*-cresol concentrations in different GLAS

To measure GC responses for phenol and *p*-cresol at each location, the chromatogram from the blank run was subtracted from the air sample chromatogram and was used for calculating concentrations. In this study, VOC concentration values obtained from field blanks ranged from 0.5 to 2 ppbv. Concentrations from different GLAS during the winter ranged from 55 to 569 ppbv (212 to 2191 μg m^{-3}) for phenol and 15 to 74 ppbv (66 to 327 μg m^{-3}) for *p*-cresol. During summer, concentrations ranged from 18 to 177 ppbv (69 to 681 μg m^{-3}) and 8 to 57 ppbv (35 to 252 μg m^{-3}) for phenol and *p*-cresol, respectively (Table 1). The average ambient temperatures were 9.8 and 31.3 °C, in winter and summer, respectively. The measured concentrations of phenol and *p*-cresol in each GLAS varied widely as indicated by large standard deviations (Table 1). This was due to spatially variable manure loading rates, manure moisture, and manure constituents (manure, soil, urine, silage, etc.) at different GLASs in the dairy. The freshly voided manure in the concrete manure lane of the barn has the potential of carrying a higher number of bacteria to produce gaseous emissions than a recently flushed manure alley. Similarly, anaerobic liquid manure in the primary lagoon and settling basin might produce higher gaseous emissions due to anaerobic degradation than other sources. The fresh and accumulated manure with sporadic urine mixed, and minor faction of the soil, made the loafing pen a different source compared to others. Previous research reported that ambient temperature, soil moisture, and manure composition are the primary factors controlling anaerobic decomposition in feedyard soils (Miller and Varel, 2001). Mukhtar et al. (2008) also reported highly variable ammonia (NH$_3$) emissions from open-lot sources in a free-stall dairy in central Texas due to variable manure loading rates.

Concentrations of odorous VOCs (phenol and *p*-cresol) measured during the summer from different GLASs were higher than those measured by sampling downwind from a smaller dairy using sorbent tubes (Rabaud et al., 2002), as would be expected since sampling was conducted directly at the sources. Rabaud et al. (2002) identified and quantified odorous and nonodorous compounds downwind of a dairy farm (90 × 93 m) located at University of California campus with 120 milking cows and 100 heifers. Air sampling was performed during the summer (June to

August) on nine separate occasions. In the authors' measurements, concentrations of VOCs (20 odorous and nonodorous compounds) measured downwind of a small dairy ranged from 0.55 to 320.20 μg m^{-3} (Rabaud et al., 2002). Currently, there are no other dairy operation GLAS phenol and p-cresol emissions studies to compare with the present study; however, three studies measuring the air quality within the dairy barns have been conducted. Sun et al. (2008) used an environmentally controlled chamber (142 m^3) with 18 cows inside to measure alcohol, VFA, phenol, and methane emissions from dairy cows and fresh manure. The air sampling point was placed at ceiling height. The VFA and phenols emitted were close to the limit of quantification (LOQ) of the measuring instrument. The LOQ for phenolic compounds ranged from 0.02 to 2.7 μg m^{-3}. Sunesson et al. (2001) reported detection of phenol (3–50 μg m^{-3}) and p-cresol (0.6–100 μg m^{-3}) from eight farms in northern Sweden where farm size ranged from 10 to 82 milking cows. Cai et al. (2010) conducted studies in two barns in Wisconsin and Indiana to quantify odor and odorous chemicals from animal buildings during four 13-week periods. Measured average concentrations for phenol and p-cresol varied from 2.06 to 4.56 and from 3.09 to 6.31 μg m^{-3}, respectively. Our values for phenol and p-cresol from the barn (manure lane and bedding area) were higher than those found in the literature since measurements were made directly at the emitting sources.

