RESEARCH REPORT
ENVIRONMENT

Title: Odor compound production, accumulation, and volatilization from swine manure storage **NPB#06-111**

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II. Industry Summary

The objectives of this project were to determine the changes in odor compound content and composition of three swine manure storage systems over the course of a year characterize and compare the relative emission of volatile odor compounds in simulated manure applications. Alcohols, volatile fatty acids (VFA), and aromatic compounds were detected in manure samples from lagoons, deep pits, and above ground slurry storage tanks. There were substantial differences in the content of these odor compounds and other nutrients between the three types of structure and even within the type of structure. Generally, lagoon slurries had lowest nutrient and odor compound content, and pits and tanks had the greatest. The differences between individual pits (or lagoons or tanks) were attributed to different management practices (manure inputs, types of animals, or diet). Looking at emissions of odor compounds, aromatic compounds (rather than alcohols or VFA) were especially important based on their high relative emission from stored manure and when applied to soil. For soil application, this was based on the large amount emitted over a longer period of time compared to the other two classes of odor compounds. There were no odor compounds emitted from sub surface (6" depth) soil applications. Finally, seasonal effects, particularly on aromatic compounds, were strongest during winter and spring and lowest during summer and fall. These finding affirm practices involving subsurface manure injection during fall as the best practice for limiting odor compound emissions.

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III. Scientific Abstract

The objectives of this project were to determine the changes in odor compound content and composition of three swine manure storage systems over the course of a year characterize and compare the relative emission of volatile odor compounds in simulated manure applications. Alcohols, volatile fatty acids (VFA), and aromatic compounds were detected in manure samples from lagoons, deep pits, and above ground slurry storage tanks. There were substantial differences in the content of these odor compounds and other nutrients between the three types of structure and even within the type of structure. Generally, lagoon slurries had lowest nutrient and odor compound content, and pits and tanks had the greatest. The differences between individual pits (or lagoons or tanks) were attributed to different management practices (manure inputs, types of animals, or diet). Looking at emissions of odor compounds, aromatic compounds (rather than alcohols or VFA) were especially important based on their high relative emission from stored manure and when applied to soil. For soil application, this was based on the large amount emitted over a longer period of time compared to the other two classes of odor compounds. There were no odor compounds emitted from sub surface (6" depth) soil applications. Finally, seasonal effects, particularly on aromatic compounds, were strongest during winter and spring and lowest during summer and fall. These finding affirm practices involving subsurface manure injection during fall as the best practice for limiting odor compound emissions.

IV. Introduction

Swine manure storage has been optimized to reduce the time and cost associated with swine production with little thought given to controlling odor emissions. Typical production in Nebraska involves either long term manure accumulation in deep pits with annual manure application or short-term accumulation within a pull-plug system where manure accumulates under the pens for a few weeks and then is flushed into a lagoon for long term storage. A third manure storage alternative is above ground manure storage. In this practice the manure slurry is pumped out into a storage tank and subsequently applied later in the year to surrounding cropland like deep pit and pull-plug/lagoon manure storage systems. One benefit to the above ground manure storage system is that natural manure crusts tend to form on top of the manure, which limits the emission of greenhouse gases and odors compared to the other storage types (Petersen and Miller, 2006). Quantifying and controlling odor emissions from manure storage is becoming one of the top priorities for swine producers as legal action and regulation regarding odor emission pose an increasing difficult challenge to current production practices. Perhaps the most difficult barrier to developing better manure storage practices is the difficulty associated with odor measurement.

Over 150 different chemical compounds have been detected in the air emitted from livestock facilities (O'Neill and Phillips, 1992). Ascribing the human-perceived odor measures to specific volatile chemical constituents has been a challenge, but a growing body of work has emerged implicating volatile organic compounds (VOC), in particular volatile fatty acids (VFA) and aromatic ring-containing compounds, as the dominant constituents associated with odor (Zhan et al., 1997; Wright et al., 2005). Diet is thought to play a significant role in manure composition and the emissions of VOCs and other gases. Although the links between diet, manure composition, and numerous manure emissions are becoming clearer (Sutton et al., 1999), the specific relationships with odor compound production and volatilization are poorly established. In vitro incubations of swine manures imply that unutilized starch in the manure is also a prominent source of VFA during manure slurry storage (Miller and Varel, 2003), whereas aromatic compounds arise primarily from protein fermentation (Mackie et al. 1998). Establishing the links between diet, manure composition, VOC production and accumulation during manure storage, and VOC volatilization from the manure after application would speed efforts to reduce swine odors through low-cost diet modification and a combination of optimal manure storage to minimize emissions during storage and at the time of manure application.

Analysis of odor compounds can be accomplished most easily by extraction or direct measurement from the manure liquid fraction. Typically ether or another organic phase is used to concentrate and purify odor compounds before injection and separation of individual compounds during gas chromatography. Quantification involves the use of internal standards and reference compounds detected by flame ionization or mass spectroscopy. Currently accepted protocols will quantify several dozen different compounds including several different alcohols, volatile fatty acids, methyl sulfides, phenols, and indoles (Miller and Varel, 2003). Analysis of airborne malodorous VOC is a much more challenging multi-step process that involves initial concentration on an adsorbent matrix, elution of the compounds from the matrix by thermal or chemical methods, separation using gas chromatography (GC) techniques, and finally detection and quantification of individual compounds using a mass spectroscopy (MS) or flame ionization. Currently, adsorbent tubes are utilized for the capture and concentration of VOC (see Zahn et al., 1997 for an example). However, the potential for incomplete capture or the breakthrough of select compounds in the VOC mixture during long sampling times is an issue. Furthermore, there are processing issues associated with adsorbent tubes. Thermal desorption tubes require a high initial investment for desorption equipment, tubes, and tube conditioners, plus a GC must be dedicated to the thermal desorption equipment. For chemical extraction of adsorbed compounds or direct measurement of compounds in liquid extracts, the sensitivity of detection is low (only a fraction of the extract is analyzed), and often the solvent peak can mask a number of highly volatile compounds during analysis.

Solid-phase microextraction (SPME) is similar to other adsorbent methods but is not reliant upon expensive equipment for thermal desorption nor is chemical extraction necessary for sample analysis. As an alternative to other methods, SPME is fast, sensitive, and cost-effective (Koziel and Pawliszyn, 2001). In SPME, volatiles are first concentrated on an exposed fiber, and then the fiber is injected into a standard GC inlet, which volatilizes the entire sample. Odor compounds are separated and quantified using standard GC methods. SPME technology has seen some application analyzing odorous compounds associated with agriculture (Razote et al., 2004; Wright et al., 2005). Conversion of the SPME results into atmospheric concentrations is a challenge, because the amount of VOC captured on the fiber is not only dependent upon the airborne concentration of VOC, but also on numerous environmental and experimental factors. Recently, a quick, reliable, and inexpensive laboratory method utilizing SPME and dynamic flux chambers was developed to compare the types and relative amounts of volatiles emitted from manures (Miller and Woodbury, 2006). Application of the method to manures of differing origin (cattle or swine), diet, and storage conditions revealed that the types and relative amounts of emitted volatile compounds were dependent not only upon animal type, but upon diet fed and how the manure was subsequently stored.

A combination of standard extraction practices to measure the concentration of odor compounds in manure storages and newer SPME techniques to measure the emission of specific odor compounds would yield insights into the specific controls on odor compound emission from manure storages. Controlling odor emissions from manure is a top priority in the pork industry. Legal and regulatory action regarding odor emissions presents a clear challenge to the industry. Holistic solutions where odor is reduced throughout the system, both during storage and at the time of manure application, are sorely needed. This project will help to determine where odor compound emissions occur, how the emission change through time, and the relative benefit of three common manure storage systems in the context of eventual manure application.

V. Objectives

1. Determine the changes in odor compound content and composition of manure in swine manure storage systems over the course of a year (predominantly finisher) in multiple above ground, deep pits, and lagoon manure storage systems.

2. Characterize and compare the relative emission of volatile odor compounds by gas chromatography-mass spectroscopy from multiple simulated manure applications.

VI. Materials & Methods

***Field Sites*—**Five swine operations representing three common manure storage options (lagoon, deep pit, above ground slurry tank) in the upper Midwest were initially selected to provide manure samples for the project. Unfortunately, sampling issues at the second deep pit operation made it impossible to routinely access to the manure pits, and they were dropped from the research project. To compensate for this site, the remaining four replicates of each type of manure storage systems were sampled for an additional six months beyond the originally proposed period for a total period of 18 months (Dec 2006 to May 2008). Samples were collected at roughly three-week intervals in all seasons from all sites with the exception of the winter season for the two tallest above-ground manure slurry stores, since these two sites were frozen over, and a hole in the frozen manure surface permitting sample collection could not be made from the catwalk several feet above. One season (spring) was replicated (2007 and 2008) for all three types of manure storage and provided some indication of year-to-year variability.

