7-14-2014

Emission of volatile organic compounds after land application of cattle manure

Bryan Woodbury

USDA-ARS, bryan.woodbury@ars.usda.gov

John E. Gilley

USDA & UNL Biological Systems Engineering, john.gilley@ars.usda.gov

David B. Parker

West Texas A&M University, david.parker@ars.usda.gov

David B. Marx

University of Nebraska-Lincoln, david.marx@unl.edu

Daniel N. Miller

USDA, dan.miller@ars.usda.gov

See next page for additional authors

Follow this and additional works at: <http://digitalcommons.unl.edu/biosysengfacpub>

Part of the [Bioresource and Agricultural Engineering Commons](#), [Environmental Engineering Commons](#), and the [Other Civil and Environmental Engineering Commons](#)

Woodbury, Bryan; Gilley, John E.; Parker, David B.; Marx, David B.; Miller, Daniel N.; and Eigenberg, Roger A., "Emission of volatile organic compounds after land application of cattle manure" (2014). *Biological Systems Engineering: Papers and Publications*. 432.
<http://digitalcommons.unl.edu/biosysengfacpub/432>

This Article is brought to you for free and open access by the Biological Systems Engineering at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Biological Systems Engineering: Papers and Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Authors

Bryan Woodbury, John E. Gilley, David B. Parker, David B. Marx, Daniel N. Miller, and Roger A. Eigenberg

Emission of Volatile Organic Compounds after Land Application of Cattle Manure

Bryan L. Woodbury,* John E. Gilley, David B. Parker, David B. Marx, Daniel N. Miller, and Roger A. Eigenberg

Beef cattle manure can serve as a valuable source of nutrients for crop production. However, emissions of volatile organic compounds (VOCs) after land application may pose an odor nuisance to downwind populations. This study was conducted to evaluate the effects of land application method, diet, soil moisture content, and time since manure application on VOC emissions. Manure was collected from feedlot pens where cattle were fed diets containing 0, 10, or 30% wet distillers grains with solubles (WDGS). Land application methods included surface-applying manure (i.e., no-tillage) or incorporating manure using disk tillage. The effects of soil moisture content on VOC emissions was determined by adding water to each of the plots approximately 24 h after manure application. Isovaleric acid, butyric acid, and 4-methylphenol contributed 28.9, 18.0, and 17.7%, respectively, of the total measured odor activity values. In general, the largest emissions of volatile fatty acids and aromatics were measured during the initial collection periods on the no-tillage plots under dry soil moisture conditions. Emissions of volatile fatty acids and aromatics were reduced after water additions because these compounds were stored in the soil–water matrix rather than released into the atmosphere. In contrast, sulfide emissions generally increased with the addition of the water, especially on the plots containing manure from the 30% WDGS diet. Sulfur content of manure increases with higher percentages of WDGS feed stock. Application method, diet, soil moisture content, and time since application should be considered when estimating VOC emissions.

AIRBORNE POLLUTANTS from animal feeding operations may be a concern to downwind populations (Wright et al., 2005; Donham et al., 2007; Heederik et al., 2007; Radon et al., 2007; Thorne, 2007). Chronic exposure to these pollutants were associated with increased incidence of respiratory diseases, particularly for those responsible for the care of the animals (Omland, 2002; Mitloehner and Calvo, 2008). Work by Schiffman et al. (1995) found residents exposed to swine odors had significantly more stress, depression, anger, and fatigue than those who were not exposed. However, their findings were not able to distinguish whether the response was innate or learned.

Airborne pollutants can originate from several areas associated with beef cattle operations, including pen surfaces, manure storage facilities, runoff holding ponds, feed storage areas, and animal housing facilities (Koelsch et al., 2004). These pollutants can be in many forms, such as dust, bacteria, mold, endotoxins, ammonia, hydrogen sulfide, volatile organic compounds (VOCs), and particulate matter (Mitloehner and Calvo, 2008). Another origin of airborne pollutants associated with animal feeding operations that is sometimes overlooked is land application of manure.

Most of the research associated with land application is focused on improving the efficacy of nutrient utilization. There has been some work on mitigating odorous emissions from swine manure and poultry operations (Moore et al., 1995; Powers, 1999; Sims and Luka-McCafferty, 2002; Sharpe et al., 2004; Powers et al., 2007; Parker et al., 2013a). Most of the work on land-applied swine manure has been focused on liquid application, which is very different from most beef manure. Poultry litter, like beef manure, is a dry material but is very different in physical and chemical make-up.

Emission of VOCs from land-applied beef manure can be influenced by many factors, such as animal diets, storage time from excretion to application, amount of inert material (i.e., soil)

Copyright © American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America. 5585 Guilford Rd., Madison, WI 53711 USA. All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher.

J. Environ. Qual. 43:1207–1218 (2014)

doi:10.2134/jeq2013.05.0185

Received 12 May 2013.

*Corresponding author (bryan.woodbury@ars.usda.gov).

B.L. Woodbury and R.A. Eigenberg, USDA–ARS, U.S. Meat Animal Research Center, P.O. Box 166, Clay Center, NE 68933; J.E. Gilley and D.N. Miller, USDA–ARS, Agroecosystem Management Research Unit, Lincoln, NE 68583; D.B. Parker, West Texas A&M Univ., Canyon, Texas 79016; D.B. Marx, Dep. of Statistics, Univ. of Nebraska, Lincoln, NE 68583. USDA is an equal opportunity provider and employer. The mention of trade names of commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the USDA. Assigned to Technical Editor Robert Dungan.

Abbreviations: DMDS, dimethyl disulfide; DMTS, dimethyl trisulfide; GC, gas chromatography; MS, mass spectrometry; OAV, odor activity value; SCOT, single compound odor threshold; VFA, volatile fatty acids; VOC, volatile organic compound; WDGS, wet distillers grains with solubles.

entrained in the manure, and moisture content of the manure. Also, VOC emissions from land-applied beef manure come from more diffuse sources than typical pen surfaces or manure storage. Furthermore, land application can place the VOC emission closer to the public than would occur at the animal production facility. Despite the issues associated with VOC emissions from land-applied beef manure, its use as a fertilizer and soil amendment has many soil health benefits and contributes to improved agricultural sustainability (Tester, 1990; Fauci and Dick, 1994; Edmeades, 2003; Ferguson et al., 2005).

Malodorous VOCs, such as volatile fatty acids (VFAs), aromatics, sulfides, amides, and alcohols, are emitted during the microbial degradation of manure (Mackie et al., 1998; Miller and Varel, 2001; Miller and Berry, 2005; Rappert and Muller, 2005; Trabue et al., 2011). Research has focused on measuring emissions characteristics and rates of these compounds from feedlot sources (Auvermann et al., 2007; Kyoung et al., 2007; Todd et al., 2008; Trabue et al., 2008). Recent introduction of ethanol by-products, particularly distillers grains, over the past decade as a feed additive for beef cattle has modified the emission characteristics of manure (Gralapp et al., 2002; Varel et al., 2008; Spiehs and Varel, 2009; Varel et al., 2010). This modification is particularly important because certain compounds have much lower detection thresholds than others, and these detection limits can be altered by interactions with other airborne compounds and the environment (Trabue et al., 2011).