In this research, average concentrations of phenol and p-cresol measured from the primary lagoon of a dairy during summer were 74 ppbv (285 μg m^{-3}) and 30 ppbv (133 μg m^{-3}), respectively (Table 1). These concentration values were comparable to those measured using wind tunnel and GC/MS method from a dairy lagoon in the Texas Panhandle (Parker, 2008). Measured concentrations for phenol and p-cresol were 78.44 ppbv (302 μg m^{-3}) and 40.5 ppbv (179 μg m^{-3}), respectively (Parker, 2008). The highest phenol and p-cresol concentrations were measured from the silage pile in comparison to other sources during summer and winter (Table 1). Higher average phenol and p-cresol concentrations in this GLAS were most likely due to the fermentation of silage as this process converts sugars in the silage pile (glucose, fructose, and sucrose) into cellular energy with ethanol, VOCs (including phenols and p-cresol), and carbon dioxide as metabolic waste products (Ciccioli et al., 1993). Next to silage, the average phenol and p-cresol concentrations at the loafing pen were significantly higher than those from other GLASs during summer and winter. This was likely due to the fermentation of fresh manure with occasional urine mixed, a minor fraction of the soil giving it a greasy consistency during the winter, and a year-round compacted soil surface, producing phenol and p-cresol emissions. This fermentation was induced by the anaerobic environment of the loafing pen and the anaerobic condition of soil layers immediately under the pen manure's top surface (Saggar et al. 2004). This situation in the loafing pen emitted more phenol and p-cresol during winter than summer when it was dry. In general, average phenol concentrations measured in the winter from different GLAS were significantly higher than those measured in the summer ($P < 0.05$) with the exception of the settling basin. During winter, the prevalence of relatively high moisture conditions in the GLAS due to low temperature enhanced anaerobic degradation of the manure, which generated higher phenol emission. The average phenol concentrations measured from the barn (manure lane and bedding area combined), loafing pen, primary lagoon, silage pile, and walkway during the winter were about 4, 2, 4, 3.2, and 1.7 times significantly ($P < 0.05$) higher, respectively, than those measured in the summer (Table 1). In contrast, average phenol in the settling basin during the winter was about 2.3 times lower than those in the summer (Table 1).

In general, p-cresol concentrations measured in the manure lane, bedding area, loafing pen, and silage pile during the winter were higher than those measured in the summer, although those differences were not statistically significant. In the winter, excessive wet conditions of the GLAS caused by low temperatures (i.e., lower rates of evaporation) generated higher concentration of odorous VOCs (phenol and p-cresol). Miller and Varel (2001) reported that ambient temperature, soil moisture, and manure composition are the primary factors controlling anaerobic decomposition in feedyard soils, and are responsible for generating odorous compounds. Between summer and winter, average p-cresol concentrations in the primary lagoon were significantly different and higher during the winter. Average p-cresol concentrations between two seasons in the silage pile were statistically similar. In contrast, average p-cresol concentration in the settling basin during the winter was about 1.6 times lower than those measured during the summer. This was because of reduced bacterial degradation of freshly flushed manure in the settling basin, and a reduced evaporation of malodorous compounds (phenol and p-cresol) due to low winter temperatures. Average p-cresol concentrations measured at the primary lagoon and silage pile in the winter were about 2.5 and 1.3 times, respectively, higher than those in the summer. In the winter, higher phenol and p-cresol concentrations were measured from the barn (manure lane and bedding combined), loafing pen, primary lagoon, silage, and walk-alley, where those areas constituted about 83% of the total area (Figure 2). The loafing pen alone contributed about 53% and 77% of the total area during winter and summer, respectively (Figure 2). Therefore, mitigation strategies aimed at these areas would realize the greatest effect on overall emissions of phenol and p-cresol from the dairy. There are many commonly applied approaches to control odor and odorants, including low-nitrogen ration/diet, covering of manure storage tanks, lagoons, manure stockpiles, and anaerobic digesters. Others include frequent manure removal from emitting surfaces by flushing or scrapping alleys and injecting liquid manure under soil to a predetermined depth for reducing odor emissions.

Comparison of emission fluxes in different GLAS

The highest average phenol and p-cresol emission fluxes measured during summer and winter from the silage pile were significantly higher than those from other GLASs (Table 3). Next to the silage pile, higher phenol and p-cresol emission fluxes were measured from primary lagoon and loafing pen, although values between those two GLASs were not statistically different ($P > 0.05$). The average phenol emission fluxes measured in manure lane, bedding area, loafing pen, primary lagoon, silage pile, and walkway during winter were significantly higher

Table 3. Estimated average emission fluxes and rates for phenol and p-cresol in a free-stall dairy (mean ± standard deviation)