The southern operation consisted of four finishing farms with pull-plug manure collection emptying into four lagoons (WL1, WL2, WL3, and WL4). Each lagoon was sampled using a small boat at four locations within the lagoon. Two operations in northern Nebraska were sampled. The first northern operation utilized four deep pits beneath the production houses (LP1, LP2, LP3, and LP4) and a pull plug shallow pit that pumps manure into an above ground storage tank (LT1). The second northern operation used another shallow pull plug pit that pumps manure into an above ground storage tank (LT2). The remaining two operations in central Nebraska utilize above ground manure storage (FT1 and FT2). In each manure storage (pit, lagoon, or above-ground), surface liquid was collected along with solids and liquid at the bottom using a sediment sampler at four locations and pooled for that particular storage in order to minimize variation within the manure storage. Each manure storage site had unique characteristics that could impact odor production and emission. The manure inputs and management are detailed for each site in Table 1.

Table 1. Description of study sites.				
Storage Structure	Annual manure inputs to the storage system	Diet	Exposed manure surface area (meters^2)	Manure application
Lagoon—WL1	500 Sows 3000 Finishers	Corn/soybean	10,300	Center pivot
WL2	8800 Nursery 5400 Finishers	Corn/soybean	4100	Center pivot
WL3	3300 Finishers	Corn/soybean	4000	Flood irrigate
WL4	Second stage of WL3	Corn/soybean	7300	Flood irrigate
Pit—LP1	4000 Feeder to Finish	Corn/soybean	1400	Knifed in
LP2	500 Wean to Finish	Corn/soybean	2000	Knifed in
LP3	500 Wean to Finish	Corn/soybean	2000	Knifed in
LP4	500 Wean to Finish	Corn/soybean	2000	Knifed in
Slurry Tank—LT1	4800 Wean to Finish	Corn/soybean	740	Knifed in
LT2	5000 Wean to Finish	Corn/soybean	280	Knifed in
FT1	200 Sows, 12 Boars, 3800 Nursery	Corn/soybean with some dry distillers	280	Surface application to aerated soil
FT2	50 Sows/gilts	Corn/soybean with some dry distillers	280	Surface application to aerated soil

Manure Sampling—After testing and evaluating a variety of liquid samplers and talking with swine operation managers, we determined that existing sampling technology was inadequate for sampling swine manure at specific depths. Existing samplers either clogged easily, were not long enough to reach the bottom of a tank or lagoon, or the samples collected were not specific to a particular depth interval. Hence, two manure slurry samplers were devised, tested, and refined over the first few months of the study. The first sampler utilized a PVC capsule that was mechanically opened when the sampler reached the appropriate depth (Figure 1).


Figure 1. Pit slurry sampler used to collect slurry from deep pit swine operations. The sampler is lowered to depth and a rod is pulled that opens the sampler. The rod is connected to the cap and goes through the PVC capsule to a rubber stopper in the bottom of the PVC capsule. Manure enters through the bottom and top. Once full the sampler is closed by pushing the rod.

Initial sampling at the lagoon surface and pits proved easiest with this sampler, but the sampler design needed major modification to easily collect a sample from the bottom of a large slurry tank or lagoon. A second sampler, which utilizes the same general sample capsule, was devised (Figure 2) where the capsule is lowered by cable to depth, and a pneumatic mechanism opens and closes the sample container. Additional weight was added to the sampler in order to sample solids at the bottom of the lagoon or tank.

Figure 2. Pneumatic sampler for sampling above ground slurry tanks and the bottom of lagoons. The unit is lowered into the tank from the top/surface by rope (clipped to the weight). The weight allows the sampler to settle through the solids to the bottom. Once at the desired depth, water is forced down the hose and into a syringe inside the PVC sample container. As the syringe fills with water, the end cap is forced open and manure slurry enters the PVC capsule. The water is withdrawn (closing the end cap) and the unit is pulled back up to the top of the tank. Springs attached to the cap and side help to close the container.

***Manure Slurry/Wastewater Characterization*—**Manure temperature was determined at the site and varied greatest for the outdoor sites. Temperatures of samples from the lagoons, pits, and tanks varied from 3 to 30.6, 5 to 41, and 5 to 30°C, respectively. Several other manure slurry properties [five-day biological oxygen demand (BOD_5), pH, total solids, volatile solids, KCl-extraction for ammonia, and alkali drying for non ammonia nitrogen (NAN)] were determined within 24 hours of sampling, since they may change during storage (-20°C). Since chemical oxygen demand (COD), elemental composition (total N, C, and P), and odor compound composition and concentration do not change (or change very little) with storage, those analyses and soil incubations were conducted at the end of the sample collection in order to ensure extraction and incubation conditions were uniform. All analyses were conducted using standard methods for wastewater or soil analysis modified as necessary for manure slurry analysis.

***Odor Compound Content and Relative Storage Structure Emission*—**Odor compound content in all manure slurries/wastewater samples was determined directly in the liquid fraction. Originally, ether extraction was planned with several internal standards to account for variable extraction efficiency. Since the odor compounds were measured directly, only a single internal standard (ethylbutyrate) to account for

injection volume differences was utilized. Odor compounds (ethanol, propanol, butanol, isobutanol, acetate, propionate, butyrate, isobutyrate, valerate, isovalerate, hexanoate, and isohexanoate, phenol, para-cresol, 4-ethyl phenol, indole, and methyl indole were analyzed and detected using gas chromatography and flame ionization methods as previously described (Miller and Varel, 2003). The relative emission of odor compounds from surface samples was determined using a dynamic flux chamber/solid phase microextraction system as previously described (Miller and Woodbury, 2006). Briefly, VOC emitted from the surface of a manure sample in the controlled environment of the chamber (temperature, humidity, flow rate), were swept out the chamber, and a portion was captured on an exposed SPME fiber (carboxen/polydimethyl siloxane) for a 5 min period of time. The captured volatiles were then analyzed by gas chromatography using the same temperature and flow program used to separate odor compounds in the manure extract samples. Relative comparisons of flux were then made based upon peak area.

***Slurry/Wastewater Application to Soil*—**A series of soil columns was used to evaluate odor emissions from soils immediately after slurry/wastewater application to crop land. The volumes of stored manure slurry/wastewater samples were first measured, and the samples from each site were then combined to form a seasonal composite for a particular manure storage site. Since samples were collected over 18 months, two spring composites (2007 and 2008) were made. As mentioned earlier, no winter samples were available from the LT1 and LT2 sites, thus a total of 58 composites were made. The ammonia content was calculated for each composite, and an application rate equivalent to 175 pounds N per acre (typical for corn production) was calculated for a 6-inch diameter soil column. Application rates calculated to exceed a 1 inch of slurry/wastewater were reduced to a 1 inch rate in order to better conform to industry center pivot wastewater practices (a single application exceeding 1 inch is discouraged due to an enhanced runoff potential). Soil columns were constructed of a 15-inch length of 6-inch diameter PVC pipe with landscaping fabric affixed to the bottom of the column. The columns were initially loaded to an 8 inch height with top soil (Tomic, fine, smectitic, mesic pachic argiudoll; pH = 7.05; Moisture content = 0.23 g/g dry soil; Organic matter content = 61.7 mg/g dry soil). Manure slurry was applied, and an additional 6 inches of soil was immediately placed on the slurry, if a subsurface application mimicking knife or other subsurface injection was appropriate (i.e., slurry from a deep pit). For other samples (lagoon wastewater) where surface application is the norm, the manure slurry was applied to soil filling the column to a 14 inch depth (soil depth and flux chamber volumes would be equivalent regardless of subsurface or surface manure application). An end cap equipped with two ¼ inch Swagelok fittings was placed on the top of the soil column, and air was supplied at a rate of 400 mL per minute to each of the columns through one of the ports. A branched house vacuum line was used to remove air at the same rate from the columns using the other port. The relative emission of odor compounds was determined as described above using a modified PVC end cap equipped with a small computer fan to mix the air above the soil column and two Swagelok ports (one for air entry and one with a three-way connection to allow a SPME fiber to access the air stream leaving the column). SPME fibers were exposed for a 10 minute period. Air leaving the soil column was sampled three to four times immediately after application and then at several hour intervals over the next few days until the odor profile was indistinguishable from the soil background. All seasonal composites were evaluated by surface application, but only a limited number of pit and tank samples were evaluated in a subsurface manor due to the lack of odor emissions during the subsurface experiments (see Results and Discussion).

