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Abstract

Livestock operations are associated with emissions of odor, gases, and particulate matter (PM). Livestock odor characterization is one of the most challenging analytical tasks. This is because odor-causing gases are often present at very low concentrations in a complex matrix of less important or irrelevant gases. The objective of this project was to develop a set of characteristic reference odors from a swine barn in Iowa and, in the process, identify compounds causing characteristic swine odor. Odor samples were collected using a novel sampling methodology consisting of clean steel plates exposed inside and around the swine barn for ≤1 week. Steel plates were then transported to the laboratory and stored in clean jars. Head-space solid-phase microextraction was used to extract characteristic odorants collected on the plates. All of the analyses were conducted on a gas chromatography-mass spectrometry-olfactometry system where the human nose is used as a detector simultaneously with chemical analysis via mass spectrometry. Multidimensional chromatography was used to isolate and identify chemicals with high-characteristic swine odor. The effects of sampling time, distance from a source, and the presence of PM on the abundance of specific gases, odor intensity, and odor character were tested. Steel plates were effectively able to collect key volatile compounds and odorants. The abundance of specific gases and odor was amplified when plates collected PM. The results of this research indicate that PM is major carrier of odor and several key swine odorants. Three odor panelists were consistent in identifying p-cresol as closely resembling characteristic swine odor, as well as attributing to p-cresol the largest odor response out of the samples. Further research is warranted to determine how the control of PM emissions from swine housing could affect odor emissions.

Disciplines

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Comments

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Characterization of Livestock Odors Using Steel Plates, Solid Phase Microextraction, and Multidimensional -Gas Chromatography - Mass Spectrometry - Olfactometry

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ABSTRACT

Livestock operations are associated with emissions of odor, gases, and particulate matter (PM). Livestock odor characterization is one of the most challenging of analytical tasks. This is because odor-causing gases are often present at very low concentrations in a complex matrix of less important or irrelevant gases. The objective of this project was to develop a set of characteristic reference odors from a swine barn in Iowa, and in the process identify compounds causing characteristic swine odor. Odor samples were collected using a novel sampling methodology consisting of clean steel plates exposed inside and around the swine barn for up to one week. Steel plates were then transported to the laboratory and stored in clean jars. Headspace solid phase microextraction (SPME) was used to extract characteristic odorants collected on the plates. All analyses were conducted on a GC-MS-Olfactometry system where the human nose is used as a detector simultaneously with chemical analysis via MS. Multidimensional chromatography was used to isolate and identify chemicals with high characteristic swine odor. The effects of sampling time, distance from a source, and the presence of particulate matter (PM) on the abundance of specific gases, odor intensity and odor character were tested. Steel plates were effectively able to collect key volatile compounds and odorants. The abundance of specific gases and odor was amplified when plates collected PM. The results of this research indicate that PM is major carrier of odor and several key swine odorants. Three odor panelists were consistent in identifying p-cresol as closely resembling characteristic swine odor as well as attributing to p-cresol the largest odor response out of the samples Further

research is warranted to determine how the control of PM emissions from swine housing could affect odor emissions.

IMPLICATIONS

Characterization of aerial emissions of odor and odorous gases from livestock operations is critically important for the development of feasible control technologies. Particulate matter was found to have a great capacity for carrying odor. Technologies controlling PM emissions will likely have a positive effect on odor control. Several hazardous air pollutants (HAPs) are present in swine barn environments. P-cresol was found to be one of the key gases responsible for the overall characteristic swine odor. Multidimensional GC-MS-Olfactometry is very useful for characterization, separation, isolation and identification of key components of odor in complex air samples.