GLAS	Emission Flux (μg m⁻² min⁻¹)				Emission Rates (mg hd⁻¹ day⁻¹)			
	Phenol		p-Cresol		Phenol		p-Cresol	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
Barn								
Manure lane	$15.1 \pm 11.5^{yz*}$	$3.8 \pm 1.2^{b*}$	3.3 ± 3.4 yz	1.7 ± 0.57	$94 \pm 71 z*$	$33 \pm 10 b*$	$21 \pm 21 z$	$15 \pm 5 b$
Bedding area	$5.8 \pm 0.14^{z*}$	$1.8 \pm 0.8^{b*}$	1.7 ± 0.6 z	0.97 ± 0.6 d	$27 \pm 3 z*$	$12 \pm 5 b*$	$8 \pm 3 z$	$6 \pm 4 b$
Loafing pen	$20.9 \pm 5.9 yz*$	9.9 ± 2.9 bc*	6.0 ± 2.0 xy	4.8 ± 1.9 b	$1485 \pm 422 x*$	$978 \pm 283 a*$	$425 \pm 137 x$	$473 \pm 191 a$
Lagoon								
Primary	$26.5 \pm 7.7 y*$	7.4 ± 2.6 bcd*	$7.9 \pm 1.4 x*$	3.4 ± 1.2 bc*	$625 \pm 171 y*$	$16 \pm 5 b*$	$186 \pm 31 y*$	$7 \pm 3 b*$
Secondary	12.7 ± 0.8 yz	—	4.6 ± 0.5 yz	—	298 ± 24 yz	—	$101 \pm 10 yz*$	—
Settling basin	5.6 ± 0.9 z	13 ± 6.7 ab	$1.7 \pm 0.23 z*$	2.7 ± 0.5 cd*	$16 \pm 2 z$	50 ± 26 b	$5 \pm 2 z*$	$10 \pm 3 b*$
Silage	$57.2 \pm 22.7 x*$	$17.8 \pm 5.4 a*$	8.4 ± 4.0 x	6.6 ± 1.5 a	$86 \pm 34 z$	73 ± 23 b	$13 \pm 6 z*$	$27 \pm 5 b*$
Walkway	$11.0 \pm 1.4 yz*$	6.7 ± 2.3 cd*	$2.2 \pm 0.5 yz*$	3.7 ± 0.6 bc*	$25 \pm 3 z$	22 ± 8 b	$5 \pm 2 z*$	$12 \pm 3 b*$
Total					2656 ± 728	1183 ± 362	763 ± 212	551 ± 214

Notes: The values in a column, representing average flux and emission rate for different GLAS in a particular season, followed by common letter(s) do not differ significantly at $P \leq 0.05$. The values in a row, representing average flux and emission rate for two seasons in a particular GLAS, followed by * do not differ significantly at $P \leq 0.05$.

than those measured in summer ($P < 0.05$). Similarly, p-cresol concentrations measured in manure lane, bedding area, loafing pen, and silage pile during winter were higher than those measured in summer; however, not statistically significant.

In contrast, phenol and p-cresol emission fluxes measured during summer in dairy barns in colder regions (Wisconsin and Indiana) were higher than those in winter (Cai et al., 2010). This was likely due to the moderate winter of central Texas compared to Wisconsin and Indiana. The average temperatures at the study areas in Wisconsin and Indiana during winter (December and January) and summer (July to August) were approximately -2 and $19 °C$, respectively (US Weather; US Weather). In central Texas, winter and summer temperatures at the study area were 6.6 and $26.6 °C$, respectively (US Weather). In comparison to the Wisconsin and Indiana winter, central Texas climate was moderate with an average daily temperature of $8.9 °C$ (range: 0.6 to $15.8 °C$) during the sampling week. On the other hand, it was hotter (23.8 to $36.1 °C$) in Texas than Wisconsin and Indiana in summer and the ground sources at the Texas dairy were drier in summer than in winter. The ground sources were wetter because of low evaporation during the winter that resembled nearly anaerobic condition for manure accumulated on those surfaces. Therefore, higher phenol and p-cresol emissions resulted at the dairy when compared to those during summer.

Emission fluxes for phenol and p-cresol from lagoon were also compared with those obtained using a wind tunnel (Parker, 2008). In our research, the estimated emission fluxes from the primary lagoon during summer ranged from 4.6 to 9.8 μg m⁻² min⁻¹ (average 7.4 μg m⁻² min⁻¹) for phenol and 2.7 to 4.8 μg m⁻² min⁻¹ (average 3.4 μg m⁻² min⁻¹) for p-cresol. These emission fluxes were lower than those measured for phenol and p-cresol ranging from 7 to 155 μg m⁻² min⁻¹ and from 11 to 117 μg m⁻² min⁻¹, respectively, using the wind tunnel and GC/MS method from a dairy lagoon in the Texas Panhandle (Parker, 2008). However, there is debate about the appropriateness and accuracies of wind tunnels and flux chambers for quantifying pollutant emissions at AFOs because of small measurement footprint relative to the size of the source (Parker et al. 2010). Hudson et al. (2009) reported that wind tunnel odor emission rates were 60 to 240 times higher than those in the U.S. EPA flux chamber.