***Statistical Analyses*—**Standard ANOVA and repeated ANOVA was used to assess differences between manure storage types and individual sites. To assess changes in odor compound content or emission with season, concentrations were first normalized to their annual average and then analyzed by ANOVA.

VII. Results

Objective #1: Determine the changes in odor compound content and composition of manure in swine manure storage systems over the course of a year (predominantly finisher) in multiple above ground, deep pits, and lagoon manure storage systems.

Manure Composition

An initial step in data analysis was to calculate averages for manure constituent and odor compound and compare those averages across the three types of manure storage. Although the range of values observed was quite large and overlapped between manure-holding structures, significant differences were observed between average concentrations (Table 2).

Table 2. Averages (in bold) for manure constituents in each type of manure-holding structure and the ranges of values observed (in parentheses).

	Lagoon	Pit	Tank
BOD_5, mg/L	**1272**[a] (32 – 7012)	**14,016**[b] (1247 – 81033)	**7246**[c] (128 – 48,588)
COD, mg/L	**7996**[a] (80 – 93,477)	**63,852**[b] (768 – 579,898)	**34,259**[c] (384 – 109,200)
pH	**7.87**[a] (7.01 – 9.73)	**7.90**[a] (6.79 – 8.72)	**7.58**[b] (6.40 – 8.73)
Electrical Conductivity (EC), μS/cm	**5.84**[a] (0.87 – 14.5)	**25.42**[b] (2.40 – 40.2)	**13.87**[c] (4.72 – 39.8)
Total Suspended Solids (TSS), g/L	**14.86**[a] (0.73 – 111.0)	**60.26**[b] (10.53 – 163.9)	**34.20**[c] (2.0 – 239.2)
Volatile Suspended Solids (VSS), g/L	**6.62**[a] (0 – 39.1)	**37.93**[b] (4.84 – 117.53)	**17.74**[c] (0.61 – 113.75)
NH_3-N, g/L	**0.49**[a] (0 - 2.28)	**5.28**[b] (1.88 – 16.88)	**1.96**[c] (0.05 – 5.61)
Non-ammonia N, g/L	**0.46**[a] (0.0 – 2.75)	**1.31**[b] (0.05 – 18.70)	**0.64**[a] (0.0 – 5.47)
Total N, g/L	**0.72**[a] (0.0 – 4.37)	**6.60**[b] (2.17 – 23.79)	**2.61**[c] (0.18 – 8.27)
Starch, μmoles glucose/g dry solids	**1.33**[a] (0 – 20.6)	**2.56**[b] (0 – 11.51)	**1.72**[ab] (0 – 28.5)
Total C, % (g/100 g dry solids)	**16.45**[a] (2.21 – 29.16)	**31.63**[b] (17.15 – 217.78)	**21.94**[a] (8.24 – 39.97)
Total P, mg/L slurry	**123.0**[a] (7.1 – 1211.8)	**797.9**[b] (86.9 – 2873.4)	**554.9**[c] (5.65 – 4167.7)
Odor Compounds			
Ethanol, μmoles/L	**0.58**[a] (0 – 49.68)	**3.93**[a] (0 – 46.88)	**16.54**[b] (0 – 126.25)
Acetate, mmoles/L	**3.34**[a] (0 – 33.7)	**13.59**[b] (0.23 – 64.41)	**26.17**[c] (0.02 – 116.98)
Propionate, mmoles/L	**1.01**[a] (0 – 9.81)	**4.73**[b] (0 – 20.52)	**7.61**[c] (0 – 34.12)
Isobutyrate, mmoles/L	**0.34**[a] (0 – 1.64)	**1.27**[b] (0 – 4.45)	**1.71**[b] (0 – 6.65)
Butyrate, mmoles/L	**0.77**[a]	**2.60**[a]	**6.97**[b]

	(0 – 8.04)	(0 – 13.92)	(0 – 73.15)
Isovalerate, mmoles/L	**0.41**[a] (0 – 1.95)	**1.69**[b] (0 – 5.42)	**2.24**[b] (0 – 7.63)
Valerate, mmoles/L	**0.22**[a] (0 – 1.23)	**0.46**[a] (0 – 1.17)	**1.74**[b] (0 – 7.03)
Isohexanoate, mmoles/L	**0.15**[a] (0 – 0.53)	**0.34**[b] (0 – 0.64)	**0.32**[b] (0 – 0.67)
Hexanoate, mmoles/L	**0.02**[a] (0 – 0.39)	**0.05**[a] (0 – 0.05)	**1.31**[b] (0 – 6.61)
Heptanoate, mmoles/L	**0.06**[a] (0 – 0.57)	**0.14**[a] (0 – 0.58)	**0.33**[b] (0 – 1.05)
Octanoate, mmoles/L	**0.06**[a] (0 – 0.62)	**0.21**[b] (0 – 0.68)	**0.25**[b] (0 – 0.67)
Total Volatile Fatty Acid, mg/L	**74.4**[a] (0 – 4083)	**184.5**[b] (56 – 7593)	**458.0**[c] (2 – 18841)
Phenol, μmoles/L	**37.7**[a] (0 – 152.9)	**96.6**[b] (0 – 337.9)	**108.5**[b] (0 – 322.9)
p-Cresol, μmoles/L	**202.8**[a] (0 – 715.3)	**588.0**[b] (0 – 1314.5)	**636.3**[b] (0 – 1481.0)
4-Ethyl Phenol, μmoles/L	**54.4**[a] (0 – 185.8)	**144.6**[b] (0 – 264.7)	**151.1**[b] (0 – 853.2)
Indole, μmoles/L	**0.06**[a] (0 – 3.47)	**0**[a] (0 – 0)	**0**[a] (0 – 0)
Skatole, μmoles/L	**0**[a] (0 – 0)	**23.7**[b] (0 -252.7)	**41.5**[b] (0 – 259.4)
Total Aromatics, mg/L	**32.1**[a] (0 – 110.4)	**93.4**[b] (0 -200.6)	**102.9**[b] (0 – 322.1)

[abc]Storage structures with differing superscripts are significantly different ($P < 0.05$).

Taking a broad look at the pooled data, manure samples from pits had the greatest concentrations of solids and nutrients, followed by slurry tank manure, and finally lagoons. Compared to the odor compounds dissolved in the manure slurry, the tank and pits are flipped with tank samples having the greatest odor compound concentrations, closely followed by pits, and then lagoon samples. For the volatile fatty acids, acetate, propionate, and butyrate were the most abundant for all samples. For the aromatic compounds, p-cresol was the dominant compound, but it was roughly 50 times lower in concentration compared to acetate. Another interesting feature is that lagoon and pit samples had similar concentrations of odor compounds that largely originate from carbohydrate fermentation (ethanol, acetate, propionate, butyrate, valerate, hexanoate, and heptanoate) with octanoate as the sole exception to this trend. On the other hand, pits and tanks had similar concentrations of odor compounds that originate from protein fermentation (isobutyrate, isovalerate, isohexanoate, phenol, p-cresol, 4-ethyl phenol, and skatole). No differences were observed for indole which was generally not detected in the manure slurries.

After observing the large range of data values, one possible explanation would be that one of the four structures (replicates) within a particular type of manure-holding structure could be an outlier. Not all replicates within manure structure type were managed identically. Based upon interviews with the cooperating producers, we assumed that there would be differences in manure and water inputs between individual structures. In order to identify any particular outliers within a particular structure type, the data was analyzed by structure type. Tables 3, 4, and 5 report the averages for each manure storage segregated based upon the type of structure.