Increasing the amount of wet distillers grains with solubles (WDGS) fed to feedlot cattle can increase P, N, and S intake and excretion. This increase in N can cause greater ammonia emission, primarily from urine (Spiehs and Varel, 2009; Todd et al., 2011). Feeding WDGS has also been found to contribute to the production of odorous VOCs, such as long- and branched-chain VFAs and phenol (Spiehs and Varel, 2009). Increases in specific VFAs, however, may not lead to overall increases in total VFA emissions. Similar studies have found that total VFA concentrations in manure can decrease as WDGS increase in the diet and that the concentration of other aromatic compounds (*p*-cresol, indole, skatole) in cattle feces does not change (Spiehs and Varel, 2009; Parker et al., 2013a). Another study found that VOC flux or odor activity values (OAVs) did not differ between measured VOC emissions from feces and urine from cattle fed steam-flaked corn diets containing 0, 15, 30, or 45% WDGS (Hales et al., 2012a).

In addition to manure characteristics, the method of manure application can affect emissions of VOC after land application. It is unlikely that beef producers will alter animal diets to manage VOC emissions because animal feed is one of the largest input costs for production. Therefore, the lowest cost rations that supply the needs of the animal will be used. However, producers may consider changes in how manure is handled during land application. Research investigating changes in manure handling has shown promise. Parker et al. (2013a) reported that injection of swine manure resulted in 80 to 95% lower flux than surface-applied manure. Similarly, Hanna et al. (2000) reported that injection of swine manure reduced odor emissions by 68 to 88% relative to surface broadcasting, and Feilberg et al. (2011) reported a 75 to 90% reduction in 4-methylphenol emissions when swine manure was injected. For dairies, Brandt et al. (2008)

reported 58 to 67% lower odor concentrations for injected dairy slurry than for surface application.

There has been limited research to evaluate the effects of land application method of beef cattle manure on VOC emissions; therefore, there is limited information to develop management practices that would mitigate VOC emissions. The objective of this investigation was to evaluate the effects of land application method, diet, soil moisture content, and time since application on VOC emissions.

Materials and Methods

Study Site

Field experiments were conducted during the summer of 2012 at the University of Nebraska Rogers Memorial Farm located 18 km east of Lincoln, Nebraska. The site had been cropped using a grain sorghum [*Sorghum bicolor* (L.) Moench], soybean [*Glycine max* (L.) Merr.], winter wheat (*Triticum aestivum* L. 'Pastiche') rotation under a no-tillage management system (hereafter referred to as "no-till") and was planted to winter wheat during the 2010–2011 cropping season. The area was left undisturbed after wheat harvest in July 2011. Herbicide was applied as needed to control weed growth. Wheat residue was removed by hand raking before plot establishment.

Soil at the study site was classified as an Aksarben silt loam (fine, smectitic, mesic Typic Argiudoll). The site contained 25% sand, 52% silt, and 23% clay and had a pH of 7.2 and an organic matter content of 3.4%. Air temperatures and relative humidity at the time of the study are shown in Table 1.

Beef Cattle Manure

Beef cattle manure was collected from feedlot pens located at the U.S. Meat Animal Research Center near Clay Center, NE. Calves born during the spring of 2011 were placed in the pens in October 2011. Cattle were fed a corn-based diet that contained 0, 10, or 30% WDGS. Animals were removed from the pens, and the surface was allowed to dry. The manure was collected from behind the feed bunk apron of the pens using a front-end loader and placed in a truck. The manure from the respective diets was stored in separate piles at a manure handling facility until it could be ground and mixed using a gas-powered tree branch chipper. The ground and mixed manure was placed in 125-L plastic containers until it was land applied. For each diet, 10 grab samples were removed and composited. A subsample from each composited sample was used to determine the physical and chemical characteristics of the manure (Table 2) (Servi-Tech Laboratories).

Table 1. Mean temperature and humidity at the study site during the two sampling periods.

Date	Mean air temperature	Average humidity
	°C	%
14 May 2013	18	54
15 May 2013	21	50
16 May 2013	17	48
4 June 2013	24	61
5 June 2013	23	59
6 June 2013	24	51

Experimental Design

Twelve plots (0.75 m × 2.0 m) were established across the slope using a randomized block design. The plots were planted to wheat the previous year, and the stubble was left standing through the winter. The plot area was fallowed during the study. The experimental treatments, which were replicated twice, included land application method (tilled or no-till) and diet (0, 10, or 30% WDGS). Each of the plots received an application of water after the 24-h sampling period to evaluate the effect of water on odor emissions. Although antecedent moisture conditions of the plot soils were not measured, vegetative growth was eliminated. Therefore, it was assumed the soil moisture condition was at or below field capacity during the study. After the addition of water, another series of air samples was collected using the same sampling intervals. Field tests for replications 1 (six plots) and 2 (six plots) were conducted from 14 to 16 May and from 4 to 6 June 2012, respectively.

Beef cattle manure was applied to meet the 1-yr N requirement for corn (151 kg N ha⁻¹ yr⁻¹ for an expected yield of 9.4 Mg ha⁻¹). Based on laboratory analysis of the manure, application rates for each plot were calculated assuming that the first-year N availability from the manure was 40% (Eghball et al., 2002). This resulted in more manure being applied to plots receiving 0% WDGS diet manures because the concentration of N was less when compared with the other diets. This approach was selected because it more accurately reflects procedures used by producers, thereby allowing better evaluation of application method for developing mitigating management practices. Manure was uniformly applied by hand across the plot surfaces using 19-L buckets. Applications covered an area slightly larger than the final plot dimensions to ensure uniform application on the tilled plots. Immediately after land application, a 5-m tandem disk was used to incorporate the applied manure to a depth of approximately 8 cm. A single pass occurred up and down the slope in the direction of overland flow.

Experimental Procedures

After manure application, plots were established within the no-till and tilled areas using 20-cm-wide sheet metal frames driven approximately 10 cm into the soil. Measurements for VOC fluxes were conducted using a wind tunnel chamber on each of the two sampling dates. On Day 1 (dry condition), the wind tunnel chamber was placed on the soil surface and pressed into the soil to a depth sufficient to ensure soil contact around

the parameter of the tunnel. Air flow was introduced into the flux chamber to establish equilibrium conditions.

Collection of air samples for VOC measurements began 0, 1, 2, 6, and 23 h after equilibrium was established. The flux chamber was removed after the 23-h sampling interval had been completed. The effects of a single application of water on VOC measurements were identified during Day 2. On Day 2 (wet condition), water was applied to the plot surfaces with a hand-operated irrigation wand until the surface soil was saturated and runoff began. Measurements of VOCs from the saturated soil surface were conducted using the wind tunnel flux chamber and the same experimental procedures as described for dry conditions.

Background emissions for the site were determined by establishing six plots adjacent to the test site. Metal frames were installed as describe earlier. Three of the plots had water applied in a manner similar to the test plots, and three were left dry. Wind tunnels were installed, and background measurements were collected using the same procedure used previously. Background values for each of the measured compounds are listed in Table 3.

Wind Tunnel Flux Measurements

Details on the operation of the small wind tunnel can be found in Parker et al. (2013b). The small wind tunnel had a 51 mm height, 305 mm length, and 152 mm width, with a footprint of 0.046 m² and internal volume of 2.36 L. The sweep air entered the wind tunnel through 17 holes (6-mm diam.) in three rows at heights of 17 mm (six holes), 30 mm (five holes), and 43 mm (six holes) above the base. Air exited the tunnel through three 10-mm-diameter holes equally spaced at a height 27 mm above surface at the opposite end of the tunnel. Sweep air (1 L min⁻¹) was supplied via Teflon tubing from a compressed air cylinder (Linweld).