Estimation of emission rates in different GLAS

In the winter, estimated average ERs for phenol and p-cresol in this study ranged from 16 to 1485 and from 5 to 425 mg hd⁻¹ day⁻¹, respectively. Similarly, estimated ERs for phenol and p-cresol ranged from 12 to 978 and from 6 to 473 mg hd⁻¹ day⁻¹, respectively, in the summer (Table 3). The estimated average ERs for phenol and p-cresol within the GLAS varied widely as indicated by the large standard deviations (Table 3). Variations were likely attributable to variations in the air temperature, moisture content of manure, and spatially variable manure loading rates at different GLAS areas in a dairy operation. Miller and Varel (2001) reported that air temperature, moisture, and manure composition are three primary factors controlling the rate and extent of anaerobic manure decomposition in the cattle feedyard soils that supplies the pool of odorous

compounds. Mukhtar et al. (2008) also reported variations in ammonia emissions in a dairy operation due to air temperature and manure loading rates. During winter, phenol ERs estimated from the loafing pen and the primary lagoon were significantly ($P < 0.05$) higher than those estimated from other GLASs (Table 3). The highest average phenol ERs were from the loafing pen and estimated to be 1485 and 978 mg hd^{-1} day^{-1} during winter and summer, respectively, and they were significantly different from each other GLAS ($P < 0.05$). Average phenol ER estimated at the loafing pen during winter was about 1.5 times higher than that in summer. Phenol and p-cresol ERs estimated from the primary lagoon were 16 and 7 mg hd^{-1} day^{-1}, respectively, and were much lower than the range reported previously (Parker, 2008). This was because the primary lagoon was almost empty during summer and its surface area at the water line was 6.73% of the winter (Table 1) surface area. To remove the sludge from the primary lagoon, the wastewater was continuously pumped out to irrigate the nearby crop field. Assuming the normal lagoon area as winter, the estimated phenol and p-cresol ERs during summer equate to 238 and 104 mg hd^{-1} day^{-1}, respectively. These extrapolated ER values for phenol and p-cresol fall within the range (Parker, 2008) estimated previously for a dairy lagoon. Parker (2008) reported that ERs for phenol and p-cresol were from 33 to 735 mg hd^{-1} day^{-1} and from 52 to 555 mg hd^{-1} day^{-1}, respectively, for a dairy lagoon at Texas Panhandle with 9890 m^2 surface area and 3000 dairy cows.

In this study, phenol ERs from the barn manure lane and bedding area were 121 and 45 mg hd^{-1} day^{-1}, respectively, for winter and summer. Similarly, p-cresol ERs estimated from manure lane and bedding area were 29 and 21 mg hd^{-1} day^{-1}, respectively, between winter and summer. The phenol and p-cresol ERs estimated from the barn during summer and winter were lower than those measured in the mechanically ventilated barns from Wisconsin and Indiana dairy (Cai et al. 2010). The estimated phenol ERs in a dairy barn in Wisconsin were 141 and 30 mg hd^{-1} day^{-1}, respectively, during summer and winter. Similarly, estimated p-cresol ERs for this dairy were 298 and 44 mg hd^{-1} day^{-1}, respectively, for the two seasons. In a dairy barn in Indiana, the estimated phenol ERs were 94 and 7 mg hd^{-1} day^{-1}, respectively, during summer and winter. Similarly, estimated p-cresol ERs for this dairy were 70 and 68 mg hd^{-1} day^{-1}, respectively, for the same periods (Cai et al. 2010). The ERs in enclosed Midwestern barns were higher because of greater gas buildup than those in a naturally ventilated barn with open sides and ends in central Texas.

There were no significant differences in the phenol ERs among the barn, settling basin, silage pile, and walkway during winter ($P > 0.05$). Similarly, phenol ERs among barn, settling basin, silage pile, and walkway were statistically similar during summer ($P > 0.05$). The loafing pen also showed significantly higher p-cresol ERs during summer and winter when compared with other GLAS. The average p-cresol ER in the winter and summer from the loafing pen (425 and 473 mg hd^{-1} day^{-1}, respectively) was the highest amongst the GLASs in both seasons and was significantly different from other GLASs ($P < 0.05$). There were no significant differences in p-cresol ERs estimated from the barn, lagoons, settling basin, silage

pile, and walkway during summer ($P > 0.05$). Therefore, for reducing phenol and p-cresol emissions, abatement and management practices must be directed to the loafing pen and lagoons, since those emission areas constituted about 87% of the total GLAS of the dairy operation during winter (Figure 2).