Table 3. Average concentration of manure constituents for individual lagoons.				
	WL1	WL2	WL3	WL4
BOD_5, mg/L	1623[a]	2123[a]	934[ab]	314[b]
COD, mg/L	6635[ab]	14,295[a]	8308[ab]	2221[b]
pH	7.61[a]	8.05[b]	7.86[ab]	7.92[ab]
Electrical Conductivity (EC), μS/cm	2.11[a]	11.47[b]	5.32[c]	3.98[d]
Total Suspended Solids (TSS), g/L	13.71[ab]	25.78[a]	15.19[ab]	3.85[b]
Volatile Suspended Solids (VSS), g/L	5.30[a]	12.31[b]	6.94[abc]	1.44[ac]
NH_3-N, g/L	0.19[a]	0.94[b]	0.50[c]	0.29[ac]
Non-ammonia N, g/L	0.30[a]	0.92[b]	0.52[ab]	0.04[a]
Total N, g/L	0.34[a]	1.40[b]	0.76[a]	0.31[a]
Starch, μmoles glucose/g dry solids	1.24[a]	2.87[a]	0.78[a]	0.31[a]
Total C, % (g/100 g dry solids)	14.1[ab]	23.8[c]	16.8[a]	9.9[b]
Total P, mg/L	45[a]	297[b]	123[a]	26[a]
Odor Compounds				
Ethanol, μmoles/L	0[a]	2.07[a]	0[a]	0[a]
Acetate, mmoles/L	0.74[a]	8.21[b]	2.44[a]	1.20[a]
Propionate, mmoles/L	0.28[a]	2.47[b]	0.70[a]	0.38[a]
Isobutyrate, mmoles/L	0.19[a]	0.55[b]	0.31[ab]	0.28[a]
Butyrate, mmoles/L	0.41[a]	1.40[b]	0.71[ab]	0.49[a]
Isovalerate, mmoles/L	0.21[a]	0.69[b]	0.42[ab]	0.31[a]
Valerate, mmoles/L	0.09[a]	0.38[b]	0.21[ab]	0.17[ab]
Isohexanoate, mmoles/L	0.12[a]	0.23[a]	0.16[a]	0.08[a]
Hexanoate, μmoles/L	1.5[a]	68.6[b]	20.8[a]	6.1[a]
Heptanoate, μmoles/L	0[a]	172.7[b]	65.3[ab]	0[a]
Octanoate, μmoles /L	0[a]	155.8[b]	66.4[ab]	0[a]
Total Volatile Fatty Acid, mg/L	162.6[a]	1037.1[b]	391.4[a]	227.4[a]
Phenol, μmoles/L	7.5[a]	68.7[b]	49.7[ab]	21.5[a]
p-Cresol, μmoles/L	78.8[a]	337.0[b]	216.0[ab]	162.0[ab]
4-Ethyl Phenol, μmoles/L	39.6[a]	102.1[b]	55.2[ab]	13.3[ab]
Indole, μmoles/L	0.1[a]	0[a]	0.1[a]	0[a]
Skatole, μmoles/L	0[a]	0[a]	0[a]	0[a]
Total Aromatics, mg/L	14.1[a]	55.4[b]	34.8[ab]	21.1[a]

Table 4. Average concentration of manure constituents for individual deep pits.				
	LP1	LP2	LP3	LP4
BOD_5, mg/L	40355[a]	5576[b]	7287[b]	2847[b]
COD, mg/L	119961[a]	50849[b]	50211[b]	34385[b]
pH	7.68[a]	7.96[b]	8.01[b]	7.95[b]
Electrical Conductivity (EC), μS/cm	31.8[a]	23.2[b]	25.8[bc]	20.8[c]
Total Suspended Solids (TSS), g/L	88.5[a]	55.5[b]	55.3[b]	41.7[b]
Volatile Suspended Solids (VSS), g/L	59.8[a]	34.3[b]	33.3[b]	24.2[b]
NH3-N, g/L	7.6[a]	4.4[b]	5.4[b]	3.7[b]
Non-ammonia N, g/L	2.0[a]	1.2[ab]	1.1[ab]	0.9[b]
Total N, g/L	9.6[a]	5.6[b]	6.5[b]	4.6[b]
Starch, μmoles glucose/g dry solids	3.0[a]	2.2[a]	2.3[a]	2.7[a]
Total C, % (g/100 g dry solids)	41.0[a]	30.5[ab]	29.6[b]	25.4[b]
Total P, mg/L	1324[a]	706[b]	665[b]	489[b]
Odor Compounds				
Ethanol, μmoles/L	15.5[a]	0[b]	0[b]	0[b]
Acetate, mmoles/L	41.07[a]	5.07[b]	4.93[b]	2.72[b]
Propionate, mmoles/L	12.99[a]	2.24[b]	2.57[b]	0.95[c]
Isobutyrate, mmoles/L	3.65[a]	0.56[b]	0.51[bc]	0.32[c]
Butyrate, mmoles/L	7.92[a]	0.94[b]	0.88[b]	0.54[b]
Isovalerate, mmoles/L	4.45[a]	0.87[b]	0.91[b]	0.49[c]
Valerate, mmoles/L	0.97[a]	0.38[b]	0.30[b]	0.16[c]
Isohexanoate, mmoles/L	0.60[a]	0.33[b]	0.30[b]	0.12[c]
Hexanoate, μmoles/L	152.7[a]	9.5[b]	26.5[b]	1.1[b]
Heptanoate, μmoles/L	538.2[a]	0[b]	33.3[b]	0[b]
Octanoate, μmoles /L	612.6[a]	109.0[b]	112.5[b]	0[b]
Total Volatile Fatty Acid, mg/L	5247.5[a]	785.1[b]	790.9[b]	390.4[b]
Phenol, μmoles/L	9.5[a]	10.4[b]	11.5[b]	6.9[c]
p-Cresol, μmoles/L	954.9[a]	608.8[b]	492.5[b]	284.0[c]
4-Ethyl Phenol, μmoles/L	217.4[a]	151.1[b]	131.6[b]	75.9[c]
Indole, μmoles/L	0[a]	0[a]	0[a]	0[a]
Skatole, μmoles/L	91.0[a]	0[b]	2.3[b]	0[b]
Total Aromatics, mg/L	161.6[a]	93.0[b]	75.9[b]	41.1[c]

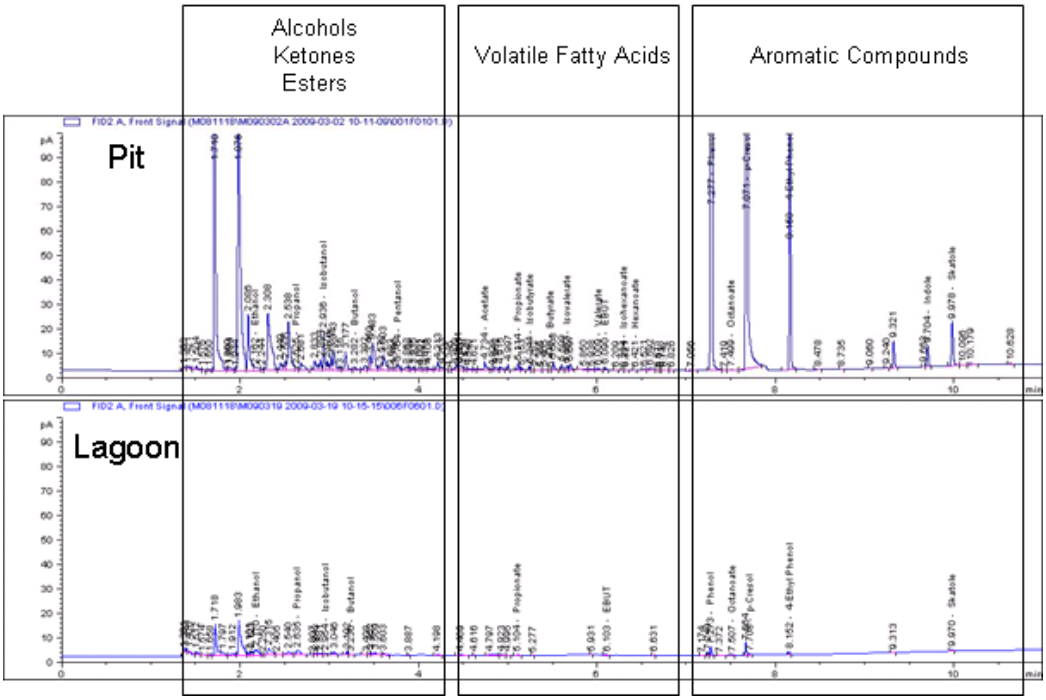
Table 5. Average concentration of manure constituents for individual slurry tanks.				
	LT1	LT2	FT1	FT2
BOD_5, mg/L	27141[a]	3734[b]	405[b]	2173[b]
COD, mg/L	48223[a]	32748[a]	15748[b]	41498[a]
pH	6.90[a]	7.94[b]	7.67[b]	7.81[b]
Electrical Conductivity (EC), μS/cm	18.4[a]	21.8[b]	8.2[c]	9.3[c]
Total Suspended Solids (TSS), g/L	35.8[ab]	43.3[a]	13.1[b]	46.1[a]
Volatile Suspended Solids (VSS), g/L	19.2[ab]	22.4[a]	6.6[b]	23.6[a]
NH_3-N, g/L	2.6[a]	2.9[a]	1.4[b]	1.2[b]
Non-ammonia N, g/L	0.5[ab]	0.9[ab]	0.2[a]	1.0[b]
Total N, g/L	3.1[ab]	3.8[a]	1.6[c]	2.2[bc]
Starch, μmoles glucose/g dry solids	1.9[a]	2.3[a]	1.1[a]	1.7[a]
Total C, % (g/100 g dry solids)	29.9[a]	25.3[a]	15.6[b]	18.8[b]
Total P, mg/L	424[a]	595[a]	352[a]	819[a]
Odor Compounds				
Ethanol, μmoles/L	45.62[a]	10.54[b]	5.50[b]	7.18[b]
Acetate, mmoles/L	69.34[a]	26.48[b]	10.76[c]	4.23[c]
Propionate, mmoles/L	18.88[a]	8.39[b]	2.85[c]	2.06[c]
Isobutyrate, mmoles/L	4.32[a]	1.75[b]	0.64[c]	0.49[c]
Butyrate, mmoles/L	3.55[a]	1.95[b]	0.75[b]	0.10[b]
Isovalerate, mmoles/L	5.50[a]	2.45[b]	0.86[c]	0.66[c]
Valerate, mmoles/L	5.17[a]	1.20[b]	0.59[b]	0.35[b]
Isohexanoate, mmoles/L	0.62[a]	0.28[b]	0.21[b]	0.21[b]
Hexanoate, μmoles/L	4606.4[a]	656.2[b]	270.2[b]	12.7[b]
Heptanoate, μmoles/L	881.6[a]	279.1[b]	222.1[b]	0[c]
Octanoate, μmoles /L	620.8[a]	247.0[b]	199.9[b]	0[c]
Total Volatile Fatty Acid, mg/L	9718.1[a]	3362.1[b]	1385.8[c]	649.3[c]
Phenol, μmoles/L	220.7[a]	116.1[b]	66.3[bc]	48.5[c]
p-Cresol, μmoles/L	1193.3[a]	752.7[b]	433.1[c]	271.0[c]
4-Ethyl Phenol, μmoles/L	272.2[a]	226.3[a]	78.4[b]	60.7[b]
Indole, μmoles/L	0[a]	0[a]	0[a]	0[a]
Skatole, μmoles/L	97.4[a]	46.6[ab]	31.6[b]	0[b]
Total Aromatics, mg/L	195.8[a]	126.1[b]	66.8[bc]	41.3[c]