After an equilibration period that allowed three volumes of sweep air to pass through the wind tunnel, VOC samples were collected from the air exiting the wind tunnel. Air samples were obtained in stainless steel sorbent tubes (89 mm × 6.4 mm OD; Markes International Inc.) filled with Tenax TA sorbent (Sigma-Aldrich). Before use, the sorbent tubes were conditioned for 30 min at 230°C. Air was pulled through the sorbent tubes at a flow rate of 75 mL min⁻¹ for 60 min using a vacuum pump (Pocket Pump 210 Series, SKC Inc.).

Flux density, J , was calculated on a mass per unit area per unit time basis ($\mu\text{g m}^{-2} \text{ min}^{-1}$) using Eq. [1]:

$$J = \frac{Q C_{\text{air}}}{A} \quad [1]$$

where Q is the sweep air flow rate (m³ min⁻¹), C_{air} is the VOC concentration of the exiting air ($\mu\text{g m}^{-3}$), and A is the footprint area of the wind tunnel (m²).

Gas Chromatography/Mass Spectrometry Analyses

Sorbent tube samples were collected in duplicate and results were averaged. A thermal desorption–gas chromatography (GC)–mass spectrometry (MS) system consisting of a Markes Unity 2 thermal desorber with Ultra 2 autosampler (Markes International Inc.) was used to analyze the sorbent tube samples. Samples were quantified with an Agilent 7890A/5975C GC/MS (Agilent Technologies, Inc.). The system used an Agilent Innobox (30 m × 0.25 mm inner diameter) capillary column

Table 2. Laboratory analysis of manure from beef cattle fed selected diets containing selected amounts of wet distillers grains.

Parameters	Wet distillers grains		
	0%	10%	30%
Total N, %	1.08	1.89	1.99
Organic N, %	1.05	1.76	1.77
Ammonium N, %	0.037	0.125	0.220
Nitrate N, %	0.001	0.001	0.001
P, %	0.275	0.390	0.676
P as P ₂ O ₅ , %	0.629	0.892	1.55
Moisture, %	38.7	23.0	21.0
Solids, %	61.4	77.1	79.0
Organic matter, %	31.6	51.8	42.9
Ash, %	29.8	25.3	36.1
C:N ratio	17.0	16.1	12.6

Table 3. Summary of the measured compounds, method detection limits, calibration statistics, and background soil emission rates under dry and wet soil moisture conditions.

Compound	MW†	Retention time	Min.	Max.	MDL‡	MDL§	RSD¶	r²	Background		Relative contribution
									Dry#	Wet††	
		min	ng		µg m⁻² min⁻¹				µg m⁻² min⁻¹		%
Volatile fatty acid											
Acetic acid	60.0	12.4	30.2	4114	32.9	0.16	0.38	0.99	0.33	0.67	0.37
Butyric acid	88.1	15.1	2.9	3723	8.6	0.042	0.87	0.99	0.03	0.04	18.00
Heptanoic acid	130.2	19.5	0.66	502	1.6	0.0077	0.25	0.98	0.02	0.02	0.48
Hexanoic acid	116.2	18.1	5.3	8244	2.2	0.011	0.50	0.98	0.08	0.08	6.80
Isobutyric acid	88.1	14.2	2.4	2239	15.1	0.073	0.82	0.99	0.01	0.01	2.06
Isovaleric acid	102.1	15.7	0.57	1810	5.9	0.028	0.80	0.99	0.00	0.01	28.91
Propanoic acid	74.1	13.8	4.2	6721	15.9	0.077	0.89	0.99	0.04	0.13	2.09
Valeric acid	102.1	16.7	1.9	807	2.5	0.012	0.62	0.99	0.02	0.03	5.85
Aromatics											
4-Ethylphenol	122.2	22.2	0.07	7.66	6.0	0.029	0.21	0.97	0.00	0.00	0.11
4-Methylphenol	108.1	21.1	0.37	871	4.0	0.019	0.11	0.97	0.00	0.01	17.60
Indole	117.1	25.2	0.07	259	3.5	0.017	0.09	0.99	0.00	0.00	4.52
Phenol	94.1	20.2	5.0	2027	6.0	0.029	0.14	0.99	0.04	0.07	0.44
Skatole	131.2	25.6	0.015	9.84	4.8	0.023	0.12	0.98	0.00	0.00	0.81
Sulfides											
Dimethyl disulfide	94.2	5.2	2.4	1281	1.0	0.005	0.04	0.99	0.01	0.01	3.28
Dimethyl trisulfide	126.2	11.0	0.40	587	2.1	0.01	0.14	0.99	0.00	0.00	8.68

† Molecular weight.

‡ Method detection limit.

§ Method detection limit for flux based on a 60-min sample time with a wind tunnel flow rate of 1 L min⁻¹.

¶ Relative standard deviation (SD/mean) from seven replications at minimum mass analyzed.

Background emission rate from soil receiving no moisture or beef manure (average of three replicates).

†† Background emission rate from soil receiving moisture but no beef manure (average of three replicates).

(polyethylene glycol, 0.25 mm film thickness) that was operated under a constant air flow rate of 1.4 mL min⁻¹.

Samples were purged for 1 min at 40 mL min⁻¹ to remove water and solvent. The tube was then desorbed for 10 min at 280°C with a carrier gas flow of 50 mL min⁻¹ and trapped on a cold trap maintained at -10°C. The cold trap was heated to 320°C for 1 min with a carrier gas flow of 20 mL min⁻¹, and 1.4 mL min⁻¹ was transferred to the GC-MS. In the GC oven, the column was held at 40°C for 3 min, and then the temperature was increased to 230°C at a rate of 8°C min⁻¹ and held at 230°C for 5 min. The polar analytical column was an Agilent Innowax, with a 30 m × 0.25 mm inner diameter capillary column (polyethylene glycol, 0.25 µm film thickness).

Samples were analyzed for eight VFAs (acetic, butyric, heptanoic, hexanoic, isobutyric, isovaleric, propionic, and valeric acids), five aromatic compounds (4-ethylphenol, indole, p-cresol, phenol, and skatole), and two sulfur-containing VOCs (dimethyl disulfide [DMDS] and dimethyl trisulfide [DMTS]). For calibration, standard solutions were prepared by diluting known masses of pure chemicals with methanol. Standards were prepared fresh and analyzed within 48 h to establish standard curves. Stored standards were periodically integrated to verify changes in sensitivity of analysis. All chemicals and solvents were FCC grade (Sigma Aldrich). Standards were prepared using serial dilutions and then injected onto clean tubes while purified air was pulled through the tubes with a vacuum pump operated at 75 mL min⁻¹. Standard solutions were stored for periodic instrument calibrations. Our experience has shown little evidence that VFAs are ionized and become nonvolatile. However, esterification

with methanol is used to convert nonvolatile VOCs into a more volatile form, such as converting fatty acids found in meat (palmitic acid, stearic acid, oleic acid, etc.) to its more volatile methyl ester form. We have seen little difference in GC response from freshly made standards to standards that have been stored, which indicates little to no ionization or response issues.

Within the linear range, standard curves were fit using linear regression with zero y-intercept. Coefficients of determination for the standard curves ranged from 97.8 to 99.7% for the eight VFAs, 97.8 to 99.3% for the five aromatics, and 99.8% for DMDS and DMTS.

