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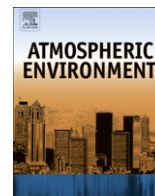
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Odororous VOC emission following land application of swine manure slurry

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ABSTRACT

Swine manure is often applied to crop land as a fertilizer source. Odor emissions from land-applied swine manure may pose a nuisance to downwind populations if manure is not applied with sufficient forethought. A research project was conducted to assess the time decay of odororous volatile organic compound (VOC) emissions following land application of swine manure. Three land application methods were compared: surface application, incorporation 24 h after surface application, and injection. Emission rates were measured in field plots using a small wind tunnel and sorbent tubes. VOCs including eight volatile fatty acids, five aromatics, and two sulfur-containing compounds were quantified by gas chromatography-mass spectrometry. In most cases, a first order exponential decay model adequately described the flux versus time relationship for the 24 h period following land application, but the model sometimes overestimated flux in the 6–24 h range. The same model but with the time term squared adequately predicted flux over the entire 24 h period. Three compounds (4-methylphenol, skatole, and 4-ethylphenol) accounted for 93 percent of the summed odor activity value. First order decay constants (k) for these three compounds ranged from 0.157 to 0.996 h⁻¹. When compared to surface application, injection of swine manure resulted in 80–95 percent lower flux for the most odororous aromatic compounds. These results show that VOC flux decreases rapidly following land application of swine manure, declining below levels of detection and near background levels after 4 to 8 h.

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1. Introduction

Odor emissions have been of great interest in recent decades. In fact, odor nuisance generates a significant fraction of the complaints in air pollution (Shusterman, 1992). The land application of municipal biosolids has been shown to emit odor and VOCs, a concern to neighbors near the land application sites (Laor et al., 2011; Kim et al., 2008). Likewise, odor and VOC emissions have been an issue at animal feeding operations (AFOs), and the issue has become more prevalent as houses encroach upon areas once occupied only by agriculture (Chen et al., 1999; Sweeten, 1995). Odors immediately adjacent to AFOs have been found to be caused

by VOCs and non-VOCs (ammonia, hydrogen sulfide) emitted from manure sources as well as other sources such as feed and silage (Montes et al., 2010; Hafner et al., 2010; Trabue et al., 2011a, b). AFOs have been identified as a source of over 200 VOCs to date (Zhang, 2001; Kai and Schäfer, 2004; Trabue et al., 2011a, b) with most VOCs at AFOs resulting from incomplete anaerobic degradation (Mackie et al., 1998). However, there is evidence that only a small percentage of those compounds are actually responsible for odor downwind from AFOs and these compounds are VOCs (Wright et al., 2005; Trabue et al., 2011a, b).

Currently, there is little data on the emission of odors and VOCs from AFOs. However, the recently completed U.S. EPA National Air Emissions Monitoring Study (NAEMS) was instituted to quantify air quality emissions from AFOs (Heber et al., 2008; Bereznicki et al., 2010). The NAEMS study mainly focused on quantifying air emissions from buildings and lagoons, while ignoring other minor emission sources such as land application of manure. However, land application of manure can be a major source of odor emission in rural communities (Brandt et al., 2008; Feilberg et al., 2010a).

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Consequently, this study was conducted for the purpose of quantifying odor (i.e., VOC) emission from the land application of manure. The objectives of the study were the following: 1) determine how specific VOC emissions decay with time following land application of swine manure slurry; and 2) compare VOC emissions using three application methods (surface application, incorporation by disking 24 h following surface application, and injection).

2. Materials and methods

2.1. Study site

Field experiments were conducted during the summer of 2011 at the University of Nebraska Rogers Memorial Farm located 18 km east of Lincoln, NE, USA. Soil at the site was classified as an Aksarben silty clay loam (*fine, smectitic, mesic Typic Argiudoll*) (Kettler et al., 2001). The soil contained 15% sand, 57% silt, and 28% clay with pH of 7.1 and organic matter content of 4.6%. Air temperatures at the time of the measurements were 32–38 °C and relative humidity varied from 50 to 95%.

Swine slurry was land-applied one day per week over a four week period using three treatments (i.e. TRT 1, 2, 3): TRT 1) surface application where the slurry was applied to the ground surface, TRT 2) the slurry was surface-applied followed by incorporation (disking), and TRT 3) the slurry was injected to a depth of approximately 11 cm (TRT 3). Disking on TRT 2 occurred 24 h after manure application so that the soil surface would not be muddy during tillage. TRT 1 was applied all four weeks. TRT 2 was applied in week 1 only, and TRT 3 was applied in week 2 only.

2.2. Swine manure slurry

Swine slurry was collected at the USDA Meat Animal Research Center in Clay Center, Nebraska, USA. Slurry was collected from a mechanically-ventilated barn (14 m × 59 m) that was stocked with 280 feeder pigs (mass range 68–120 kg). The pigs were fed with a corn and soybean-based diet (Table 1). The building had a pull-plug waste management system that was drained once a week on Tuesday evening and was then partially filled with water to 0.5 m depth.

Each week, swine slurry was collected from the pit on Monday morning at 0900 h and transported to the land application site in 20 L plastic buckets. In week 1, the swine slurry was dipped from the near-surface of the pit using an 8 L plastic bucket. In weeks 2–4, the swine slurry was collected from near the bottom of the pit using a submersible sewage pump. The slurry was pumped into 20 L plastic buckets and transported to the field site. A subsample of the swine slurry was analyzed for solids and nutrient analyses at Ward

Laboratories (Kearney, NE, USA). Swine slurry nutrient and solids concentrations are shown in Table 2.

2.3. Land application plots

Small plots (0.75 m × 2.0 m and 0.75 m × 4.0 m) were constructed using 20 cm wide sheet metal frames driven approximately 10 cm into the soil. New plots were constructed each week such that plots would receive swine slurry application only once. Swine slurry 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). When calculating manure application rates, it was assumed that the first year N availability from swine slurry was 70% of the total amount of nitrogen measured in the slurry.