Overall phenol and p-cresol emission rates

The overall estimated winter ERs for phenol and p-cresol were 2656 and 763 mg hd^{-1} day^{-1}, respectively. Similarly, the overall estimated summer ERs for phenol and p-cresol were 1183 and 551 mg hd^{-1} day^{-1}, respectively (Table 3). For this free-stall dairy, overall phenol and p-cresol ERs in winter were about 2.2 and 1.4 times higher than those in summer. The contribution of each GLAS to the overall phenol and p-cresol ERs during summer and winter for this free-stall dairy are presented in Figures 6 and 7, respectively. The loafing pen alone contributed about 56% of the overall phenol ERs and 55% of the overall p-cresol ERs during winter (Figures 6 and 7). Similarly, the loafing pen alone contributed about 82% of the overall phenol emissions and 86% of overall p-cresol emissions during
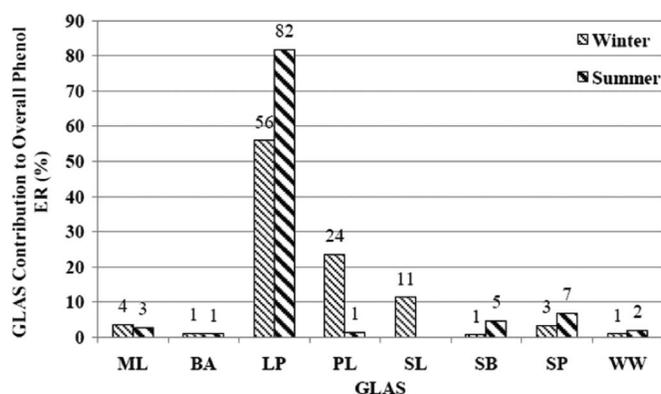
Figure 6. Seasonal GLAS contribution to overall phenol ERs at the free-stall dairy. ML = manure lane; BA = bedding area; LP = loafing pen; PL = primary lagoon; SL = secondary lagoon; SB = settling basin; SP = silage pile; WW = walkway.

Figure 7. Seasonal GLAS contribution to overall p-cresol ERs at the free-stall dairy. ML = manure lane; BA = bedding area; LP = loafing pen; PL = primary lagoon; SL = secondary lagoon; SB = settling basin; SP = silage pile; WW = walkway.
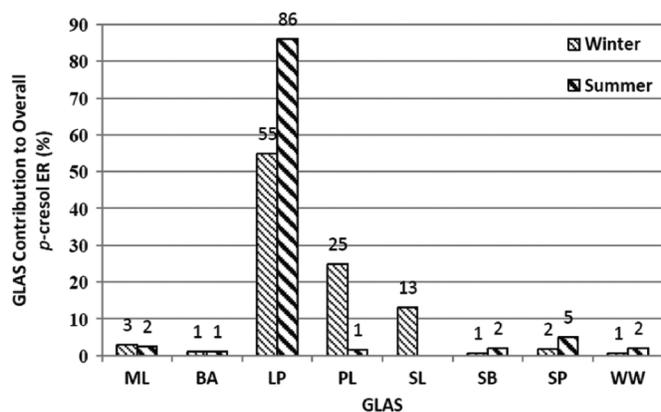
summer (Figures 6 and 7). Furthermore, the loafing pen and lagoons (primary and secondary) contributed about 91% of the overall phenol ERs during winter and comprised about 87% of the total GLAS of the dairy operation (Figures 2 and 6). Therefore, abatement and management practices that address emissions from these sources that comprise about 87% of the total GLASs area will likely be most effective for reducing facility emissions.

Summary and Conclusions

A modified EPA Method TO-14A was used for determining phenol and *p*-cresol emissions from different GLASs in a free-stall dairy operation in central Texas. This protocol employed a flux chamber and a portable GC, coupled with purge-and-trap system to quantify VOCs directly in the field. The measured concentrations of phenol and *p*-cresol within and among the GLASs in this dairy operation varied widely due to spatially variable manure loading rates and manure microbial activity. The estimated ERs for phenol and *p*-cresol ranged from 16 to 1485 and from 5 to 425 mg hd^{-1} day^{-1}, respectively, during winter. In the summer, estimated average ERs for phenol and *p*-cresol ranged from 12 to 978 and from 6 to 473 mg hd^{-1} day^{-1}, respectively.