Three of the manure storage sites, WL2, LP1, and LT1, appear to be substantially different from the others within their respective groups based upon differences in their manure composition (Table 3, 4, and 5). For WL2, a number of constituents (EC, VSS, NH_3, total N, total C, and total P) are significantly greater than the other lagoons studied and indicate that the manure content is greater than the other lagoons. The content of a number of odor compound are also greater than WL1 but did not differ with WL3 and WL4. The same is true for LP1—all constituents are significantly greater than the other pits except for starch and total C. All odor compounds, except indole were also greater than the other pit samples. For LT1, the manure constituents were also generally greater, but it was not as clear cut as the other two cases. However the case is stronger when odor compounds were considered—13 of 16 odor compounds were greater than the other three slurry tanks. Differences within manure storage site indicate that other factors such as management have a major impact on manure composition and odor compound content. Two samples were collected at each sample site, one from the surface and one from the bottom. As expected, some constituents differed considerably between the surface and bottom, but the common thread was their relationship to the solids in the manure.

Slurry Emissions

The relative emission of odor compounds was compared between all samples by using the dynamic flux chamber and solid phase microextraction (SPME) fibers to capture any volatiles emitted from the slurry. A set of typical odor emission chromatograms (fingerprints) obtained using the flux chamber and SPME technique is depicted in Figure 3. A number of very volatile peaks that elute early (1.5 to 4 minutes) during analysis were often observed. In earlier studies utilizing mass spectroscopy, these peaks were identified as alcohols, ketones, and esters (Miller and Woodbury, 2006). Normally these peaks would be undetectable when directly analyzing manure slurry since the solvent (water, alcohol, or ether) would elute at the same time and mask these peaks. Since the same gas chromatography conditions were used for both the SPME and for odor compound concentrations dissolved in the manure, the standard curves developed for the liquid samples could be used to determine the amount of those same odor compounds captured by the SPME fiber during the emission experiments. Unfortunately for a few of the

Figure 3. Typical odor compound emission profiles from a pit and a lagoon sample.



very volatile early peaks, no liquid standards were available, since those peaks eluted with the solvent peak (water or ether). A general comparison (total VOC) that included these early peaks was possible if butanol was used as a reference for every peak. Since volatiles were present in negative control (no manure) blanks at background levels, the amounts of those volatiles in the blanks was subtracted from manure samples prior to statistical analysis.

For the three types of manure storage structures, individual amounts of emitted odor compound varied between the systems (Table 6). For all structures, ethanol was the principal alcohol, and p-cresol was the dominant aromatic compound. There was no consistently dominant VFA for all three manure storage systems. Comparing the three classes of odor compounds to each other, the principal group of odor compounds emitted, by far, was the aromatic ring containing compounds (phenol, p-cresol, 4-ethyl phenol, indole, and skatole). However, there is a large discrepancy between the total VOC and the sum of identified odorants. Clearly, substantial quantities of very volatile compounds (alcohols, ketones, and esters) were not specifically monitored odor compounds (see proceeding paragraph).

Table 6. Relative emission of odor compounds (nanograms captured by the fiber) and total organic compounds (butanol equivalent) from the stored manure surface determined using the dynamic flux chamber and SPME fiber technique.

	Lagoon	Pit	Tank
Alcohols			
Ethanol	0.35^{a}	2.08^{b}	1.56^{ab}
Propanol	2.09^{a}	1.14^{a}	0.93^{a}
Isobutanol	0.72^{a}	0.64^{a}	0.07^{a}
Butanol	0.09^{ab}	0.10^{a}	0^{b}
Pentanol	0.01^{a}	0.52^{b}	0.24^{c}
Volatile Fatty Acids			
Acetate	0.09^{a}	0.43^{a}	0.32^{a}
Propionate	0.04^{a}	0.44^{ab}	0.81^{b}
Isobutyrate	0^{a}	0.29^{ab}	0.53^{b}
Butyrate	0^{a}	0.15^{ab}	0.38^{b}
Isovalerate	0^{a}	0.99^{b}	0.55^{c}
Valerate	0^{a}	0.03^{a}	0.40^{b}
Hexanoate	0^{a}	0.04^{a}	0.32^{a}
Octanoate	0.62^{a}	0^{b}	0^{b}
Aromatics			
Phenol	0.40^{a}	7.00^{b}	4.09^{ab}
p-Cresol	1.44^{a}	29.83^{b}	14.91^{c}
4-Ethyl Phenol	0.51^{a}	2.71^{b}	1.27^{a}
Indole	0^{a}	0.51^{b}	0^{a}
Skatole	0.42^{a}	1.02^{b}	1.15^{b}
Summary			
Total Alcohols	3.26^{a}	4.49^{a}	2.81^{a}
Total Volatile Fatty Acid	0.76^{a}	2.36^{ab}	3.32^{b}
Total Aromatics	2.77^{a}	41.06^{b}	21.42^{c}
Total Volatile Organic Compounds, butanol equivalent	8.70^{a}	121.41^{b}	80.51^{b}

A significant effect of structure on an odor compound or group of odor compounds is denoted by a blue font. Storage structures with differing superscripts are significantly different ($P < 0.05$).

As previously observed for dissolved manure constituents, the amount of odor compound captured by the fiber (relative emission) varied within the same manure structure (Table 7, 8, 9). For lagoons, the only significant differences observed between individual sites was that WL2 and WL3 had higher relative emissions of either p-cresol or skatole compared to WL1 or WL4. Since these differences in odor emissions were relatively small, all four lagoon sites were used to investigate seasonal emission differences.

Table 7. Relative Lagoon Emissions—Odor compounds (nanograms captured by the fiber) and total organic compounds (butanol equivalent) from slurry/wastewater samples collected at the surface determined using the dynamic flux chamber and SPME fiber technique.