Swine slurry was weighed at the field site, then land-applied starting about 1100 h. For the surface broadcast plots, the slurry was poured evenly across the entire plot area, and the wind tunnel was placed over a randomly selected location. For the injection plots, a tillage implement (four sweeps spaced 0.51 m apart) was passed over the area prior to placement of the metal borders. Swine slurry was poured into 3 cm diameter plastic pipes inserted 10 cm into the bottom of one of the slots. The wind tunnel was selectively placed over a slot area that received the injected slurry.

Because the study plots had been cropped in no-till corn and remained undisturbed following harvest the previous fall, there was considerable crop residue on the ground surface. Selected pieces of residue (corn stalks) were removed from the footprint of the wind tunnel prior to measuring the flux.

2.4. Wind tunnel flux measurement

The wind tunnel had dimensions of 51 mm (height), 305 mm (length), and 152 mm (width), with a footprint of 0.046 m² and internal volume of 2.36 L (Fig. 1). The wind tunnel was constructed of 50 mm square steel tubing and 44 × 44 mm angle iron with a 5 mm thick Plexiglas top. The sweep air entered the wind tunnel through 17 holes (6 mm dia.) in three rows at heights of 17 mm (6 holes), 30 mm (5 holes), and 43 mm (6 holes) above the base. Air exited the tunnel through three 10 mm diameter holes equally spaced at a height of 27 mm above the base of the angle iron at the opposite end of the tunnel. Sweep air (1 L min⁻¹) was supplied via Teflon[®] tubing from a compressed zero-grade air cylinder (Linweld, Lincoln, NE, USA). VOC emission rates have been shown to be dependent on sweep air flow rate, with higher sweep air flow rates producing higher VOC emission rates (Parker et al., 2010a). VOC emission rates are also positively correlated with the evaporation rate of water. For a sweep air flow rate of 1 L min⁻¹, the equivalent distilled water evaporation rate for this wind tunnel was 1.2 mm d⁻¹, measured using dry zero-grade sweep air in a 138 mm diameter Petri dish placed in the center of the wind tunnel (Parker et al., 2011).

Table 1
Composition of the diet fed to the pigs during the study.

	Percent of total (% dry matter basis)
Ground Corn	80.21
Soybean Meal	16.60
Dicalcium Phosphate	0.45
Limestone	0.80
Salt	0.30
Vitamin Premix	0.20
Trace Minerals	0.20
Phytase	0.05
L-Lysine	0.15
Theronine	0.01
Bacitracin	0.03
Soybean Oil	1.00
Total	100.00

Table 2
Slurry characteristics and nutrient concentrations of swine slurry.

	Week 1	Week 2	Week 3	Week 4
Ammonium (NH ₄), ppm N	745.7	728.5	578.5	862.3
Nitrate (NO ₃), ppm N	0.7	<0.1	0.3	1.1
Total N (TKN), ppm	809.8	863	628.4	1007
Phosphorus (as P ₂ O ₅), ppm	128.9	393.4	279.8	212.5
Potassium (as K ₂ O), ppm	630.4	615.0	486.6	772.0
Sulfur (S), ppm	82.6	51.6	63.0	56.7
Sodium Adsorption Ratio (SAR)	4.46	3.87	3.64	5.55
Elect. Cond. (EC), mmho cm ⁻¹	7.66	7.74	6.41	9.04
pH	8.0	7.2	7.4	7.6
Total Solids (%)	0.29	0.42	0.32	0.37

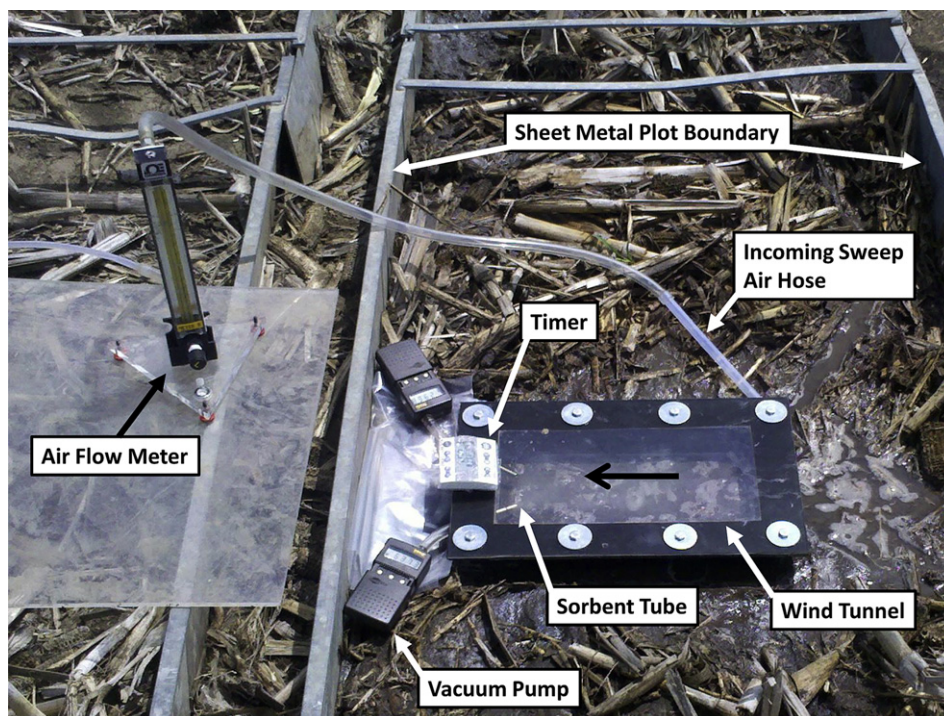


Fig. 1. Photograph of the small wind tunnel being used in the field plots to measure VOC flux shortly after land application of swine slurry. To the immediate left of the wind tunnel are the two portable vacuum pumps and sorbent tubes being used to collect samples from air as it leaves the wind tunnel, and further left is the rotameter used for metering the sweep air flow rate. Flow in the wind tunnel is from right to left as indicated by the black arrow.

Following an equilibration time allowing three volumes of sweep air to pass through the wind tunnel, VOC samples were collected from the air exiting the wind tunnel. Samples were collected in stainless steel sorbent tubes (89 mm × 6.4 mm OD, Markes International Inc., Wilmington, DE, USA) filled with Tenax TA[®] sorbent. Prior to use, 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 10 min using a vacuum pump (Pocket pump 210 series, SKC Inc., Eighty Four, PA, USA).