INTRODUCTION

Odor emissions from confined animal feeding operations affect air quality in surrounding communities.[1] The chemical makeup of odor emitted from swine manure has been a focus of several previous studies.[2-7] Schaeffer (1977) reported concentrations of indole, skatole, p-cresol, phenol, and volatile fatty acids (VFAs) measured in the exhaust air of 17 swine buildings.[2] Spoelstra (1980) reviewed literature and reported a total of 87 compounds associated with swine manure.[3] Yasuhara (1984) reported 31 compounds in association with either fresh or aged swine manure.[4] O'Neil and Phillips reported 168 compounds reported by various researchers in livestock wastes and air around them.[5] Zahn et al. (1997) reported 22 organic compounds in liquid manure and air in and around swine production facilities.[6] To date, the most comprehensive list of VOCs and fixed gases in air around swine production facilities was published by Schiffman et al., (2001) in which 331 compounds were tentatively identified.[7] Koziel et al. (2005) reported 63 gases emitted from swine manure.[8] Day et al. (1965) reported that most of the swine odor was carried on particulate matter (PM).[9] Hammond et al. (1979) and Hammond et al. (1981) concluded that PM plays a crucial role in transporting and magnifying swine odor.[10-11] Razote et al.(2004) identified 84 compounds in swine barn PM.[12] Cai et al (2005) used SPME to characterize VOCs and semi-VOCs associated with swine dust.[13] Still relatively little is known about swine odor, odor-causing chemicals, odor-particulate matter

interactions, and persistence of swine odor. Table 1 compares methods used and number of compounds identified between several of these studies.

Livestock odor can be measured using dynamic forced choice olfactometry which relies on air sample collection in polymeric (e.g., polyvinyl fluoride, polyethylene terephthalate) bags for subsequent evaluation with an olfactometer.[14,15] Air sample collection is relatively short (typically a few minutes). Air samples are then presented to trained panelists at various dilutions with clean air to determine odor strength and intensity relative to n-butanol standard.[1] While such standardized approach allows for quantification of the overall odor, it does not allow for (1) identification of individual odor-causing compounds that might be examined in an attempt to control the odor, (2) it is not suited for long-term sampling of odor, and (3) it requires significant investment in air sampling and olfactometry analysis equipment and the compensation necessary for the panelists' time and training. In addition, polymeric materials used in bags are associated with impurities and poor recoveries of polar and semivolatile odorous gases typical to livestock environment gases.[16]

Several techniques for chemical identification of odorants exist and generally involve the use of gas chromatography-mass spectrometry (GC-MS). Rabaud et al. (2003) used sorbent tubes with Carboxen and Tenax.[17] Willig et al. (2004) used various sorbent cartridges to collect air samples.[18] Techniques such as these do have some disadvantages however. Air must be drawn through such devices in order to collect samples. This requires precisely calibrated pumps be brought into the field and repeatedly monitored to ensure similar results between samples. Analyses of some compounds of interest, e.g., carboxylic acids can be affected by the presence of water in air and loading of that water on sorbent tubes and subsequently on a GC-MS.[19] Most recently, Pelletier et al (2005) published an interesting summary of investigations of emissions of odor and selected gases (NH_3, N_2O, CO_2 and CH_4) from common building materials submerged previously in swine manure in laboratory conditions.[20] It is now known that all tested materials are capable of re-emitting odor and the selected gases. However, there is still no linkage between priority odor-causing gases and such materials for swine operations.

Our goal for this project was to develop a novel method for sampling the ambient air in livestock facilities capable of long-term sampling. The sampling was intended to be used for qualitative analysis. We attempted to create a sampling method that would be inexpensive and easy to deploy in field conditions. Such a method would allow for efficient long-term storage of samples with characteristic odor in the laboratory, multiple sampling and analysis of odor with a SPME and GC-MS-O system. Previous studies by these authors show that simple carbon steel plates exposed to ambient air in and near beef cattle feedyards can adsorb odorous gases.[21] Thus, we selected the same type of material for long-term sampling of odors at swine operations. In this research, we also further investigated the effects of exposure time, distance, and dust of odor and odorants. In addition, further use of such a system will allow for the identification of key compounds causing characteristic swine odor. This was accomplished using the multidimensional capability of the GC-MS-olfactometry system.[21-23] Chromatographic retention times associated with characteristic odors were identified and then used to determine optimum Dean switch 'heart-cut regions' . During heart-cutting, compounds with retention times coinciding with characteristic compounds only were passed into a second column for improved separation and odor characterization.