Odor Activity Value and Analysis

Concentrations of individual compounds were converted to their respective OAVs. An assessment of the relative impact of each individual odor compound is provided by OAV analyses. Details of the conversion can be found in Parker et al. (2013a); a brief description is provided below.

The OAV is a ratio of the measured concentration of a single compound normalized to the single compound odor threshold (SCOT) for that compound (Patton and Josephson, 1957; Friedrich and Acree, 1998; Trabue et al., 2006; Parker et al., 2010b; Parker et al., 2013b). Therefore, the higher the OAV for an individual compound, the more likely that compound will contribute to the overall odor of a complex odor mixture.

The single compound odor threshold values for each compound were obtained using values from published odor thresholds (Table 4). The relative contribution of each compound was calculated by subtracting background emission for each

Table 4. A summary of published single compound odor thresholds (SCOT) for the 15 compounds measured in this research is shown. Different statistical measures of central tendency are provided.†

Compound	n‡	Min.	Max.	Arithmetic mean	SD	Geometric mean	Harmonic mean	Median	Geometric mean§
$\mu\text{g m}^{-3}$									
Volatile fatty acids									
Acetic acid	8	25	7500	2480	2754	578	85	2050	467
Butyric acid	11	0.4	105	25	34	6.9	1.4	13	23
Heptanoic acid	3	22	300	118	157	60	38	33	–
Hexanoic acid	5	12	510	182	226	69	31	40	83.1
Isobutyric acid	2	0.8	285	145	198	38	10	145	41
Isovaleric acid	5	0.22	14	5.0	5.5	2.3	0.81	4.1	4.7
Propionic acid	7	3	890	303	344	106	18	80	101
Valeric acid	6	0.8	75	24	30	8.8	3.0	9.0	11.7
Aromatics									
4-Ethylphenol¶	1	6.3	6.3	6.3	–	6.3	6.3	6.3	–
4-Methylphenol	4	0.05	24	9.2	11.5	1.3	0.16	6.3	2.6
Indole	2	0.6	7.1	3.8	4.6	2.1	1.1	3.8	1.9
Phenol	9	39	4000	734	1290	206	88	200	127
Skatole	4	0.35	0.78	0.51	0.19	0.48	0.46	0.45	1.6
Sulfides#									
DMDS	5	1.6	64	25	28	12	5.3	8.5	–
DMTS	3	0.08	14	7.2	7.0	2.0	0.24	7.5	–

† All raw data on thresholds from van Gemert (2003) unless otherwise noted.

‡ Number of independent odor threshold observations used in the calculations.

§ SCOT values from the compilation of Parker et al. (2010a) are provided for comparison.

¶ 4-Ethylphenol threshold from Trabue et al. (2008).

DMDS, dimethyl disulfide; DMTS, dimethyl trisulfide.

compound and dividing by the sum of the OAV for all measured compounds. This approach does not account for possible synergistic or other complex interactions of the compounds (DiSpirito et al., 1994; Powers, 2001; Zahn et al., 2001).

Statistical Analyses

The effects of land application method, diet, soil moisture condition, and sample collection time on VOCs were determined using repeated-measures ANOVA (SAS Institute, 2011). For a given plot, duplicate readings collected for a particular test interval and sample collection time were treated as repeated measures. Significant treatment differences were further evaluated by using post hoc multiple comparison tests (Fisher's LSD). A probability level < 0.05 was considered significant.

Results and Discussion

Isovaleric acid, butyric acid, and 4-methylphenol accounted for 28.9, 18.0, and 17.6%, respectively, of the total OAV (Fig. 1). Three other VFAs with notable contributors to the total OAV were valeric, propanoic, and isobutyric acid, with contributions of 5.85, 2.09, and 2.06%, respectively. Indole was the only other aromatic that contributed substantially to the total OAV, with a value of 4.52%. Dimethyl trisulfide and

DMDS contributed 8.68 and 3.28%, respectively, to the total OAV. Heptanoic acid, acetic acid, skatole, 4-methylphenol, and phenol each had contributions that were less than 1% of the total OAV and were not included in further discussion (Fig. 1).

Tillage did not significantly change the emission for any of the measured VOCs (Tables 5 and 6). Emissions from the no-till plots, however, tended to be greater than from the tilled plots. The ratio of VOC emissions from the no-till-to-disked plots ranged from 1.3 for isovaleric acid to 15.7 for indole.

Fig. 1. Relative contribution of odorant to the overall odor activity value (OAV). Each compound is adjusted for background emission and normalized for its specific odor threshold.

The sulfide compounds, DMDS and DMTS, were the only VOCs that were significantly influenced by the amount of WDGS in the diet (Tables 5 and 6). Emissions of DMDS and DMTS were significantly greater for the 30% WDGS diet than for the 0 and 10% WDGS diets. Flux measurements of DMDS for the 30% WDGS diet were over 4 times higher than those measured for the 0 and 10% WDGS diets. Flux measurements of DMTS for the 30% WDGS diet were 3 times higher than the 0% WDGS diet and 8 times higher than the 10% WDGS diet.

Flux measurements for each of the VFAs and aromatic compounds were generally higher under dry than wet soil conditions, although differences were not significant for all compounds. Only DMDS emissions were significantly affected

by moisture content, which were 2.5 times higher for wet than for dry soil conditions (Table 5).

Each of the VOCs was significantly influenced by sampling time (Tables 5 and 6). Flux measurements for propionic acid, isobutyric acid, butyric acid, isovaleric acid, and indole were highest at the 1-h sampling period. Flux measurements were lowest at the 23-h sampling period for isobutyric acid, butyric acid, isovaleric acid, valeric acid, hexanoic acid, indole, DMDS, and DMTS.

Volatile Fatty Acids

All six VFAs measured in this investigation had significant three-way treatment interaction effects (Table 6). Emissions of all VFAs except hexanoic acid were affected by the interaction of

Table 5. Odorous volatile organic compound emissions as affected by application method, diet, soil moisture condition, and time since application. Values listed for a variable are averaged across all other variables.

	Volatile fatty acids						Aromatic		Sulfides†	
	Propan	Isobut	Butyr	Isoval	Valer	Hexan	4-Meth	Indole	DMDS	DMTS
	$\mu\text{g m}^{-2} \text{min}^{-1}$									
Application method										
Disk	0.222	0.053	0.134	0.436	0.188	1.83	0.023	0.006	0.487	0.116
No-till	1.93	0.705	1.11	0.576	0.429	3.69	0.232	0.094	0.720	0.219
Diet										
0%WDGS‡	1.94	0.462	0.656	0.333	0.164	0.956	0.300	0.088	0.301	0.109
10%WDGS	1.02	0.618	1.05	0.532	0.468	4.34	0.070	0.055	0.281	0.040
30%WDGS	0.268	0.574	0.158	0.064	0.293	2.97	0.013	0.007	1.23	0.353
Moisture										
Dry	1.94	0.708	1.12	0.568	0.439	4.00	0.199	0.082	0.337	0.148
Wet	0.206	0.050	0.127	0.052	0.177	1.52	0.056	0.017	0.870	0.187
Hour										
0	0.872b§	0.301bc	0.541bc	0.259bc	0.359ab	3.11ab	0.255a	0.077ab	0.057b	0.180b
1	1.89a	0.681a	1.11a	0.534a	0.353ab	3.30ab	0.200ab	0.089a	0.556b	0.147b
2	1.15b	0.365bc	0.613b	0.305b	0.418a	3.89a	0.113b	0.047b	0.643b	0.171b
6	1.05b	0.409b	0.620b	0.327b	0.284b	2.55b	0.052b	0.023bc	1.02a	0.203ab
23	0.399b	0.139c	0.220c	0.122c	0.127c	0.930c	0.018b	0.008c	0.22c	0.035c

† DMDS, dimethyl disulfide; DMTS, dimethyl trisulfide.