The overall calculated ERs for phenol and *p*-cresol were 2656 ± 728 and 763 ± 212 mg hd^{-1} day^{-1}, respectively, in winter. Overall calculated phenol and *p*-cresol ERs were 1183 ± 361 and 551 ± 214 mg hd^{-1} day^{-1}, respectively, in summer. In general, overall phenol and *p*-cresol ERs in the winter were about 2.2 and 1.4 times higher than those in the summer for this free-stall dairy. The loafing pen alone contributed about 82% of the overall phenol ERs and 86% of overall *p*-cresol ERs during summer. The loafing pen and lagoons (primary and secondary) contributed about 91% of the overall phenol emissions during winter and represented about 87% of the total area of GLASs at the dairy operation. Therefore, for reducing phenol and *p*-cresol emissions, abatement and management practices directed at the loafing pen and lagoons would likely be most effective for reducing facility-wide emissions.

Acknowledgments

References

Air Resources Board (ARB), 2005. *Air Pollution Control Officer's Determination of VOC Emission Factors for Dairies—August 1, 2005. Final Report: Dairy Emission Factors for Volatile Organic Compounds*. Dairy Permitting Advisory Group (DPAG) Recommendation to the San Joaquin Valley Air Pollution Control Officer regarding VOC emission from Dairies. May 6, 2005. Sacramento, CA: Air Resources Board.

ATAS GL Science Company, 2001. Determination of breakthrough volume for optical liner. Application note no. 052. http://www.atasgl.com/ap-note/052_LVI%20Breakthrough%20Volume.pdf (February 8, 2010).

Auvermann, P.W., J.A. Koziel, D.B. Parker, S.A. Amosson, L.W. Greene, N. Chirase, N.A. Cole, C. Parnell, and J.M. Sweeten, 2001. Cattle feedlot odor and dust control: approaches and recent results. Abstract presented at the annual meeting of the American Agricultural Economist Association, Chicago, IL, August 6–9, 2001.

Bourque, D., J. Bisaillon, R. Beaudet, M. Sylvestre, M. Ishaque, and A. Morrin. 1987. Microbiological degradation of malodorous substances of swine wastewater under aerobic conditions. *Appl. Environ. Micro.* 53:37-141.

Buser, Z., D.B. Parker, K. Casey, G. Green, E. Caraway, and M.B. Rhoades, 2007. Quantification ambient *p*-cresol concentration downwind of beef cattle feedyards. In *International Symposium on Air Quality and Manure Management for Agriculture*, Bloomfield, CO, September 16, 2007. ASABE Publication No. 701P0907cd.

Cai, L., J.A. Koziel, J. Davis, Y.C. Lo, and H. Xin. 2006. Characterization of VOCs and odors by in-vivo sampling of beef cattle rumen gas, using solid-phase microextraction, and has chromatography-mass spectroscopy-olfactometry. *Anal. Bioanal. Chem.* 386:1791–1802.

Cai, L., S. Zhang, J.A. Koziel, G. Sun, K.Y. Heathcote, S.J. Hoff, D.B. Parker, E.A. Caraway, L.D. Jacobson et al., 2010. Odor and odorous chemical emissions from animal buildings: part 3—chemical emissions. In *International Symposium on Air Quality and Manure Management for Agriculture*, Dallas, TX, September 13, 2010. ASABE Publication No. 711P0510cd.

Capareda, S.C., C.N. Boriack, S. Mukhtar, A. Mutlu, B.W. Shaw, R.E. Lacey, and C.B. Parnell Jr.. 1995. The recovery of ammonia and hydrogen sulfide from ground level area sources using dynamic isolation flux chambers: bench-scale studies. *J. Air Waste Mange. Assoc.* 55:999–1006.

Capareda, S.C., C.B. Parnell, B.W. Shaw, R.E. Lacey, and S. Mukhtar, 2005. New protocol for the determination of reactive organic gases in animal feeding operations. Presented at the ASABE Annual International Meeting, St. Joseph, MI, July 17–20, 2005; Paper 054028.

Ciccioli, P., E. Branceleoni, A. Cecinato, R. Sparapani, and M. Franttoni. 1993. Identification and determination of biogenic and anthropogenic volatile organic compounds in forest areas of northern and southern Europe and a remote site of the Himalaya region by high resolution gas chromatography mass spectrometry. *J. Chromatogr.* 643:55–69.

Code of Federal Regulations (CFR), 2008. *National Primary and Secondary Ambient Air Quality Standards. 40CFR, Part 50. Office of the Federal Register, National Archives, and Records Administration*. Washington D.C: U.S. Government Printing Office.