METHODOLOGY

Preparation of Plates and Jars

Carbon steel plates approximately 6 cm × 3 cm × 0.25 cm were fabricated by cutting down stock 1018 grade cold drawn flat steel purchased from Iowa State General Stores. Each end of the plates was smoothed out with a grinder. Additionally, a small hole was drilled into each plate to facilitate hanging. Each of the plates was hand washed in a lab detergent solution two times. The plates were then rinsed in de-ionized water. After rinsing, the plates were cleaned in batches of about 14 plates in an ultrasonic cleaner for 1 hr. Again, the plates were rinsed before being baked in an oven for 8 hrs at 200 °C and then 110 °C overnight. After baking, the plates were individually wrapped in sheets of aluminum foil to await sampling. Aluminum wire that would be used to hang the plates at the individual sampling sites was also washed, baked and stored in the same manner. Glass jars were also prepared to store the samples once they had been collected. Glass jars, metal rings and lids, and PTFE disks were washed in a detergent solution

and then baked for 8 hrs at 200 °C and kept in an oven at 110 °C until used for sample storage.

Sampling

Plates were deployed and collected at the Iowa State University swine research farm. The selection of sampling locations was driven by the need to represent air inside a barn immediately before exhaust, outside of a barn and very close to the same air exhaust location, and a distant location where the effects of air dilution and pollutant/odor dispersion were likely to occur. One set consisting of one plate from each location was collected at 1, 4, and 7 days after deployment. Figure 1 shows the locations used for sampling at the swine barn.

The first set of plates was hung directly above a pig pen on the inside of the barn, approximately 2 m above ground; this spot was called the inside location. The second set of plates was hung on some aluminum wire strung up in the corner of a fence on the property line, approximately 100 m from the barn. This location was the distant site. A third set of plates was hung on some aluminum wire suspended between two steel t-posts driven into the ground approximately 1m away from a continuous exhaust fan. The fan blew directly onto the plates when they had been suspended. Additional plates were deployed at each location at the swine site to test for the effects of particulate matter (PM) on odor sampling. Particulate matter is a term used to describe dispersed airborne solid or liquid particles larger in size than a molecule but smaller than10^{-4} cm. Particles of this size have a lifespan from anywhere between several seconds to several months.[24] These plates were collected on the 7th day. Additionally, two more sets were deployed at the swine barn to be collected on the 7th day for replications. Table 2 shows the plate number, sampling location, treatment after collection, and the number of precipitation events which may have affected outside sampling. No data for wind direction and velocity was collected for the distant location.

Storage of Sampled Plates

Plates were brought back into the lab wrapped in aluminum foil. Once back in the lab, the plates were rinsed 1 min each in tap water, with the exception of the plates to be used to test for the effects of PM. After the plates had dried in a fume hood, they were placed into the previously prepared jars. PTFE disks were placed underneath the lids before the jars had been sealed to

prevent any odor contamination from metal or paint on the lid. Once the plates had been placed in the jars and the jars sealed, they were placed in a wooden cabinet in the atmospheric air quality lab. The jars were then stored for 2-3 months at room temperature (~22 ºC) to allow the headspace within the jar to become saturated with the compounds adsorbed to the steel plates. Many odor causing compounds are semi-volatile, characterized by low vapor pressure. Thus, longer equilibration time allows for increased concentration in the jar headspace. Two control jars were also prepared for analysis of blanks. Both jars were washed and baked in the same manner as the other jars. One was left empty and sealed. A metal plate that had been washed and baked was placed in the other. The two jars were stored in the same location as the exposed plates for an equivalent amount of time. These controls would allow for the identification of any background gases and odor found in the jars and steel plates.

Analysis

Headspaces of jars with plates were sampled using solid phase microextraction (SPME). In this methodology, explained in Koziel et al. (2001) sampling, preconcentration, and direct transfer of analytes into a standard gas chromatograph are combined. As such, this method has many advantages when compared to traditional analytical methods. [25] SPME fibers also allow for excellent recovery, shown to be approximately 90% for VFAs and phenolics.[16] Standard push pins were baked in an oven to minimize contamination before being used to puncture the lids of the jars to allow SPME insertion. When a jar lid had been punctured, the air inside would be sampled by inserting a Carboxen/PDMS 85 μm SPME fiber into the hole. The fiber was allowed to sample the headspace of the jars for 24 hrs. Once the headspace had been sampled, the jars were closed with the push pins and again stored.