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

$$J = \frac{VA_T C_{\text{air}}}{A_S} = \frac{QC_{\text{air}}}{A_S} \quad [1]$$

where V is the average cross-sectional air velocity in the wind tunnel (m min^{-1}), A_T is the cross-sectional area of the wind tunnel (m^2), C_{air} is the VOC concentration in the exiting air ($\mu\text{g m}^{-3}$), and A_S is the footprint area of the wind tunnel (m^2). It should be noted that the sweep air flow rate, Q ($\text{m}^3 \text{min}^{-1}$), is equal to the average velocity times the cross sectional area of the wind tunnel ($Q = VA_T$). As such, the flux density formula derived for the wind tunnel investigated in this study is essentially identical to that often used for dynamic flux chambers. The sweep air flow rate entering the wind tunnel was controlled using a valved rotameter (Omega Engineering, Stamford, CT, USA). VOC flux was measured 15 min, 30 min, 1 h, 2 h, 6 h (for weeks 3 and 4 only), and 24 h following land application. Background flux was also measured in week 1 on four plots that did not receive swine slurry.

2.5. Gas chromatography/mass spectrometry analyses

All sorbent tube samples were collected in duplicate and results were averaged. Sorbent tube samples were analyzed using

a thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) system. The TD system was a Markes Unity 2 (Markes International Inc., Wilmington, DE, USA) with autosampler (Ultra 2, Markes International, Inc.) coupled to an Agilent GC-MS (7890A/5975C, Agilent Technologies, Inc., Santa Clara, CA, USA). The system used an Agilent Innowax, 30 m × 0.25 mm ID capillary column (polyethylene glycol, 0.25 μm film thickness). The column was run in constant flow of 1.4 mL min⁻¹.

Samples were purged at 40 mL min⁻¹ for 1 min prior to TD, desorbed for 10 min at 280 °C with a purge flow of 50 mL min⁻¹ (with no split) and trapped at -10 °C. The cold trap was rapidly heated to 320 °C and held for 1 min with a carrier gas flow of 20 mL min⁻¹, and 1.4 mL min⁻¹ was split and transferred to the GC-MS. The GC oven temperature program was the following: 1) initial temp, 40 °C hold 3 min; 2) ramp 8 °C min⁻¹ to 230 °C; and hold 5 min for total run time of 31.8 min.

Samples were analyzed for eight volatile fatty acids (VFA: acetic, propionic, butyric, isobutyric, valeric, isovaleric, hexanoic, and heptanoic acid), five aromatic compounds (phenol, 4-methylphenol, 4-ethylphenol, indole, and skatole), and two sulfur-containing VOCs (dimethyl disulfide and dimethyl trisulfide). For calibration, standard solutions were prepared ranging in concentration from 2.5 to 2500 ng μL^{-1} by diluting known masses of pure chemicals with methanol. All chemicals and solvents were FCC grade (Sigma Aldrich, St. Louis, MO, USA). Calibration standards in methanol were injected (2–10 μL) onto clean sorbent tubes using a calibration solution loading rig (CSLR, Markes International Inc., Wilmington, DE, USA). The liquid calibration standard was introduced through the CSLR injector septum in nitrogen carrier gas (75 mL min⁻¹) using a standard GC syringe.

MDLs for each target compound were calculated per U.S. EPA guidelines as the product of the standard deviation of seven replicates and the Student's t -value at the 99% confidence level (6 df, $t = 3.14$). The MDLs for all compounds, if expressed on a flux

Table 3
Summary of compounds quantified in the study, method detection limits, calibration statistics, and background soil emission rates.

Compound	MW	Retention time (min)	Min (ng)	Max (ng)	MDL (ng)	MDL ^a (ug m ⁻² min ⁻¹)	RSD ^b	r ²	Background ^c (ug m ⁻² min ⁻¹)
Phenol	94.1	20.2	5.5	1105	6.0	0.17	0.14	0.99	0.14
4-Methylphenol	108.1	21.1	5.2	1045	4.0	0.12	0.11	0.97	0.13
4-Ethylphenol	122.2	22.2	5.2	1055	6.0	0.17	0.21	0.97	0.01
Indole	117.1	25.2	6.3	1283	3.5	0.10	0.09	0.99	0.01
Skatole	131.2	25.6	7.1	1444	4.8	0.14	0.12	0.98	0.01
Dimethyl disulfide	94.2	5.2	5.3	2742	1.0	0.03	0.04	0.99	0.02
Dimethyl trisulfide	126.2	11.0	5.9	3084	2.1	0.06	0.14	0.99	0.01
Acetic acid	60.0	12.4	8.0	2602	32.9	0.96	0.38	0.99	1.63
Propanoic acid	74.1	13.8	7.5	2485	15.9	0.46	0.89	0.99	0.24
Isobutyric acid	88.1	14.2	7.3	2345	15.1	0.44	0.82	0.99	0.06
Butyric acid	88.1	15.1	7.3	2401	8.6	0.25	0.87	0.99	0.12
Isovaleric acid	102.1	15.7	7.1	2290	5.9	0.17	0.80	0.99	0.02
Valeric acid	102.1	16.7	7.1	2342	2.5	0.07	0.62	0.99	0.04
Hexanoic acid	116.2	18.1	7.0	2348	2.2	0.06	0.50	0.98	0.03
Heptanoic acid	130.2	19.5	7.0	2278	1.6	0.05	0.25	0.98	0.01

^a MDL for flux based on 10 min sampling time with wind tunnel flow rate of 1 L min⁻¹.

^b RSD = Relative standard deviation (standard deviation/mean) from 7 replications at minimum mass analyzed.

^c Background emission rate from soil receiving no swine slurry (average of 4 replicates in week 1).

basis, ranged from 0.03 to 0.96 μg m⁻² min⁻¹ which were similar to background emission rates measured separately on untreated soils (0.01–1.63 μg m⁻² min⁻¹) (Table 3).