	WL1	WL2	WL3	WL4
Alcohols				
Ethanol	0.26[a]	0.47[a]	0.30[a]	0.36[a]
Propanol	0.04[a]	1.32[a]	6.18[a]	1.21[a]
Isobutanol	0[a]	0[a]	3.15[a]	0[a]
Butanol	0.06[a]	0.10[a]	0.05[a]	0.16[a]
Pentanol	0[a]	0.03[a]	0[a]	0[a]
Volatile Fatty Acids				
Acetate	0.18[a]	0.16[a]	0[a]	0[a]
Propionate	0.18[a]	0[a]	0[a]	0[a]
Isobutyrate	0[a]	0[a]	0[a]	0[a]
Butyrate	0[a]	0[a]	0[a]	0[a]
Isovalerate	0[a]	0[a]	0[a]	0[a]
Valerate	0[a]	0[a]	0[a]	0[a]
Hexanoate	0[a]	0[a]	0[a]	0[a]
Octanoate	0.71[a]	0.65[a]	0.76[a]	0.39[a]
Aromatics				
Phenol	0.07[a]	0.64[a]	0.57[a]	0.32[a]
p-Cresol	0.62[a]	2.91[b]	1.21[ab]	0.86[a]
4-Ethyl Phenol	0.24[a]	0.66[a]	0.66[a]	0.48[a]
Indole	0[a]	0[a]	0[a]	0[a]
Skatole	0[a]	0.67[ab]	0.88[b]	0.13[a]
Summary				
Total Alcohols	0.36[a]	1.93[a]	9.69[a]	1.73[a]
Total Volatile Fatty Acid	1.07[a]	0.81[a]	0.76[a]	0.39[a]
Total Aromatics	0.93[a]	4.89[b]	3.32[ab]	1.79[ab]
Total Volatile Organic Compounds, butanol equivalent	2.61[a]	13.12[a]	13.84[a]	5.29[a]

A significant effect of site on an odor compound or group of odor compounds is denoted by a blue font. Storage structures with differing superscripts are significantly different ($P < 0.05$).

Table 8. Relative Pit Emissions—Odor compounds (nanograms captured by the fiber) and total organic compounds (butanol equivalent) from slurry samples collected at the manure surface determined using the dynamic flux chamber and SPME fiber technique.

	LP1	LP2	LP3	LP4
Alcohols				
Ethanol	1.86[a]	2.11[a]	2.62[a]	1.74[a]
Propanol	1.73[a]	1.24[a]	1.20[a]	0.39[a]
Isobutanol	0.87[a]	0.41[a]	0.68[a]	0.60[a]
Butanol	0.41[a]	0[b]	0[b]	0[b]
Pentanol	0.48[a]	0.51[a]	0.53[a]	0.57[a]
Volatile Fatty Acids				
Acetate	0.39[a]	0.51[a]	0.50[a]	0.31[a]
Propionate	1.06[a]	0.23[a]	0.22[a]	0.25[a]
Isobutyrate	0.63[a]	0.18[a]	0.16[a]	0.18[a]
Butyrate	0.42[a]	0.06[a]	0.05[a]	0.06[a]
Isovalerate	2.15[a]	0.90[b]	0.64[b]	0.26[b]
Valerate	0.13[a]	0[a]	0[a]	0[a]
Hexanoate	0.17[a]	0[a]	0[a]	0[a]
Octanoate	0[a]	0[a]	0[a]	0[a]
Aromatics				
Phenol	22.17[a]	2.49[b]	1.94[b]	1.39[b]
p-Cresol	70.74[a]	25.89[b]	16.79[b]	5.91[b]
4-Ethyl Phenol	4.79[a]	2.59[b]	2.23[b]	1.22[b]
Indole	1.58[a]	0.27[b]	0.11[b]	0.06[b]
Skatole	1.42[a]	0.98[ab]	0.94[ab]	0.73[b]
Summary				
Total Alcohols	5.34[a]	4.28[a]	5.03[a]	3.30[a]
Total Volatile Fatty Acid	4.96[a]	1.87[b]	1.57[b]	1.06[b]
Total Aromatics	100.71[a]	32.22[b]	22.00[b]	9.32[b]
Total Volatile Organic Compounds, butanol equivalent	269.14[a]	94.03[b]	78.66[b]	43.79[b]

A significant effect of site on an odor compound or group of odor compounds is denoted by a blue font. Storage structures with differing superscripts are significantly different ($P < 0.05$).

Relative emissions from the pit were broadly similar to lagoon emissions. Aromatics were the largest emission relative to the other identified odor groups (alcohols and volatile fatty acids), but a large amount of highly volatile emissions (alcohols, ketones, esters) were identified and contributed to the total VOC for each sample. Comparing the different pit sites with each other, LP1 emitted greater amounts of butanol, isovalerate, and all aromatic compounds compared to the other three sites. For this reason, it was omitted from the other pit samples for analysis of seasonal differences in emission.

Table 9. Relative Tank Emissions—Odor compounds (nanograms captured by the fiber) and total organic compounds (butanol equivalent) from slurry samples collected at the manure surface determined using the dynamic flux chamber and SPME fiber technique.

	LT1	LT2	FT1	FT2
Alcohols				
Ethanol	0.65[a]	1.01[a]	0.84[a]	3.49[a]
Propanol	0.61[a]	0.42[a]	1.18[a]	1.39[a]
Isobutanol	0[a]	0.29[a]	0.03[a]	0[a]
Butanol	0[a]	0[a]	0[a]	0[a]
Pentanol	0.24[a]	0.63[b]	0.16[a]	0[a]
Volatile Fatty Acids				
Acetate	1.36[a]	0.05[b]	0[b]	0[b]
Propionate	2.79[a]	0.57[b]	0[b]	0.18[b]
Isobutyrate	2.07[a]	0.26[b]	0[b]	0[b]
Butyrate	1.40[a]	0.28[b]	0[b]	0[b]
Isovalerate	1.33[a]	1.09[a]	0[b]	0[b]
Valerate	1.77[a]	0[b]	0[b]	0[b]
Hexanoate	1.12[a]	0.30[a]	0[a]	0[a]
Octanoate	0[a]	0[a]	0[a]	0[a]
Aromatics				
Phenol	8.32[a]	4.97[ab]	1.81[b]	2.13[b]
p-Cresol	36.59[a]	22.20[b]	3.97[c]	1.71[c]
4-Ethyl Phenol	2.03[a]	1.59[ab]	1.02[ab]	0.61[b]
Indole	0[a]	0.01[a]	0[a]	0[a]
Skatole	1.21[a]	1.17[a]	1.43[a]	0.79[a]
Summary				
Total Alcohols	1.50[a]	2.35[a]	2.20[a]	4.88[a]
Total Volatile Fatty Acid	11.84[a]	2.55[b]	0[b]	0.18[b]
Total Aromatics	48.15[a]	29.94[a]	8.23[b]	5.24[b]
Total Volatile Organic Compounds, butanol equivalent	174.6[a]	120.57[ab]	31.57[bc]	17.67[c]

A significant effect of site on an odor compound or group of odor compounds is denoted by a blue font. Storage structures with differing superscripts are significantly different ($P < 0.05$).

For the tank samples, the pattern of relative emission for the groups of compounds was similar to both lagoon and pit samples—aromatic compounds were proportionately greater than volatile fatty acids and alcohols. Examining differences in relative emissions between sites, one site (LT1) showed significantly higher relative emissions of volatile fatty acids and phenolic compounds compared to the other three sites. When analyzing the data set for seasonal emission differences, LT1 was omitted from the analysis of the other tank sites.

Seasonal Patterns

Identifying differences in manure composition through time was the major focus of this project. The relative emission of groups of odor compounds from the three types of swine manure storage (lagoons, pits, and tanks) is presented in Table 10.

Table 10. Seasonal Comparison of Relative Emission from the Three Manure Storage Types					
	Fall	Winter	Spring 07	Spring 08	Summer
Lagoons					
Total Alcohols	1.42^{a}	1.39^{a}	6.05^{a}	0.95^{a}	4.77^{a}
Total Volatile Fatty Acid	0^{a}	0^{a}	3.03^{b}	0^{a}	0^{a}
Total Aromatics	0.53^{a}	5.22^{b}	5.13^{b}	4.14^{b}	0.52^{a}
Total Volatile Organic Compounds, butanol equivalent	2.76^{a}	14.00^{a}	14.33^{a}	10.67^{a}	5.20^{a}
Pits (LP1 omitted)					
Total Alcohols	3.88^{ab}	5.61^{b}	4.88^{ab}	4.81^{ab}	1.69^{a}
Total Volatile Fatty Acid	1.84^{a}	1.86^{a}	1.00^{a}	1.68^{a}	0.87^{a}
Total Aromatics	12.39^{ab}	32.82^{a}	20.63^{ab}	33.11^{a}	4.62^{b}
Total Volatile Organic Compounds, butanol equivalent	50.38^{ab}	100.25^{c}	73.43^{abc}	97.23^{ac}	33.19^{b}
Tanks (LT1 omitted)					
Total Alcohols	0.52^{a}	7.12^{a}	3.50^{a}	3.73^{a}	3.66^{a}
Total Volatile Fatty Acid	1.76^{a}	1.08^{a}	0.95^{a}	0.54^{a}	0.31^{a}
Total Aromatics	3.75^{a}	8.19^{ab}	20.20^{ab}	40.44^{b}	8.23^{a}
Total Volatile Organic Compounds, butanol equivalent	11.74^{a}	43.84^{a}	104.54^{a}	106.03^{a}	33.63^{a}
A significant effect of season on an odor compound group is denoted by a blue font. Seasons with differing superscripts are significantly different ($P < 0.05$).					