Eniola, B., Z. Perschbacher-Buser, E. Caraway, N. Gosh, M. Olsen, and D.B. Parker, 2006. Odor control in waste management lagoons via reduction of *p*-cresol using horseradish peroxidase. Presented at the ASABE Annual International Meeting, St. Joseph, MI, July 9–12, 2006; Paper 064044.

Gholson, A.R., J.R. Albriton, and R.K.M. Yayanti, 1989. *Evaluation for the Flux Chamber Method for Measuring Volatile Organic Emissions from Surface Impoundments*. Project Summary EPA/600/S3-89/008. U.S. Environmental Protection Agency: Washington, DC.

Higashi, R.M., and T.A. Cassel. 2004. *Whitepaper: Analysis of Volatile Organic Tropospheric Ozone Precursors from Biogenic Sources. Center for Health and Environment*. Davis, CA: University of California, Davis.

Howard, C.J., A. Kumar, F. Mitloehner, K. Stackhouse, P.G. Green, R.G. Flochini, and M. Kleeman. 2010. Direct measurement of ozone formation potential from livestock and poultry waste emissions. *Environ. Sci. Technol.* 44:2292–2298.

Hudson, N., G.A. Ayoko, M. Dunlop, D. Duperouzel, D. Burrell, K. Bell, E. Gallagher, P. Nicholas, and N. Heinrich, 2009. Comparison of odor emission rates measured from various sources using two sampling devices. *Bioresource Tech.* 100(1): 118-124.

Idaho Department of Environmental Quality (IDEQ), 2003. *Treasure Valley Air Quality Issues: Ammonia, Particulate, and VOC Emissions*. IDEQ: Boise, ID

Karger, B.L., L.R. Snyder, and C. Horvath. 1973. *An Introduction to Separation Science*. Hoboken, NJ: John Wiley & Sons.

Kienbusch, M.R.. 1986. *Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber—User's Guide. EPA/600/8-86/008*. Washington, DC: U.S. Environmental Protection Agency.

Koziel, J.A., L. Cai, D. Wright, and S. Hoff. 2006. Solid phase microextraction as a novel air sampling technology for improved, GC-olfactometry-based, assessment of livestock odors. *J. Chromatogr. Sci.* 44:451–457.

Lu, M., O. Lamichhane, F. Liang, and M. Chai. 2008. Identification of odor causing compounds in a commercial dairy farm. *Water Air Soil Pollut. Focus.* 8:359–367.

McGinn, S.M., H.H. Janzen, and T. Coates. 2003. Atmospheric ammonia, volatile fatty acids, and other odorants near beef feedlots. Atmospheric pollutants and trace gases. *J. Environ. Qual.* 32:1173–1182.

Miller, D.N., and V.H. Varel. 2001. In vitro study of the biochemical origin and production limits of odorous compounds in cattle feedlots. *J. Anim. Sci.* 79:2949–2956.

Mukhtar, S., A. Mutlu, S.C. Capareda, and C.B. Parnell. 2008. Seasonal and spatial variations of ammonia emissions from an open-lot dairy operations. *J. Air Waste Manage. Assoc.* 58:369–378. doi: 10.3155/1047-3289.58.3.369

National Oceanic and Atmospheric Administration (NOAA), Cautionary Response Information of *p*-cresol. http://cameochemicals.noaa.gov/chris/CSO.pdf (accessed June 14, 2011).

Parker, D.B.. 2008. Reduction of odor and VOC emissions from a dairy lagoon. *Appl. Eng. Agric.* 24:647–655.

Parker, D.B., Z. Buser, E. Caraway, M. Rhoades, M. Olsen, K. Casey, J. Spears, and G. Green, 2007. VOC concentrations downwind of beef feedlots during intense odour events. In *Proceedings of 14th IUAPPA World Congress*, Brisbane, Australia. September 9–13, 2007. Briton, United Kingdom: IUAPPA.

Parker, D.B., Z. Buser, N.A. Cole, and J.A. Koziel. 2010. Recovery of agricultural odors and odorous compounds from polyvinyl fluoride film bags. *Sensors.* 10:8536–8552.

Parker, D.B., E.A. Caraway, M.B. Rhoades, N.A. Cole, R.W. Todd, and K.D. Casey. 2010. Effect of wind tunnel air velocity on VOC flux from standard solutions and CAFO manure/wastewater. *Trans ASABE.* 53:831–845.

Rabaud, N.E., S.E. Ebeler, L.L. Ashbaugh, and R.G. Flocchini. 2002. The application of thermal desorption GC/MS with simultaneous olfactory evaluation for the characterization and quantification of odor compounds from a dairy. *J. Agric. Food Chem.* 50:5139–5145.