An Agilent Technologies GC-MS system (Agilent 6890N GC / 5973 MS, Agilent Inc., Wilmington, DE) modified with MDGC-Olfactometry system and Aromatrax software (Microanalytics, Round Rock, TX) for recording odor events was used to analyze all samples. This system allows for the simultaneous identification and analysis of chemicals and corresponding odors. The system was equipped with a non-polar pre-column and polar analytical column in series as well as system automation and data acquisition software (MultiTrax™ V. 6.00 and AromaTrax V. 6.61, Microanalytics and ChemStation, Agilent). The pre-column was a

12 m × 0.53 mm ID BP5 × 1.0 µm and analytical column was a 25 m × 0.53 mm ID BP20 × 1.0 µm both from SGE (Austin, TX). The general run parameters used were as follows: injector, 260 °C; FID, 280 °C, column, 40 °C initial, 3 min hold, 7 °C/min, 220 °C final, 10 min hold; carrier gas, helium. Scan mode MS acquisition was utilized with mass/molecular weight to charge ratio (m/z) range set between 33 and 280. Spectra were collected at 6/sec and electron multiplier voltage was set between 1100 to 1200 V. The detector was auto-tuned weekly.

Multidimensional GC capabilities for 'heart-cutting" were based on the Dean switch principle. In such a dual column system, heart-cutting is a pressure balance based flow switch process in which, to enhance resolution, a small, 'chromatographic/odor region of interest' from the first column separation is transferred to a second column, representing different phase selectivity. The heart-cut valve was used to transfer specific pre-separated retention regions with characteristic swine odor from the pre-column to the analytical column. Back-flush of the pre-column was activated between 36 and 40 min. The system operated in constant pressure mode. The olfactory detector allowed the panelist to apply an odor tag to a peak or a region of the chromatographic separation. The odor tag consists of editable odor character descriptors, an odor event time span and perceived odor intensity. Dual column MDGC systems with heart-cutting capability enable isolation of critical trace level odorants from complex background matrices.[20-22]

Multidimensional GC-MS-O was used for separation and identification of compounds with the characteristic swine odor. Three panelists analyzed headspace samples from the Day 7 sample plate which was exposed to continuous barn exhaust air immediately outside the barn. The panelists consisted of two full time researchers with at least 100 previous analyses done, many concerning swine odor, as well as a student who had been trained over the course of 5-10 practice analyses using various odor samples including swine dust samples. This approach was used so that variation between panelists could be studied. Lastly, one of the panelists analyzed the same plate's headspace three consecutive times, again to study variance between analyses. Each of the panelists analyzed the sample once without heart-cutting to determine appropriate pre-column retention times to isolate. Retention times were selected in which characteristic swine odor was detected. "Characteristic swine odor" was defined as the composite smell

emanating from the sampled plate with swine dust Panelist responses were compared based on odor character and odor intensity associated with separated compounds in headspace.

After the SPME fibers had been analyzed with the MDGC-MS-O, results files were interpreted using single ions and peak area counts for selected compounds which were then compared with each other. In addition, odor character and intensity were compared among various samples. Compounds were identified with three sets of criteria: (1) match of the retention time with the retention time of pure compounds run as standards, (2) matching mass spectra of unknown compounds with BenchTop/PBM MS library search system and spectra of pure compounds, and (3) matching odor character. Qualitative assessment of VOC abundance and odor abundance was measured as area counts under peaks for separated VOCs and odor/aroma events.

RESULTS

Blank Samples

Initially, approximately 20 representative compounds were selected from among the plates used for swine odor collections to compare throughout analysis. However, upon comparing these compounds to the compounds found in our jar and plate blank sample, we chose to remove several of the compounds. These compounds which had originally been identified but were removed because they were deemed to be background interferences included pentanal, toluene, 3-heptanone, 2-ethyl hexanol, benzaldehyde, benzene methanol, and phenol. An air sample was also collected inside the cabinet in which the jars containing the plates were stored using a SPME fiber. This was done in attempt to explain the source of the background compounds. Pentanal, toluene, benzaldehyde, and phenol were all present in the cabinet air. This indicates that at least some compounds found in blanks were impurities introduced during sample storage. From their presence, it can be concluded that it is quite possible the jars were not completely sealed.