All manure storage sites had at least one group of odor compounds that exhibited a seasonal difference in emission. For the lagoon sites, the relative emission of volatile fatty acids was higher in spring of 2007 and higher than spring 2008, which did not differ from the other seasons. The relative emission of aromatic compounds was also higher, but only during the winter and spring (both years). For the pit sites, alcohols were emitted higher in winter compared to summer with emissions during fall and spring in between the two extremes. Emissions of aromatic compounds from the pits were highest during winter and spring 2008 and lowest during summer. The intervening seasons emitted aromatics at rates between the two extremes. For the tank samples, only aromatics showed a seasonal effect—largest emissions were during the spring and lowest emissions during summer and fall. The most notable observation that could impact producers was the consistent higher emissions of aromatic compounds (the largest component emitted of the three groups of identified odor compounds) from manure slurry/wastewater surfaces during winter and spring for all three types of manure storage. In reality, the emissions from lagoons and tanks would be moderated by the low outdoor temperatures, but pit emissions of aromatic compounds would be expected to be greater in the winter and spring.

Objective #2: Characterize and compare the relative emission of volatile odor compounds by gas chromatography-mass spectroscopy from multiple simulated manure applications.

The same general pattern of odor compound emission through time was seen for nearly all samples when they were applied to the soil columns. A series of odor compound profiles for one sample illustrates the general pattern (Figure 5). In this example, the highly volatile compounds (HVC) alcohols, ketones, and esters were detected from 1.5 to 4 minutes into the analysis. As time progressed, the amount of the HVC collected on the fiber decreased drastically to near background levels within four hours. The next group of compounds, volatile fatty acids (VFA), was not regularly detected, but when they were, they would slowly disappear from the profile and were usually at background levels within 24 hours. During that period a few new HVC would appear (in this example the peak at 2.5 minutes), which may represent a break down product of the volatile fatty acid. The

last odor compound peaks to go were the aromatic compounds (phenol, p-cresol, 4-ethyl phenol, and skatole). Typically the aromatic compounds would linger for 48 hours or longer.

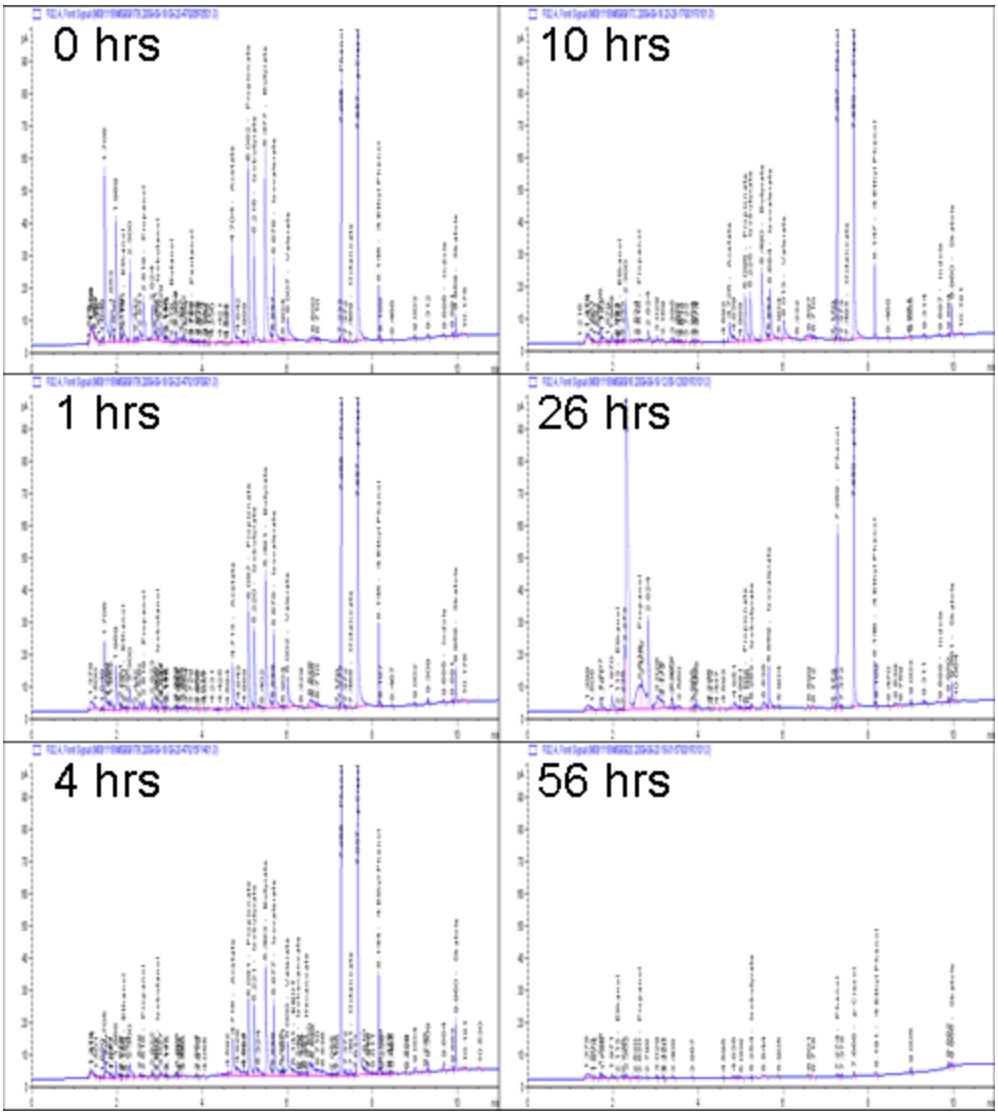
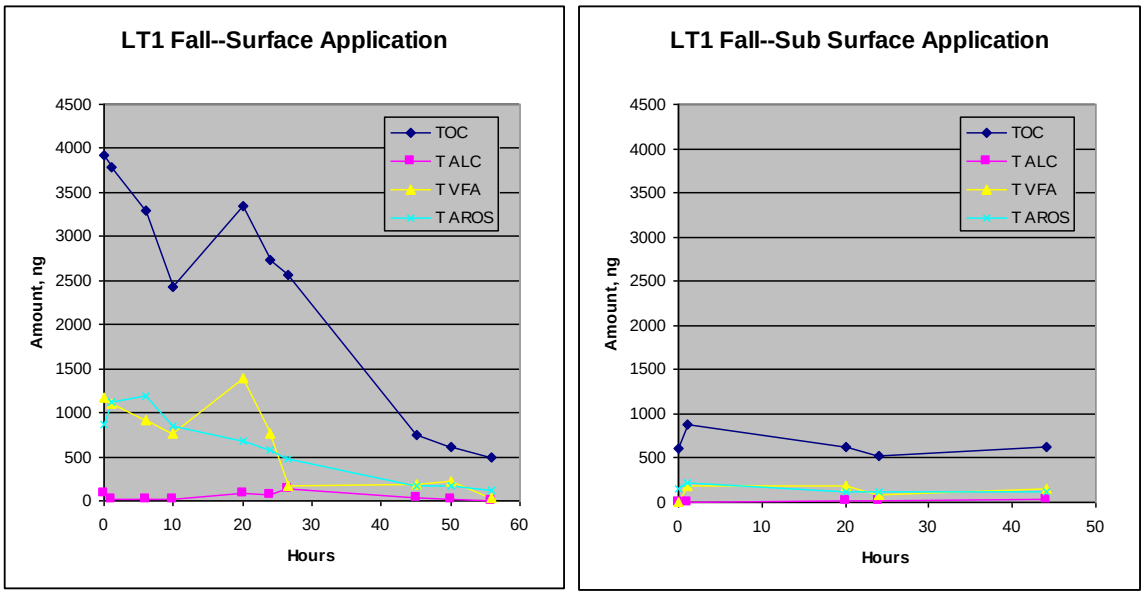


Figure 4. The odor compound profile for LT1 Fall composite surface applied over a period of two days.