Rabaud, N.E., S.E. Ebeler, L.L. Ashbaugh, and R.G. locchini. 2003. Characterization and quantification of odorous compounds near a commercial dairy in California. *Atmos. Environ.* 37:933–940.

SAS. 1999. *SAS User's Guide: Statistics Ver. 8.* Cary, NC: SAS Institute, Inc.

Saggar, S., R. Bhandral, C.B. Hedley, and J. Luo. 2004. A review of emissions of methane, ammonia, and nitrous oxide from animal excreta deposition and farm effluent application in grazed pastures. *N. Z. J. Agric. Res.* 47:513–544.

Scott Specialty Gases, 2004. *Protecting Against Condensation Improves Calibration Accuracy.* Scott Tech Newsline 1(5). Plumsteadville, PA: Scott Specialty Gases.

Spinhirne, J.P, J.A. Koziel, B.H. Baek, and D. Parker, 2004. Measurements of volatile fatty acids flux from cattle pens in Texas. In *Proceedings of the 2004 AWMA Annual Meeting and Exhibition,* June 2004, Indianapolis, IN: AWMA; Paper 04-A-646.

SRI Instruments. 2008. *SRI Instruments Operation Manual and Reference Guide.* Torrance, CA: SRI Instruments.

Steel, R.C.D., J.H. Torrie, and D.A. Dickey. 1997. *Principles and Procedures of Statistics: A Biometrical Approach.* Singapore: McGraw-Hill.

Sun, H., S. Trabue, K. Scoggin, W.A. Jacson, Y. Pan, Y. Zhao, L. Malkina, J.A. Koziel, and F.M. Mitloehner. 2008. Alcohol, volatile fatty acid, and methane emissions from dairy cows and fresh manure. *J. Environ. Qual.* 37:615–622.

Sunesson, J.P., J. Gullberg, and G. Blomquist. 2001. Airborne chemical compounds on dairy farms. *J. Environ. Monit.* 3:210–216.

The United State Library of Medicine, 1981. Toxnet. http://toxnet.nlm.nih.gov/cgi-bin/sis/search (accessed on May 31, 2011).

Trabue, S., K. Scoggin, L. McConnell, R. Maghirang, and J. Hatfield. 2011. Identifying and tracking key odorants from cattle feedlots. *Atmos. Environ.* 45(25):4243–4251. doi: 10.1016/j.atmosenv.2011.04.081.

U.S. Environmental Protection Agency (EPA). 1999. *Compendium Method TO-14A: Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography.* Cincinnati, OH: EPA.

U.S. Environmental Protection Agency. 1995. *Definition and Procedure for the Determination of the Method Detection Limit Revision 1.11. 40CFR Part 136.* Washington, DC.: Government Printing Office.

U.S. Environmental Protection Agency (EPA), 2001. *Emissions from Animal Feeding Operations (Draft).* EPA Contract No. 68-D6-0011. U.S. EPA: Washington, DC. http://www.epa.gov/ttn/chief/ap42/ch09/draft/draftanimalfeed.pdf (accessed on June 16, 2011).

U.S. Weather, 2009. Wisconsin weather. http://countrystudies.us/united-states/weather/wisconsin/ (accessed on July 20, 2011).

U.S. Weather, 2009. Indiana weather. http://countrystudies.us/united-states/weather/indiana/ (accessed on July 19, 2011).

U.S. Weather, 2009. Texas weather. http://countrystudies.us/united-states/weather/texas/ (accessed on July 22, 2011).

Wright, D.W., D.K. Eaton, L.T. Nielsen, F.W. Kuhrt, J.A. Koziel, J.P. Spinhirne, and D.B. Parker. 2005. Multidimensional gas chromatography-olfactometry for identification and prioritization of malodors from confined animal feeding operations. *J. Agric. Food Chem.* 53:8663–8672.

Wright, D.W., D.K. Eaton, L.T. Nielsen, F.W. Kurt, J.A. Koziel, J.P. Spinherne, and D.B. Parker, 2004. Multidimensional gas chromatography-olfactometry for identification and prioritization of malodors from confined animal feeding operations. Presented at the ASAE/CSAE Annual International Meeting, Ottawa, Ontario, Canada, August 1–4, 2004; Paper 044128.

Yu, J.C., C.E. Isaac, R.N. Coleman, J.J.R. Feddes, and B.S. West. 1990. Odorous compounds from treated pig manure. *Can. Agric. Eng.* 33:131–136.

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