2.6. Regression analyses

Regression was used to fit the flux versus time data to standard first-order exponential decay curves (Eq. (2)) and modified exponential decay curves (Eq. (3)).

$$J(t) = J_0 e^{-kt} \quad [2]$$

$$J(t) = J_0 e^{-kt^2} \quad [3]$$

where $J(t)$ = flux (μg m⁻² min⁻¹) at time t (hours), and J_0 = initial flux (μg m⁻² min⁻¹) at $t = 0$ h. In Eq. (2), k is the first order decay constant (hr⁻¹) and the value $-k$ is the slope of the curve $\ln(J)$ versus t . A large k value is indicative of a steep decay curve.

Regression coefficients, standard errors, and coefficient of determination (r^2) were calculated for each compound for selected land application tests. Nonlinear regression techniques were used, including the PROC NLIN procedure of SAS version 9.2 (SAS Institute, 2008) and the SOLVER function in Microsoft Excel (Brown, 2001). The Newton search method algorithm was used for both SAS and Excel.

Table 4
Regression coefficients for flux of individual compounds with time, $J(t)$, using the exponential decay curve of Eq. (2). Swine slurry was applied using the broadcast method at the rate of 1 × the annual nitrogen requirement.

	J_0 (μg m ⁻² min ⁻¹)				k (hr ⁻¹)				r^2			
	Wk 1	Wk 2	Wk 3	Wk 4	Wk 1	Wk 2	Wk 3	Wk 4	Wk 1	Wk 2	Wk 3	Wk 4
Phenol	0.821	4.02	6.05	8.28	0.069	0.161	0.358	0.214	0.801	0.980	0.953	0.906
4-Methylphenol	10.1	58.2	42.9	60.8	0.996	0.400	0.630	0.297	0.931	0.988	0.971	0.928
4-Ethylphenol	0.378	3.25	2.21	4.05	0.157	0.421	0.434	0.297	0.940	0.973	0.922	0.894
Indole	0.205	0.564	0.633	0.933	0.661	1.19	0.603	0.400	0.875	0.985	0.926	0.923
Skatole	0.298	4.91	2.48	4.87	0.812	0.838	0.584	0.385	0.854	0.958	0.911	0.918
Dimethyl Disulfide	0.405	0.086	1.20	0.073	1.74	0.025	0.831	0.018	0.784	0.845	0.980	0.353
Dimethyl Trisulfide	0.409	0.051	0.609	0.038	5.57	0.064	1.02	0.167	0.816	0.904	0.965	0.615
Acetic Acid	3.06	23.5	3.73	2.98	-0.011	0.067	0.018	0.005	0.241	0.454	0.106	0.011
Propionic Acid	0.514	8.64	0.988	0.330	-0.006	0.085	0.048	0.0004	0.032	0.526	0.422	0.000
Isobutyric Acid	0.415	2.59	0.341	0.342	-0.013	0.081	0.048	0.072	0.111	0.514	0.547	0.337
Butyric Acid	0.345	3.85	0.574	0.387	0.035	0.086	0.102	0.072	0.453	0.534	0.512	0.192
Isovaleric Acid	0.094	1.89	0.161	0.189	0.074	0.085	0.092	0.099	0.706	0.521	0.462	0.215
Valeric Acid	0.103	0.471	0.069	0.086	0.059	0.089	0.015	0.060	0.760	0.606	0.091	0.263
Hexanoic Acid	0.040	0.061	0.048	0.106	0.031	0.014	-0.007	0.048	0.584	0.342	0.045	0.338
Heptanoic Acid	0.032	0.033	0.028	0.048	0.034	0.018	0.006	0.064	0.366	0.153	0.078	0.876

Although a true r^2 value is not defined for a nonlinear regression model, a “pseudo r^2 ” (SAS, 2011; Brown, 2001) was calculated from the sum of squares (SS) as shown in Eq. (4).

$$r^2 = 1 - \frac{SS_{\text{residual}}}{SS_{\text{total}}} \quad [4]$$

To determine the mass of each compound emitted per unit area (μg m⁻²), the area under the curve of Eq. (2) was calculated using integration over the first 24 h following land application using Eq. (5):

$$\int J_0 e^{-kt} dt = \frac{J_0 e^{-kt}}{-k} \quad [5]$$

2.7. Odor activity value analyses

To assess the relative importance of each individual compound on odor, the concentrations of individual compounds were converted to their respective odor activity values (OAV). The OAV is defined as the ratio of the concentration of a single compound to the odor threshold for that single compound (i.e. single compound odor threshold, SCOT) (Friedrich and Acree, 1998; Trabue et al., 2006; Parker et al., 2010b; Patton and Josephson, 1957). Conceptually, the larger the OAV, the more likely that compound will contribute to the overall odor of a complex odor mixture. Scientists