‡ Wet distillers grains with solubles.

§ Mean values in a column followed by different letters are significantly different at the 0.05 probability level based on the LSD test.

Table 6. Analysis of variance results ($P > F$) as affected by application method, diet, soil moisture condition, and time since application.

	Volatile fatty acids						Aromatic-		Sulfides	
	Propan	Isobut	Butyr	Isoval	Valer	Hexan	4-Meth	Indole	DMDS	DMTS
Tillage	0.19	0.19	0.17	0.19	0.37	0.49	0.29	0.18	0.30	0.22
Diet	0.52	0.59	0.54	0.59	0.62	0.58	0.43	0.53	0.02*	0.04*
Moisture	0.17	0.18	0.16	0.20	0.11	0.13	0.27	0.20	0.04*	0.62
Hour	0.01*	0.01*	0.01*	0.01*	0.01*	0.01*	0.01*	0.01*	0.01*	0.01*
Tillage × diet	0.54	0.59	0.52	0.60	0.44	0.41	0.48	0.54	0.81	0.86
Tillage × moisture	0.2	0.2	0.17	0.21	0.22	0.35	0.25	0.20	0.62	0.35
Diet × moisture	0.54	0.59	0.53	0.60	0.46	0.48	0.49	0.58	0.13	0.58
Tillage × diet × moisture	0.58	0.61	0.54	0.62	0.41	0.39	0.46	0.65	0.99	0.88
Tillage × hour	0.01*	0.01*	0.01*	0.01*	0.05*	0.18	0.01*	0.01*	0.40	0.06
Diet × hour	0.24	0.23	0.13	0.16	0.03*	0.02*	0.01*	0.04*	0.01*	0.01*
Tillage × diet × hour	0.24	0.25	0.12	0.21	0.01*	0.01*	0.01*	0.13	0.09	0.24
Moisture × hour	0.01*	0.01*	0.01*	0.01*	0.09	0.09	0.01*	0.01*	0.01*	0.01*
Tillage × moisture × hour	0.01*	0.01*	0.01*	0.01*	0.03*	0.13	0.01*	0.01*	0.01*	0.01*
Diet × moisture × hour	0.24	0.25	0.14	0.21	0.25	0.33	0.03*	0.32	0.01*	0.01*
Tillage × diet × moisture × hour	0.32	0.26	0.15	0.20	0.21	0.26	0.01*	0.34	0.02*	0.13

* Significant at the 0.05 probability level.

application method, moisture content, and sampling time. The largest emissions of propionic, isobutyric, butyric, isovaleric, and valeric acid occurred for the dry condition under no-tillage (Fig. 2A–E). In general, emissions were greater during the first 6 h of sampling compared with the emissions at 23 h. Specifically, the 1-h emission measurements for propionic, isobutyric, butyric, and isovaleric acid were substantially higher than any of the other emission measurements obtained during the 24-h period. Emission values for propionic, isobutyric, butyric, isovaleric, and valeric acid were near minimum detection limits (MDLs) for wet soil moisture conditions on the no-till plots and for both dry and wet soil moisture conditions on the tilled plots.

The relatively large flux values obtained at the 1-h sampling interval under dry soil moisture conditions on the no-till plots may indicate that the odor compounds generated during storage were released when the manure was applied to the soil. The no-till plots retained the greatest amount of VOCs in the manure on the soil surface. Once the manure was spread on the plot surface, the increased surface area may have facilitated additional exposure to direct sunlight, facilitating drying beyond the storage moisture content. With the loss of moisture, the odor compounds contained in the manure were released to the atmosphere. Not all of the VFAs contained in the manure were released during the initial sampling period; the peak loss of the VFAs was measured after the first 1-h

Fig. 2. Flux values for propionic, isobutyric, butyric, isovaleric, and valeric acid as affected by application method, soil moisture content, and time since application.

sample period. Additional work is needed to further quantify this process. Incorporating the manure into the soil during disking may have released odorous compounds from the manure, and those odorous compounds may have been trapped within the soil matrix and not released to the atmosphere. Adding water to increase soil moisture after land application reduced VFA emissions to near the MDL for each of the VFAs except valeric acid.

Emissions of hexanoic acid were affected by the interaction of application method, diet, and sampling time. The largest hexanoic acid emission occurred on the no-till plots that received manure generated from the 10% WDGS diet (Fig. 3A). The hexanoic acid emission peaked at the 2-h sampling time, and the smallest values occurred at the 23-h sampling time (Table 5). The largest hexanoic acid emissions from the tilled soils occurred for the manure generated from the diet containing 30% WDGS (Fig. 3B). As was true for no-till conditions, the peak emission occurred at the 2-h sampling time, and the lowest emissions were found at the 23-h sampling time.

Aromatics

The two aromatics measured in this investigation were 4-methylphenol and indole (Fig. 1). Of these two compounds, flux values for 4-methylphenol were nearly four times higher than indole. The largest emission of aromatics occurred for dry soil moisture conditions under no-till (Fig. 4A–D).

The largest emission of 4-methylphenol occurred under dry soil moisture conditions on the no-till plots that received manure generated from the 0% WDGS diet (Table 5; Fig. 4A–D). Flux measurements under dry soil moisture conditions on the no-till plots containing manure from the 10% WDGS diet were slightly higher than the plots containing manure obtained from the 30% WDGS diet. Measurements of 4-methylphenol were near MDL after 6 h for each of the treatments. Applying manure from the 0% WDGS diet on the soil surface under dry conditions for no-till increased 4-methylphenol emissions nearly 10 times compared with the tilled condition (Fig. 4A, B). The largest 4-methylphenol emissions occurred at 0 h, and the smallest emissions occurred at 23 h. Adding water on day 2 to no-till, surface-applied manure obtained from the 0% WDGS diet reduced emissions of 4-methylphenol (Fig. 4A–D). Measurements of 4-methylphenol were minimal for manure generated from diets containing 10 and 30% WDGS.

These findings of higher 4-methylphenol flux from 0% WDGS manures were different from results reported elsewhere (Cole et al., 2005; Galles et al., 2011; Todd et al., 2011; Hales et al., 2012b). These fresh WDGS manures contain a higher content of aromatic fermentation products, leading to higher initial fluxes of aromatics. However, as manure ages there is a loss of volatile odor compounds originally present in the manure, and subsequent fermentation can produce a different suite of odor compounds depending on the available substrate (Miller and Varel, 2001). Miller and Varel (2001) found that fresh manure from standard rations of dry rolled corn contain residual starch and a suite of fermentation products originating from carbohydrate fermentation. Aged manure from these standard rations has much lower starch content and, when subjected to additional fermentation, consumes protein and yields aromatic fermentation products (Miller and Varel, 2001). Most of the easily fermentable protein may have been used and already emitted from the WDGS. In the 0% WDGS manures, starch was broken down as the manure aged, and at the point when the aged manure was used, the microbes responsible for manure decomposition were using residual, more recalcitrant protein. Additional studies are needed to better understand manure aging and how the emissions of odorous fermentation products change over time.