By plotting the amount of odor compound for each group, interesting changes in odor compound emissions were observed (VFA), or if the change was linear (aromatics), rates of odor compound loss could be calculated. In the LT1 Fall example, the amount of VFA captured on the fiber was steadily dropping with time but suddenly increased 10 to 25 hours after slurry application. It is also reflected in total VOC, but the rate of total VOC detected declined at a similar rate before and after the event (140 and 100 ng/hr, respectively). Whether this is a result of the soil surface drying or a change in pH is unknown and will be investigated in future experiments. For the aromatics, there was a steady decline in the amount leaving the soil columns. The calculated rate of loss was 20.4 ng/hr.

Initial work with application of slurry (composited by season) to the soil columns examined both surface and subsurface (6" depth) applications. A comparison between surface and subsurface applied slurry is depicted in Figure 5. For all subsurface applications, emissions were comparable to soil only controls, whereas emissions of odor compounds were always detected from surface applied manure. Eight of the 58 seasonal composite samples were evaluated at both surface and subsurface applications. Those eight composites were selected from the samples indicated to have the greatest emissions based upon the flux chamber/SPME work (see above). All samples were evaluated using surface application even if the typical management practices indicate a subsurface application to conserve nutrients and decrease odor emissions.

Figure 5. Comparison of relative odor emission from LT1 slurry applied to soil on the surface and on the subsurface. TOC is the total volatile organic compounds detected using a butanol reference, T ALC was total alcohols, T VFA was total volatile fatty acids, and T AROS was total aromatic compounds.



Two comparisons were made in order to identify any seasonal differences for manure applications. The first comparison was to compare initial (T = 0) emissions based upon manure storage type and then by season for each type of structure. Differences were observed between the types of manure structure (Table 11), but the pattern was consistent with the earlier flux chamber/SPME findings in Table 6. When the data was examined by season, significant differences in emission were observed only in the lagoon samples (Table 12). Specifically, emissions of VFA during winter and spring (both 2007 and 2008) were greater than in the summer and fall. Emissions of aromatic compounds were greater in the spring 2007 samples compared to fall, and the emission of total VOC was greater for spring 2007 when compared to fall and spring 2008.

Table 11. Comparison of initial emissions during soil surface application			
	Lagoon	Pit	Tank
Total alcohols, ng	41.7[a]	121.8[b]	37.6[a]
Total volatile fatty acids, ng	20.9[a]	73.3[a]	224.3[b]
Total aromatic compounds, ng	47.8[a]	407.9[b]	310.9[b]
Total volatile organic compounds, ng	424.1[a]	1671.3[ab]	2114.9[b]

Table 12. Initial odor compound emissions from soil columns with seasonal composites of manure slurry					
	Fall	Winter	Spring 07	Spring 08	Summer
Lagoon					
Total Alcohols	15.8[a]	6.5[a]	71.6[a]	5.9[a]	108.5[a]
Total VFA	0[a]	34.8[b]	34.8[b]	34.8[b]	0[a]
Total aromatics	0[a]	60.2[ab]	96.7[b]	61.2[ab]	21.1[ab]
Total VOC	364.0[a]	447.9[ab]	646.1[b]	360.4[a]	413.7[ab]
Pit					
Total Alcohols	121.5[a]	161.7[a]	90.2[a]	65.4[a]	180.0[a]
Total VFA	46.1[a]	60.8[a]	133.7[a]	58.4[a]	64.1[a]
Total aromatics	450.7[a]	489.4[a]	581.8[a]	260.6[a]	277.6[a]
Total VOC	1783.4[a]	1540.2[a]	2050.8[a]	1386.1[a]	1540.2[a]
Tank					
Total Alcohols	39.2[a]	19.9[a]	38.8[a]	11.4[a]	69.8[a]
Total VFA	309.7[a]	56.3[a]	262.7[a]	97.1[a]	311.6[a]
Total aromatics	268.1[a]	79.1[a]	462.1[a]	289.8[a]	339.4[a]
Total VOC	1397.2[a]	738.6[a]	5192.8[a]	1055.6[a]	1502.3[a]

Another way to examine seasonal differences is to compare the length of time for emissions to return to background levels. A slurry application was deemed at background levels were both the total VOC and the total aromatics were less than 400 and 20 ng, respectively. In figure 5, that amount of time was close to 56 hours. Table 13 summarizes the data for slurry composites.

Table 13. Comparison of the number of hours needed for emissions to return to background levels after the application of seasonal slurry composites.					
Manure storage structure	Fall	Winter	Spring 2007	Spring 2008	Summer
WL1	0	1	22	2	1
WL2	1	21	1	23	22
WL3	0	0	22	23	0
WL4	0	1	2	2	0
LP1	48	28.5	45	48	46
LP2	48	28.5	45	48	46
LP3	48	25	45	48	25
LP4	48	19.5	45	31	46
LT1	56	No sample	26	26	24
LT2	45	No sample	30	30	19
FT1	1	26	24	24	1
FT2	2	26	24	1	24

A general observation of the time to reach background after application in Table 13 is that the pit and LT tank samples took much longer than the lagoon and FT tank samples to reach the background state. Some interesting patterns in the LP samples were that WL2 and WL3 (receiving the greatest annual manure inputs) took longer than the other two lagoons to reach background. For the tank samples the FT samples appeared to have much lower capacity to emit odor compounds through time compared to the LT samples. This was consistent with odor compound contents. Further analyses should help to clarify differences in how the soils metabolize or emit odor compounds in the slurries.

VIII. Discussion

A number of factors differed between types of manure storage, individual manure storages (within type), and even within individual manure storage by season. Preliminary statistical analysis indicates that there are some interesting differences between manure storage structures, with depth in structure, and with season. The differences in pH were minor, but could affect the amount of easily volatilized odorous fatty acids and ammonia. As expected, chemical oxygen demand (COD), total suspended solids (TSS) and volatile suspended solids (VSS) trends showed highest concentrations in the bottom samples, where most of the solids were located. Comparing the differences and ratios of COD, TSS, and VSS yields some clues to the nature of the manure solids, organic matter content, and indicates that ammonia concentrations are likely higher in some storage structures compared to other storage structures. Slurry samples having low VSS (lagoon surface) have solids in it that are largely mineralized and not likely to degrade further into odor compounds. Samples having a high COD and VSS (lagoon bottom, tank, and pit) are likely to produce copious odor compounds during storage if no oxygen is available while the organic matter degrades.

In some cases (pH for instance), statistical differences were detectible, but may have had only a minor impact on manure odor—VFA and NH_3 volatility would have been slightly higher and lower, respectively, in the slurry tanks due to the 0.3 unit lower pH. In one instance, though, it seems that pH did have an impact on odor. For LT1, pH was lower than the other sites, and it is interesting to note that only the LT1 site emitted volatile fatty acids during from the manure slurry and after soil application. It is possible that the quality of manure inputs in LT1 affected pH. Controlling the pH at this site during manure storage or immediately prior to slurry application could benefit the producer by decreasing the emission of malodorous VFA.

In other cases, pH differences would have a profound impact on manure management and odor impacts by affecting the amount of ammonia retained in the manure. For instance, application rates of pit slurry and some tanks would have to be much lower, if N rate were the determinant. How would this potentially impact odor emission? Given a surface application of pit slurry (not a typical method) and the small amount needed relative

to the other manures (tank and lagoon), the impact of odor emission after application would be proportionately higher since a larger surface area would receive the manure. Other factors impacting this calculation would be odor compound content and manure volume.

An informative comparison to make is the comparison between odor compounds dissolved in the manure and odor compounds emitted from the manure surface. Although VFA concentrations were always quite high in the pit and tank samples, the amount observed in odor emissions was quite low. Conversely, although the content of aromatic compounds was usually only a fraction of the VFA, the emission of aromatic compounds was many times greater than that of the VFA. This was observed for both stored manure slurry and when it was applied to the soil surface. Clearly, understanding the formation of aromatic compounds and the factors controlling its emission would have a proportionately greater impact on odor emissions than work on alcohols, ketones, or VFA.

Another factor affecting emissions is the amount of exposed surface for odor compounds to be emitted. A relationship between odor compound content and surface area is straight-forward to understand (large area with low odor emission capacity may emit more odor compounds than a small area with high odor emission capacity). Further analysis of this data set factoring in slurry/wastewater surface area will provide a better understanding of the system's emission. This analysis will be made and reported in future research articles.

One of the final conclusions to impart, subsurface manure applications reduced odor emissions. The results of this study are clear on this point. Ensuring that the manure is incorporated, and not hanging around on the surface will have a great impact on odor emissions and neighbor relations.

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