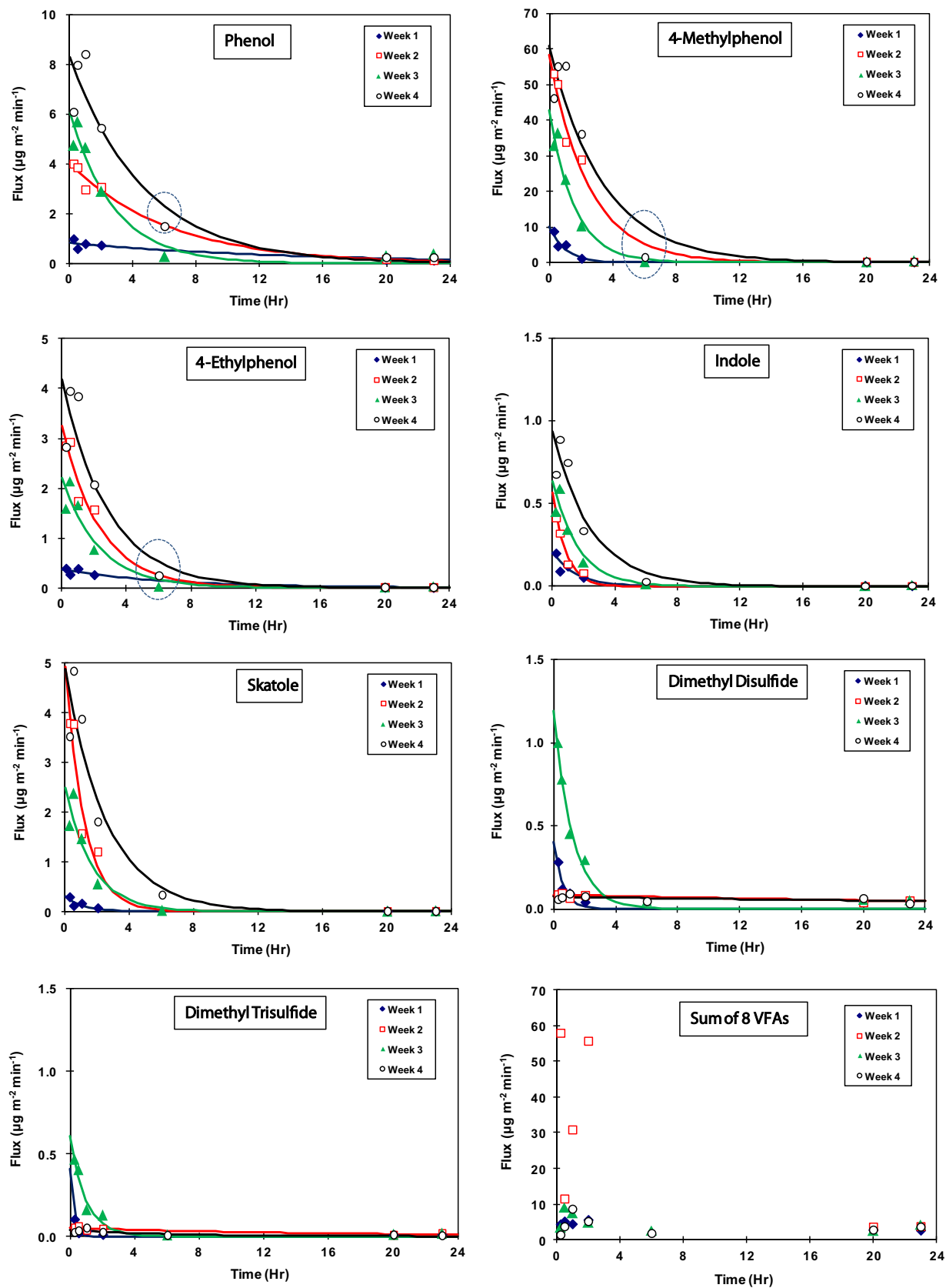


Fig. 2. Flux as a function of elapsed time following land application using the surface broadcast method. The first order exponential decay curves provided a reasonable estimate of flux versus time, with the exception of phenol, 4-methylphenol, and 4-ethylphenol for the 6 h time in week 4 (circled).

in the food and beverage industries have used OAV extensively in their research to determine the most important aroma contributors (Hansen and Schieberle, 2005; Grosch, 1994; Fritsch and Schieberle, 2005).

Because published SCOT values can vary as much as an order of magnitude, OAV calculation can be difficult. In this research, the average SCOT values were calculated for each compound using the numerous values from a compilation of published odor thresholds (Parker et al., 2010b). Average concentrations were calculated for each compound in the first 24 h following land application, and then these values were converted to OAVs by dividing by the SCOT value. The relative contribution of each compound was calculated by dividing the OAV for the individual compound by the sum of the OAV values for all compounds. The idea of summing the individual OAVs to assess overall odor potential was initially proposed by Guadagni et al. (1963) and later by Leffingwell and Leffingwell (1991). However, it should be noted that one of the arguments against the use of the summed OAVs, and OAV in general, is that it does not account for possible synergistic or other complex interactive effects (DiSpirito et al., 1994; Powers, 2001; Zahn et al., 2001).

3. Results and discussion

3.1. Flux decay following application

Regression coefficients and coefficient of determination values for the first-order exponential decay of Eq. (2) are presented for each compound by week in Table 4. For the first-order exponential decay curves, coefficient of determination values were higher for the aromatic and sulfide compounds ($r^2 = 0.8$ to 0.9 typical) than for the VFAs ($r^2 = 0.1$ to 0.7 typical). For the most part, the first order

exponential decay curves adequately described the degradation of VOC flux from land-applied swine slurry for the first 24 h after land application (Fig. 2). Likewise, first order exponential decay models have been used to describe the flux decay of oil-based varnishes (Lee et al., 2003), wood stains (Tichenor and Guo, 1991), and dry cleaning chemicals (Tichenor et al., 1990).

For three of the compounds (phenol, 4-methylphenol and 4-ethylphenol) examined in week 4, the first-order exponential decay curves overestimated the measured flux values at 6 h after land application. Upon further investigation, we determined that a modified exponential decay curve in which the time term was squared (Eq. (3)) resulted in a better fit for the time period from 6 to 24 h on the week 4 data (Fig. 3). This was evident by both larger r^2 values for the modified curves, and a better eyeball fit for the entire 24 h time period (Fig. 3). Because the primary objective of this study was to determine and predict VOC and odor emissions following land application of swine slurry, we view the modified curve as a better predictor of actual flux decay. The standard first order exponential decay curve would overestimate flux values for certain compounds in the 4–12 h range following land application.

Both the data and the modified exponential decay models suggest that VOC emissions after 6–24 h of land application were near the levels of detection and/or corresponding background levels shown in Table 3. In addition, based on field observations there was no swine slurry odor evident at 6 h. Similarly, Hanna et al. (2000) reported that odor emissions from land-applied swine manure, as measured by olfactometry with human panelists, were indistinguishable from the background soil after 24 h. Conversely, Brandt et al. (2008) reported only a 50% reduction in odor after 24 h for dairy manure slurry when measured by human panelists using field olfactometers.