Significant interactions for indole were measured among application method, soil moisture content, and sampling time (Table 6). Diet did not significantly affect emission rates for indole (Table 5). Peak emission rates for indole were measured at the 1-h sampling interval. The largest emission flux was obtained for dry soil moisture conditions under no-till (Fig. 5). The next largest emission flux occurred on the no-till plots under wet conditions.

The relatively large emission of aromatics on the no-till plots with dry soil conditions indicates the aromatics may have been trapped in the manure particles during storage and were released when they were applied to the plots. The addition of water may have retained the aromatic compounds in the soil–water matrix rather than releasing them to the atmosphere. The interaction effects involving soil moisture had the least impact on flux measurements for indole. This could have been influenced by the relative insolubility of indole in water compared with the other measured compounds (Houlihan, 1972).

Fig. 3. Hexanoic acid flux values for the no-till condition as affected by diet and time since application. WDGS, wet distillers grains with solubles.

Fig. 4. Flux values for 4-methylphenol as effected by application method, soil moisture content, and time since application. WDGS, wet distillers grains with solubles.

Indole solubility in pure water is more comparable to DMDS and DMTS than any of the OAV contributing VFAs or 4-methylphenol. Indole is at least five times less soluble; however, the comparison of relative solubility may be somewhat simplistic when other chemical and physical parameters are considered. Chemical parameters, such as competing dissolved salts or the presence of soil organic material, can influence how these less-soluble compounds are partitioned in the soil–water matrix. Also, the physical parameters, such as thickness of the hydrated

layer covering the soil/manure particles, can greatly influence the effective solubility of these compounds. The dynamic nature of these parameters in a changing environment creates a very complicate system. Despite the complicated nature, relative solubility can explain some tendencies.

Sulfides

The DMDS flux measurements were significantly influenced by diet, soil moisture condition, and sampling time (Table 6). The emission rate of DMDS was nearly 4 times greater for the 30% WDGS diet than for the other two diets (Table 5). Wet soil moisture conditions increased the DMDS emissions by approximately 2.6 times. The largest DMDS measurements occurred at the 6-h sampling interval.

The largest DMDS emissions were measured under wet soil moisture conditions on the plots that received manure obtained from the 30% WDGS (Fig. 6A–D). On these plots, the largest DMDS emission rates occurred at the 6-h sampling interval. For dry soil moisture conditions, the tilled plots that received manure from the 30% WDGS had the largest emission values. Emissions under dry soil moisture conditions on plots that were tilled remained relatively constant during the 24-h sampling period for all diets. In contrast, DMDS measurements for the wet condition on the plots containing manure from the 30% WDGS diet consistently increased during the first 6 h of measurement. This indicates that DMDS may have been produced on the plots

Fig. 5. Flux values for indole as affected by application method, soil moisture content, and time since application.

Fig. 6. Dimethyl disulfide (DMDS) flux values for till and no-till condition under dry and wet soil moisture conditions as affected by diet and time since application. WDGS, wet distillers grains with solubles.

containing manure from the 30% WDGS diet once water was added. Also, the WDGS is highly digested and has a higher sulfur content, which may result in rapid conversion to DMDS under specific anaerobic conditions.

Recently, Andersen et al. (2012) detailed an evaluation of this method for recovery of methanethiol and found it to be converted readily to DMDS, but methanethiol was retained in the sorbent tubes if they were not handled appropriately. This process has the potential to bias analysis if appreciable quantities of methanethiol are expected. Justification for using this method is based on work by Beard and Guenzi, (1983). They showed that DMDS was produced appreciably from cattle manure slurries from redox +300 – 100 mV potential. They also found that small amounts of methanethiol were achieved in these slurries across a wide range of redox potential but was not appreciably produced until – 100 mV potential or less. Redox potentials of – 100 mV or less are typically achieved in rice fields when flooded (Hou et al., 2000). The soils used during this study were typical agricultural loess soils found throughout the Midwest. The two methods of application were broadcast or tillage into the soil. Neither of these methods would typically produce redox potential sufficient for appreciable production of methanethiol.

Emissions of DMTS were significantly affected by diet and sampling time (Table 6). There were also significant interactive effects with application method, soil moisture content, and sampling time in addition to diet. The DMTS emissions were 3.2

times greater for manure derived from the 30% WDGS diet than for manure from the diet containing 0% WDGS. There were no significant differences in DMTS emissions between the manure derived from diets containing 0 and 10% WDGS.

The emission pattern for the sulfide compounds was very different from those of the VFAs and aromatics. Figure 7A illustrates the increase of DMTS emissions for the wet soil moisture conditions under till and no-till conditions from the initial sampling period until the 6-h sampling interval. Application method had little effect on emission rates. The no-till plots with dry soil moisture conditions had emission fluxes similar to the 1-h sampling time for the wet soil moisture condition. Emission of DMTS dropped to $<0.1 \text{ mg m}^{-2} \text{ min}^{-1}$ by the 2-h sampling period.

The effect of soil moisture content on the emission of DMTS, particularly for manure generated from the 30% WDGS diet, is illustrated in Fig. 7B and 7C. Under dry soil conditions (Fig. 7B), the largest emission rate was measured during the initial sampling period and then decreased to $<0.2 \text{ mg m}^{-2} \text{ min}^{-1}$ for the manure generated from the 30% WDGS diet and $<0.1 \text{ mg m}^{-2} \text{ min}^{-1}$ for the manure from the diets containing 0 and 10% WDGS. In contrast, for the wet soil moisture condition (Fig. 7C), the manure from the 30% WDGS diet had an initial emission flux of $0.2 \text{ mg m}^{-2} \text{ min}^{-1}$ and then steadily increased to $>0.9 \text{ mg m}^{-2} \text{ min}^{-1}$ by the 6-h sampling period.

Fig. 7. (A) Dimethyl trisulfide (DMTS) flux values as affected by application method, soil moisture content, and time since application. (B and C) Dimethyl trisulfide flux values for dry and wet soil moisture conditions as affected by diet and time since application. WDGS, wet distillers grains with solubles.

The increase in sulfide emissions from manure generated by diets with higher percentages of WDGS is influenced by the higher sulfur content of the WDGS feed stock. The removal of the starch component of corn during the creation of ethanol concentrates most of the conserved elements in the by-product. The increase in flux rates with sampling time appears to have been caused by the reduction in oxidation status of the wet soils. Reducing conditions favors the formation of reduced sulfur compounds.

Conclusions

The addition of animal manure to soil as a fertilizer amendment has benefits for sustaining or improving qualities for agricultural production. However, odors resulting from its use can affect those living nearby. Therefore, improved management is necessary to mitigate these unintended negative consequences.

Almost 65% of the offensive odors were reduced by only three compounds, and these emissions were released shortly after manure application. Although they were not directly measured, many of these odorous compounds may have been generated during manure storage. The addition of irrigation after application was found to reduce emissions of many of these compounds by retaining them in the soil-water solution. However, as the soils dry, the retained odors may be released.

Although some emissions were reduced by the addition of water, sulfide emissions were increased. This increase was greatest

for diets that contained 30% WDGS due to the increased sulfur content of the feed. The peak of sulfide emissions occurred several hours after irrigation and decreased rapidly as the soils dried. Manure incorporation combined with irrigation was found to reduce almost all of the measured odor compounds. However, the manure needs to be incorporated immediately after application to be most effective.