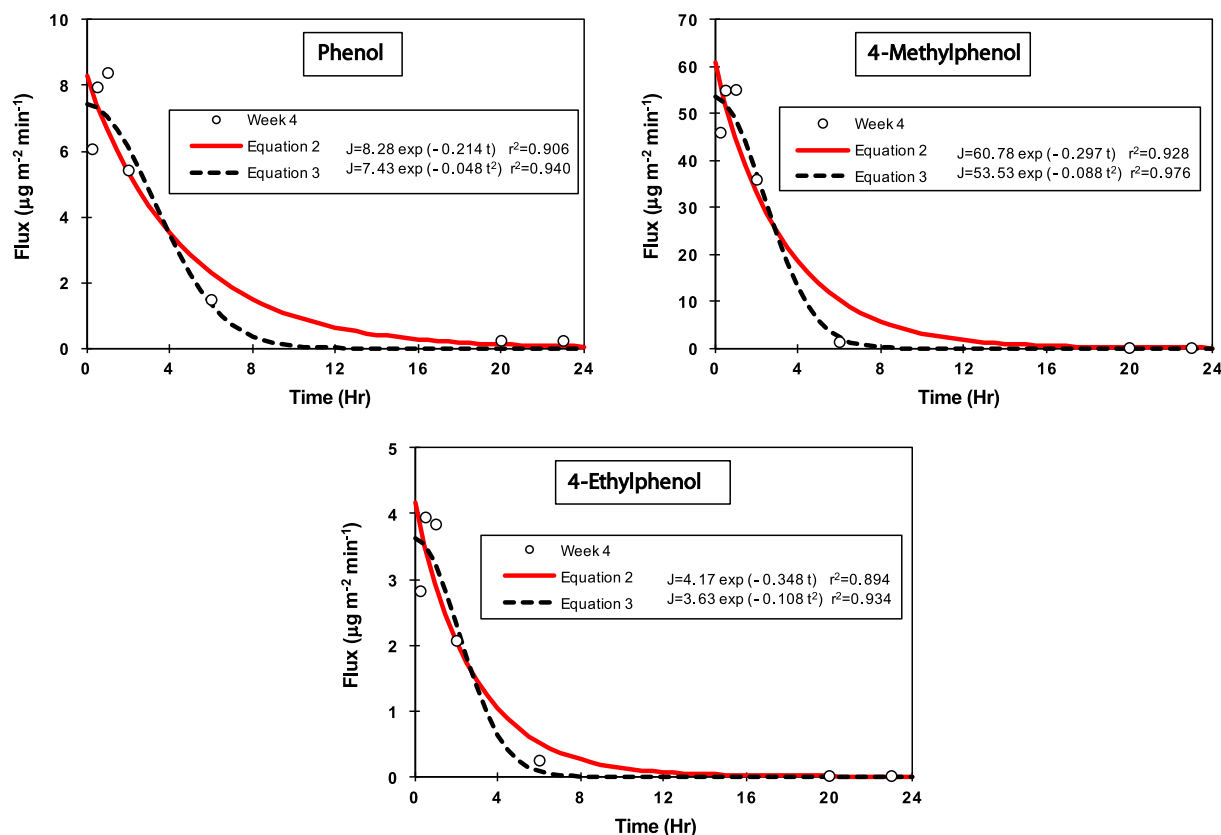


Fig. 3. A comparison of the standard first order exponential decay model (Eq. (2)) to the modified exponential decay model (Eq. (3)). The modified decay model had an overall better fit than the standard first order exponential decay model for the compounds of phenol, 4-methylphenol, and 4-ethylphenol.

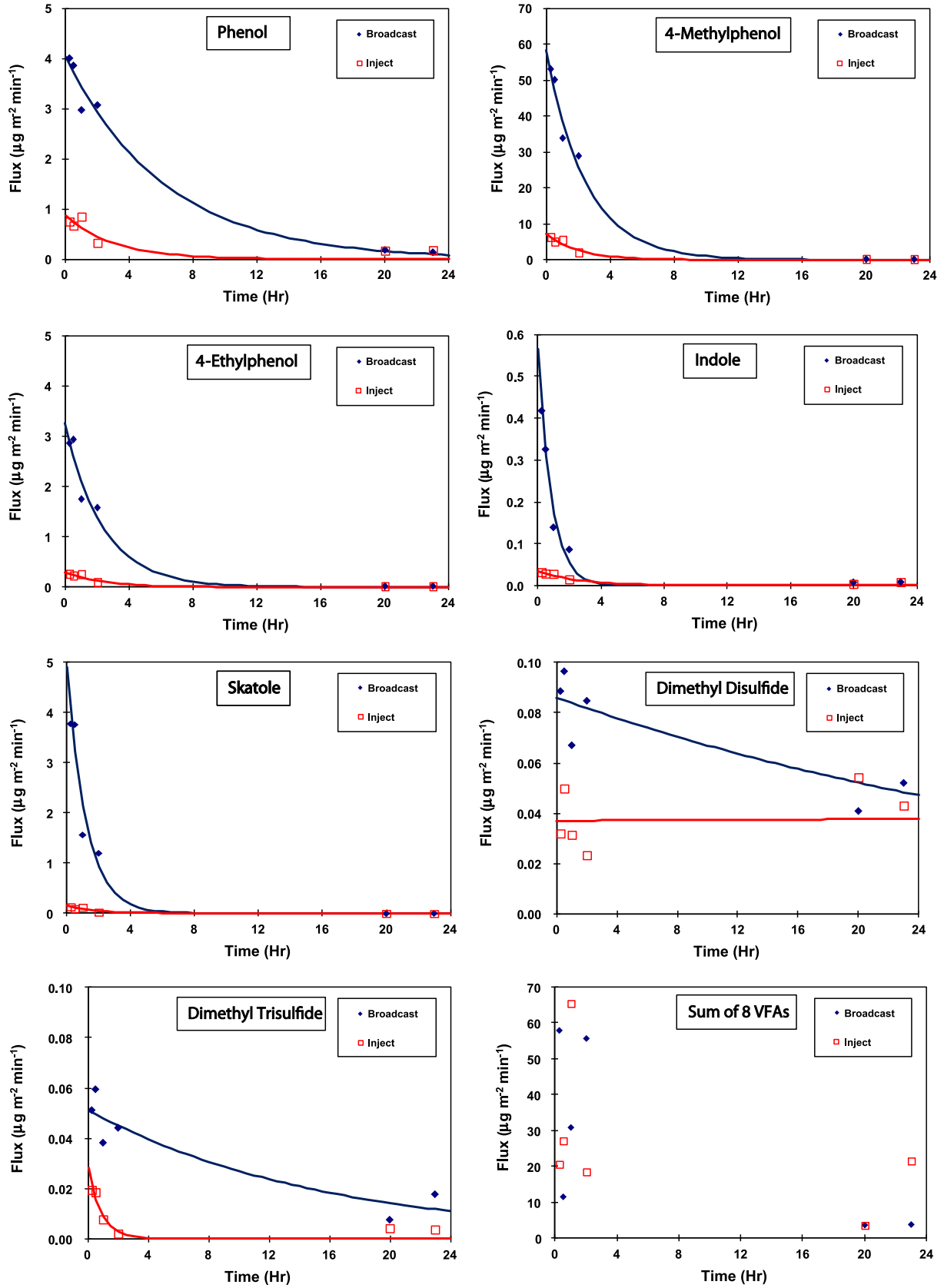


Fig. 4. A comparison of flux values for broadcast (surface-applied) versus injected swine slurry. This comparison was conducted on swine slurry collected in week 2.

Of all the VOCs, 4-methylphenol had the highest initial flux (J_0) values. These results are similar to those presented by Feilberg et al. (2010a), who also reported that 4-methylphenol had the highest concentrations within a static chamber placed above land-applied swine manure slurry. Three aromatic compounds (4-methylphenol, indole and skatole) have been reported as those most responsible for odors at a distance of several kilometers downwind of AFOs (Wright et al., 2005; Parker et al., 2007; Trabue et al., 2011b). Of these three compounds, 4-methylphenol is often implicated as the most important compound, and it has been the target for odor abatement in swine and beef manure (Eniola et al., 2006; Govere et al., 2005). This result is likely due to two factors: 1) the production and release of 4-methylphenol is high, and 2) 4-methylphenol has a low SCOT value of 2–5 $\mu\text{g m}^{-3}$ (Parker et al., 2010b). For the first order exponential decay curves of Fig. 2, the decay constants (k values) for 4-methylphenol ranged from 0.297 h^{-1} in week 4 to 0.996 h^{-1} in week 1. The background flux was 0.13 $\mu\text{g m}^{-2} \text{min}^{-1}$ for 4-methylphenol and 2.2 $\mu\text{g m}^{-2} \text{min}^{-1}$ for the summed VFAs. The 4-methylphenol flux values decreased to below detection limits and near background levels after about 8–12 h in week 4, and 6–8 h in week 1 (Figs. 2 and 3).

As discussed further in Section 3.3, the contribution of the VFAs to the overall odor was very low compared to the aromatic compounds. For this reason, the flux values from the eight VFAs were summed as shown in Fig. 2. Regression coefficients for the individual VFAs are presented in Table 4.

3.2. Effect of land application method

After 24 h, fluxes had decreased to background levels for both the surface broadcast (TRT 1) and incorporation 24 h following broadcasting (TRT2), thus preventing any meaningful comparison between these two treatments. There were, however, considerable differences in flux between the broadcast (TRT 1) and injection (TRT 3) methods. As shown in Fig. 4, the flux for the aromatic and sulfur-containing compounds was considerably less for the injected slurry (TRT 3) than for the surface broadcast (TRT 1). There were minimal differences between TRT 1 and TRT 3 for the summed VFAs. However, the overall impact of the VFAs in terms of odor emission was low, as discussed further in the next section.

For the aromatic compounds, there was an 80–95% decrease in the total mass emitted over the 24 h period for the injected manure (TRT 3) as compared to the surface broadcast (TRT 1) (Table 5). For the sulfur-containing compounds dimethyl sulfide and dimethyl trisulfide, injection (TRT 3) resulted in a 24 and 97% decrease,

respectively, as compared to the surface broadcast treatment (TRT 1). There were smaller decreases in VFA flux between the injected and surface broadcast manure. Although hexanoic and heptanoic acids showed an overall increase in flux, their emission rates were at or near their respective MDLS, and thus subject to high relative error.

For comparison, Brandt et al. (2008) reported 67% lower odor concentrations for injected dairy slurry than for surface-applied dairy slurry after 1 h, and 58% after 4 h. Hanna et al. (2000) reported 68–88% reduction in odor emissions as measured by olfactometry for injected swine manure as compared to surface broadcast. Feilberg et al. (2011) reported 75–90% reduction in 4-methylphenol emissions when swine manure was injected.

The depth of injection could have an effect on VOC emissions, and it seems logical that deeper injection depths would result in lower emissions. In our research, the manure slurry was injected to a depth of 10 cm, which is a typical depth of injection for land-applied manure with current equipment availability. Potential drawbacks to deeper injection would be the requirement for heavier injection equipment, larger tractor requirements, and higher fuel use.

3.3. Odor activity value

Based on the OAV analyses, the compound most responsible for the overall odor impact from the VOC emissions was 4-methylphenol. On average, 4-methylphenol accounted for 79.5% of the summed OAV, followed by skatole, the summed VFAs, and 4-ethylphenol at 12.3%, 4.8%, and 1.2%, respectively (Fig. 5). The two sulfide compounds combined accounted for 0.3–2.4% of the OAV for all the VOCs. The summed VFA flux was dominated by acetic acid and propionic acid, which comprised 65% and 18% of the summed VFAs, respectively. Although these two compounds had the highest concentrations out of all the VFAs, their overall contribution to OAV was minimal because of their high odor thresholds. Butyric acid and isovaleric acid accounted for 36 and 46%, respectively, of the total OAV for the VFAs, but still only a small percentage (<4.8%) of the OAV for all the VOCs.

In comparison, Trabue et al. (2008) reported that butyric acid made the single largest contribution to OAV (35.2%) in a swine finishing building with a pull-plug waste management system (a system similar to the swine building we tested), followed closely by indole (22.9%) and 4-methylphenol (22.2%). When Trabue et al. (2008) tested swine manure stored in simulation tanks resembling a deep-pit waste management system, they reported that

Table 5
A comparison of initial flux (J_0), and k values (from the regressions) for the surface broadcast and injection methods (data from week 2). Also shown is the total mass emitted per unit area during the first 24 h after application (calculated by integrating the area under the flux versus time regression curves).