References

- Andersen, K.B., M.J. Hansen, and A. Feilberb. 2012. Minimization of artifact formation of dimethyl disulfide during sampling and analysis of methanethiol in air using solid sorbent material. *J. Chromatogr. A* 1245:24–31. doi:10.1016/j.chroma.2012.05.020
- Auermann, B.W., A.N. Paila, N. Hiranuma, and J. Bush. 2007. Open-path transmissometry to determine atmospheric extinction efficiency associated with feed yard dust. In: *Proc. Int. Symp. on Air Quality and Waste Manage. for Agric.* ASABE Pub. No. 701P0907cd. 16–19 Sept. 2007, Broomfield, CO.
- Beard, W.E., and W.D. Guenzi. 1983. Volatile sulfur compounds from a redox-controlled-cattle-manure slurry. *J. Environ. Qual.* 12(1):113–116. doi:10.2134/jeq1983.00472425001200010020x
- Brandt, R.C., H.A. Elliott, M.A. Adviento-Borbe, E.F. Wheeler, P.J. Kleinman, and D.B. Beegle. 2008. Field olfactometry assessment of dairy manure land application methods. ASABE paper no. 08–4939. American Society of Agricultural and Biological Engineers, St. Joseph, MI.
- Cole, N.A., R.N. Clark, R.W. Todd, C.R. Richardson, A. Gueye, L.W. Green, and K. McBride. 2005. Influence of dietary crude protein concentration and source on potential ammonia emissions from cattle manure. *J. Anim. Sci.* 83:722–731.
- DiSpirito, A.A., J.A. Zahn, D.W. Russell, E.E. Cooper, and J.L. Hatfield. 1994. Development of a standardized method for odor quantification from livestock wastes: Development of an odor index. Final report 97e1994. Presented to the National Pork Producers Council, Washington, DC. <http://www.pork.org/FileLibrary/ResearchDocuments/97-1994-DISPIRITO-ISU.pdf> (accessed 12 Nov. 2013).