Chemical compound	J_0 ($\mu\text{g m}^{-2} \text{min}^{-1}$)		k (hr^{-1})		Total mass emitted per unit area in 24 h period ($\mu\text{g m}^{-2}$)		
	Surface broadcast	Injection	Surface broadcast	Injection	Surface broadcast	Injection	% decrease
Phenol	4.02	0.860	0.161	0.331	1497	156	89.6
4-Methylphenol	58.2	7.13	0.401	0.499	8721	858	90.2
4-Ethylphenol	3.25	0.299	0.421	0.427	463	42.0	90.9
Indole	0.564	0.035	1.19	0.389	28.3	5.46	80.7
Skatole	4.91	0.158	0.838	0.555	351	17.1	95.1
Dimethyl Disulfide	0.086	0.037	0.025	-0.001	144	109	24.3
Dimethyl Trisulfide	0.051	0.028	0.064	1.156	46	1.5	96.7
Acetic Acid	23.5	16.4	0.067	0.080	20087	12711	36.7
Propionic Acid	8.64	9.30	0.085	0.094	5990	5861	2.2
Isobutyric Acid	2.59	2.80	0.081	0.114	1872	1463	21.8
Butyric Acid	3.85	3.10	0.086	0.137	2637	1354	48.7
Isovaleric Acid	1.89	1.79	0.085	0.128	1306	837	35.9
Valeric Acid	0.471	0.446	0.089	0.105	311	251	19.3
Hexanoic Acid	0.061	0.080	0.014	0.025	128	134	-4.7
Heptanoic Acid	0.033	0.035	0.018	0.015	65.1	70.2	-7.7

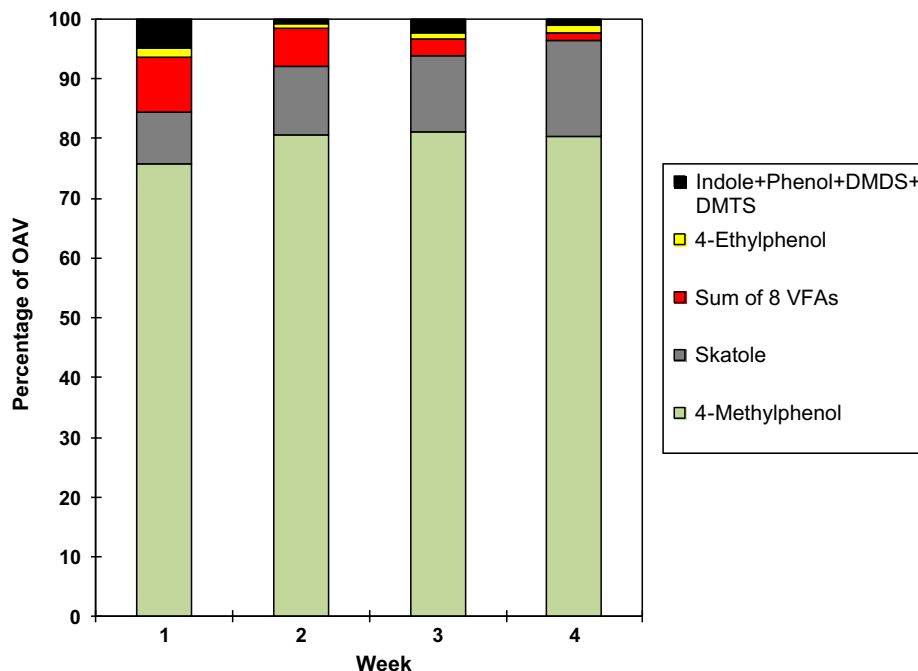


Fig. 5. The relative percentages of odor activity value (OAV) were dominated by 4-methylphenol (avg. 79.5%), skatole (avg. 12.3%), the summed VFAs (4.8%), and 4-ethylphenol (1.2%). The combined indole, phenol, DMDS and DMTS averaged 2.2%.

indole accounted for the most OAV (69.7%) followed by skatole (22.3%), 4-methylphenol (4.7%) and 4-ethylphenol (3.0%).

The three compounds 4-methylphenol, skatole, and 4-ethylphenol accounted for 93.0% of the OAV. VFAs are often implicated as the primary odor causing agents in beef cattle manures (Spiehs and Varel, 2009), and methods for reducing emissions by altering the diet have been proposed (Miller and Varel, 2002, 2003; Archibeque et al., 2005). However, similar to what was reported by others (Trabue et al., 2008, 2011a; Feilberg et al., 2010b, 2011), this research suggests that the aromatic compounds are most responsible for odor in swine manure slurry, thus these compounds should be the target for odor reduction technologies.

3.4. Implications for timing of land application

These results have implications for the timing of land application. The results demonstrate that adequate time, on the order of 6–8 h, should be allowed for the VOC flux from the application site to occur prior to any significant public event, such as a major holiday event or large weekend gathering. Although the emissions of VOC decrease substantially after land application, about 6–8 h is necessary before the emissions approach background levels. This information, together with anticipated weather conditions such as wind speed and direction, should help producers make management decisions on how and when to properly apply swine manure and minimize downwind odor impacts.

4. Conclusions

The following conclusions were drawn from this research:

1. VOC emission rates declined rapidly after land application, and were below levels of detection and near background levels within 4 to 8 h. In most cases, the first order exponential decay model adequately described the flux versus time relationship for the 24 h period following land application, but the model

sometimes overestimated flux in the 6–24 h range. The exponential decay model with time squared term provided a better overall fit to the flux versus time data. Among all the compounds analyzed, a single compound (4-methylphenol) accounted for 80 percent of the odor activity value. First order decay constants (k) for 4-methylphenol ranged from 0.297 to 0.996.

2. Injection of swine manure resulted in an 80–95% decrease in VOC flux as compared to surface application. Because flux had decreased to near background levels after 24 h (i.e. at the time of incorporation), no differences were observed between the surface-applied and incorporation methods. Incorporation would have to be conducted soon after land application to make a difference in VOC emissions.

This research showed that the method of land application had a greater effect on reducing VOC emission rates than did the decay of flux over time. For example, with surface application it took about 6 h for the VOC flux to reach 10 percent of the original flux value, which is equivalent to the same VOC flux at time zero when the manure was injected. The combining of land application methods that reduce VOC flux with management factors related to timing of land application should allow producers to better manage their land application to minimize downwind odor impacts.

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