- Donham, K.J., S. Wing, D. Osterberg, J.L. Flora, C. Hodne, and K.M. Thu. 2007. Community health and socioeconomic issues surrounding concentrated animal feeding operations. *Environ. Health Perspect.* 115:317–320. doi:10.1289/ehp.8836
- Edmeades, D.C. 2003. The long-term effects of manure and fertilizers on soil productivity and quality: A review. *Nutr. Cycling Agroecosyst.* 66:165–180. doi:10.1023/A:1023999816690
- Eghball, B., B.J. Wienhold, J.E. Gilley, and R.A. Eigenberg. 2002. Mineralization of manure nutrients. *J. Soil Water Conserv.* 57:470–478.
- Fauci, M.F., and R.P. Dick. 1994. Soil microbial dynamics: Short and long-term effects of inorganic and organic nitrogen. *Soil Sci. Soc. Am. J.* 58:801–806. doi:10.2136/sssaj1994.03615995005800030023x
- Feilberg, A., T. Nyord, M. Hansen, and S. Lindholm. 2011. Chemical evaluation of odor reduction by soil injection of animal manure. *J. Environ. Qual.* 40:1674–1682. doi:10.2134/jeq2010.0499
- Ferguson, R.B., J.A. Nienaber, R.A. Eigenberg, and B.L. Woodbury. 2005. Long-term effects of sustained beef feedlot manure application on soil nutrients, corn silage yield, and nutrient uptake. *J. Environ. Qual.* 34:1672–1681. doi:10.2134/jeq2004.0363
- Friedrich, J.E., and T.E. Acree. 1998. Gas chromatograph olfactometry (GC/O) of dairy products. *Int. Dairy J.* 8:235–241. doi:10.1016/S0958-6946(98)80002-2
- Galles, K., J. Ham, E. Westover, J. Stratton, J. Wagner, T. Engle, and T.C. Bryant. 2011. Influence of reduced nitrogen diets on ammonia emissions from cattle feedlot pens. *Atmosphere (Toronto)* 2:655–670. doi:10.3390/atmos2040655
- Gralapp, A.K., W.J. Powers, M.A. Faust, and D.S. Bundy. 2002. Effects of dietary ingredients on manure characteristics and odorous emissions from swine. *J. Anim. Sci.* 80:1512–1519.
- Hales, K.E., D.B. Parker, and N.A. Cole. 2012a. Potential odorous volatile organic compound emissions from feces and urine from cattle fed corn-based diets with wet distillers grains and solubles. *Atmos. Environ.* 60:292–297. doi:10.1016/j.atmosenv.2012.06.080
- Hales, K.E., N.A. Cole, and J.C. MacDonald. 2012b. Effects of corn processing method and dietary inclusion of wet distillers grains with solubles on energy metabolism, carbon-nitrogen balance, and methane emissions of cattle. *J. Anim. Sci.* 90:3174–3185. doi:10.2527/jas.2011-4441
- Hanna, H.M., D.S. Bundy, J.C. Lorimor, S.K. Mickelson, S.W. Melvin, and D.C. Erbach. 2000. Manure incorporation equipment effects on odor, residue cover, and crop yield. *Appl. Eng. Agric.* 16:621–627. doi:10.13031/2013.5376
- Heederik, D., T. Sigsgaard, P.S. Thorne, J.N. Kline, R. Avery, J.H. Bonlokke, E.A. Chrischilles, J.A. Dosman, C. Duchaine, S.R. Kirkhorn, K. Kuhnokova, and J.A. Merchant. 2007. Health effects of airborne exposures from concentrated animal feeding operations. *Environ. Health Perspect.* 115:298–302. doi:10.1289/ehp.8835
- Hou, A.X., G.X. Chen, Z.P. Wang, O. Van Cleemput, and W.H. Patrick, Jr. 2000. Methane and nitrous oxide emissions from a rice field in relation to soil redox and microbiological process. *Soil Sci. Soc. Am. J.* 64:2180–2186. doi:10.2136/sssaj2000.6462180x
- Houlihan, W.J. 1972. The chemistry of heterocyclic compounds: Indoles. Part 1. Wiley-Interscience, Chichester, UK.
- Koelsch, R.K., B.L. Woodbury, D.E. Stenberg, D.N. Miller, and D.D. Schulte. 2004. Total reduced sulfur concentration in the vicinity of beef cattle feedlots. *Appl. Eng. Agric.* 20:77–85. doi:10.13031/2013.15684
- Kyoung, S.R., P.G. Hunt, M.H. Johnson, A.A. Szogland, and M.B. Vanotti. 2007. Path integrated optical remote sensing technique to estimate ammonia and methane emissions from CAFOs. In: *Proc. Int. Symp. on Air Quality and Waste Manage. for Agric.* ASABE Pub. 701P0907CD. 16–19 Sept. 2007, Broomfield, CO.
- Mackie, R.I., P.G. Stroot, and V.H. Varel. 1998. Biochemical identification and biological origin of key odor components in livestock waste. *J. Anim. Sci.* 76:1331–1342.
- Miller, D.N., and E.D. Berry. 2005. Cattle feedlot soil moisture and manure content: I. Impacts on greenhouse gases, odor compounds, nitrogen losses, and dust. *J. Environ. Qual.* 34:644–655. doi:10.2134/jeq2005.0644
- 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.
- Mitloehner, F.M., and M.S. Calvo. 2008. Worker health and safety in concentrated animal feeding operations. *J. Agric. Saf. Health* 14:163–187. doi:10.13031/2013.24349
- Moore, P.A., T.C. Daniel, D.R. Edwards, and D.M. Miller. 1995. Effect of chemical amendments on ammonia volatilization from poultry litter. *J. Environ. Qual.* 24(2):293–300. doi:10.2134/jeq1995.00472425002400020012x
- Omland, O. 2002. Exposure and respiratory health in farming in temperate zones: A review of the literature. *Ann. Agric. Environ. Med.* 9:119–136.
- Parker, D.B., E.A. Caraway, M.B. Rhoades, N.A. Cole, R.W. Todd, and K.D. Casey. 2010a. Effect of wind tunnel air velocity on VOC flux from standard solutions and CAFO manure/wastewater. *Trans. ASABE* 53:831–845. doi:10.13031/2013.30066
- Parker, D.B., Z.L. Perschbacher-Buser, N.A. Cole, and J.A. Koziel. 2010b. Recovery of agricultural odors and odorous compounds from polyvinyl fluoride film bags. *Sensors (Basel Switzerland)* 10:8536–8552. doi:10.3390/s100908536
- Parker, D.B., J.E. Gilley, B. Woodbury, K.H. Kim, S. Bartelt-Hunt, X. Li, D. Snow, and G. Galvin. 2013a. Odorous VOC emission following land application of swine manure slurry. *Atmos. Environ.* 66:91–100. doi:10.1016/j.atmosenv.2012.01.001
- Parker, D., J. Ham, B. Woodbury, L. Cai, M. Spiehs, M. Rhoades, S. Trabue, K. Casey, R. Todd, and N. Cole. 2013b. Standardization of flux chamber and wind tunnel flux measurements for quantifying volatile organic compound and ammonia emissions from area sources at animal feeding operations. *Atmos. Environ.* 66:72–83. doi:10.1016/j.atmosenv.2012.03.068
- Patton, S., and D.V. Josephson. 1957. A method for determining significance of volatile flavor compounds in foods. *Food Res.* 22:316–318. doi:10.1111/j.1365-2621.1957.tb17017.x
- Powers, M.J. 1999. Odor control for livestock systems. *J. Anim. Sci.* 77:169–176.
- Powers, W.J. 2001. Development of procedures for odor evaluation techniques. In: *Proc. 1st IWA Int. Conf. on Odour and VOC's: Measurement, Regulation and Control Techniques.* Sydney, Australia.
- Powers, W.J., S.B. Zamzowand, and B.J. Kerr. 2007. Reduced crude protein effects on aerial emissions from swine. *Appl. Eng. Agric.* 23(4):539–546. doi:10.13031/2013.23487
- Radon, K., A. Schulze, V. Ehrenstein, R.T. van Strien, G. Praml, and D. Nowak. 2007. Environmental exposure to confined animal feeding operations and respiratory health of neighboring residents. *Epidemiology* 18:300–308. doi:10.1097/01.ede.0000259966.62137.84
- Rappert, S., and R. Muller. 2005. Odor compounds in waste gas emission from agricultural operation and food industries. *Waste Manag.* 25:887–907. doi:10.1016/j.wasman.2005.07.008
- SAS Institute. 2011. SAS/STAT user's guide. Version 9.3. Vol. 1, 4th ed. SAS Institute, Cary, NC.
- Schiffman, S.S., E.A. Miller, M.S. Suggs, and B.G. Graham. 1995. The effect of environmental odors emanating from commercial swine operations on the mood of nearby residents. *Brain Res. Bull.* 37(4):369–375. doi:10.1016/0361-9230(95)00015-1
- Sharpe, R.R., H.H. Schomberg, L.A. Harper, D.M. Endale, M.B. Jenkins, and A.J. Frazluebbbers. 2004. Ammonia volatilization from surface-applied poultry litter under conservation tillage management practices. *J. Environ. Qual.* 33(4):1183–1188. doi:10.2134/jeq2004.1183
- Sims, J.T., and N.J. Luka-McCafferty. 2002. On-farm evaluation of aluminum sulfate (alum) as a poultry litter amendment. *J. Environ. Qual.* 31(6):2066–2073. doi:10.2134/jeq2002.2066
- Spiehs, M.J., and V.H. Varel. 2009. Nutrient excretion and odorant production in manure from cattle fed corn wet distillers grains with solubles. *J. Anim. Sci.* 87:2977–2984. doi:10.2527/jas.2008-1584
- Tester, C.F. 1990. Organic amendment effect on physical and chemical properties of sandy soil. *Soil Sci. Soc. Am. J.* 54:827–831. doi:10.2136/sssaj1990.03615995005400030035x
- Thorne, P.S. 2007. Environmental health impacts of concentrated animal feeding operations: Anticipated hazards—Searching for solutions. *Environ. Health Perspect.* 115:296–297. doi:10.1289/ehp.8831
- Todd, R.W., N.A. Cole, L.A. Harper, and T.K. Flesch. 2008. Ammonia emissions from a beef cattle feedyard on the southern High Plains. *Atmos. Environ.* 42:6797–6805. doi:10.1016/j.atmosenv.2008.05.013
- Todd, R.W., N.A. Cole, M.B. Rhodes, D.B. Parker, and K.D. Casey. 2011. Daily, monthly, seasonal, and annual ammonia emissions from southern high plains cattle feed yards. *J. Environ. Qual.* 40:1090–1095. doi:10.2134/jeq2010.0307
- Trabue, S.L., J.C. Anhalt, and J.A. Zahn. 2006. Bias of Tedlar bags in the measurement of agricultural odorants. *J. Environ. Qual.* 35:1668–1677. doi:10.2134/jeq2005.0370
- Trabue, S.L., K.D. Scoggins, H. Li, R. Burns, and H. Xin. 2008. Field sampling method for quantifying odorants in humid environments. *Environ. Sci. Technol.* 42:3745–3750. doi:10.1021/es7031407
- Trabue, S.L., K. Scoggins, L. McConnell, R. Maghirang, E. Razote, and J. Hatfield. 2011. Identifying and tracking key odors associated with cattle feedlots. *Atmos. Environ.* 45:4243–4251. doi:10.1016/j.atmosenv.2011.04.081
- van Gemert, L.J. 2003. Odour thresholds: Compilations of odour thresholds in air, water, and other media. Oliemans Punter and Partners, Utrecht, the Netherlands.
- Varel, V.H., J.E. Wells, E.D. Berry, M.J. Spiehs, D.N. Miller, C.L. Ferrell, S.D. Shackelford, and M. Koohmaria. 2008. Odorant production and persistence of *Escherichia coli* in manure slurries from cattle fed zero, twenty, forty, or sixty percent wet distillers grains with soluble. *J. Anim. Sci.* 86:3617–3627. doi:10.2527/jas.2008-1118
- Varel, V.H., J.E. Wells, E.D. Berry, and D.N. Miller. 2010. Manure odor potential and *Escherichia coli* concentrations in manure slurries of feedlot steers fed 40% corn wet distillers grains. *J. Environ. Qual.* 39:1498–1506. doi:10.2134/jeq2009.0472
- 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 the identification and prioritization of malodors from confined animal feeding operations. *J. Agric. Food Chem.* 53:8663–8672. doi:10.1021/jf050763b
- Zahn, J.A., A.A. DiSpirito, Y.S. Do, B.E. Brooks, E.E. Cooperand, and J.L. Hatfield. 2001. Correlation of human olfactory responses to airborne concentrations of malodorous volatile organic compounds emitted from swine effluent. *J. Environ. Qual.* 30:624–634. doi:10.2134/jeq2001.302624x