The results of the analysis were also compared with the list of hazardous air pollutants (HAPs) as identified by the amended U.S. Clean Air Act of 1990.[26] The amendments made required the Environmental Protection Agency to set standards for any industry emitting any of the identified pollutants. Two of the compounds identified, carbon disulfide (CAS 75-15-0) and p-cresol (CAS

106-44-5) are classified as HAPs. Acetophenone (CAS 98-86-2) was also identified in the outside PM sample only.

Effects of Sampling Time

Comparisons of seven compounds collected with steel plates in ambient air are shown in Figure 2. Plates were exposed inside, outside, and at distance from a swine barn for 1, 4, and 7 days, respectively. Plates at the distant location collected significantly less compounds compared to the inside and outside locations. Only 2 compounds were present at the distant location, i.e., p-cresol and CS_2. The presence and importance of p-cresol as a key priority odorant downwind of beef cattle feedyards was also reported by Wright et al. (2005).[21] Particularly interesting was the predominance of p-cresol at distant location which is present there even after the rinsing. This result is consistent with the finding of p-cresol in soils and common building materials in and around beef cattle feedlot.[21] P-cresol is a polar and semivolatile compound which can easily "stick" on exposed surfaces. There were no apparent trends concerning the effects of sampling time to the amount of compounds. There is an apparent trend for both the inside and outside locations for the highest amount of compounds being found on day 4 for several compounds including dimethyl trisulfide (DMTS), dimethyl disulfide (DMDS), CS_2 and p-cresol. In contradiction to this trend is the inside sampling of CS_2, which shows a much higher concentration present on day 7. One explanation for this could be (a) possible loss of analytes during the rain and snow events between days 4 and 7 (Table 2) (b) the cumulative effect of shifting wind direction and velocity, (c) the plate positioning, i.e., the angle at which plates were exposed to the air flow was not controlled, and (d) the loss of compounds from plates through rinsing after the collection. This variability seems to introduce a large amount of error into the experiment, and is further investigated by comparing the triplicate samples below. In addition, adsorption and condensation on steel plates was likely a function of physicochemical properties associated with gases present in air. Finding the exact relationships between these properties and particular compounds collected by plates was not the scope of this experiment.

To further investigate the potential error associated with this methodology, we compared the odorants present on 3 plates exposed at each location, inside, outside, and distant from the swine barn. We averaged the amount of odorants present in plates exposed at the same location for the

same duration of time. We then calculated the standard deviation among the identical plates which was ultimately used to calculate the relative standard deviation (RSD). The results of the calculation can be found in Table 3. The RSDs were high for all compounds compared. In fact, the only compound below a 10% threshold was CS_2, as sampled by the inside plates. These large RSDs indicate that our methodology was not very repeatable nor is it well suited for quantitative comparisons. Uncertainties associated with rinsing of plates may be one explanation for the large variability between replicates.

The Role of Particulate Matter

In order to test the effects of PM on the concentration of chemical compounds and odors, we did not rinse one set of samples. This set was collected on day 7 and consisted of one plate from each sampling location. These PM samples were then compared with plates treated identically with the exception of having been rinsed. In order to compare the relative concentrations of chemical compounds, we compared the abundance measured as peak area counts for a characteristic single ion between the PM and no-PM samples using equation 1 below.

Equation 1: Relative difference for specific odorants in PM samples vs. no-PM samples

$$T_i = \frac{AC_{PM(i)} - AC_{NoPM(i)}}{AC_{PM(i)}} \times 100\%$$

Where:

T_i	=	Relative difference for odorants in PM samples vs. no-PM s samples for compound "i",
$AC_{PM(i)}$	=	Peak area count for single ion used to quantify compound "i" from plates with PM,
$AC_{NoPM(i)}$	=	Peak area count for single ion used to quantify compound "i" from plates with no PM.

The resulting average differences between the inside, outside and distant locations were 90.3, 92.8, and 36.2% for inside, outside, and distant location, respectively. Table 4 below shows the results of this calculation. A visual representation of the difference between the PM and no PM

samples can be found in Figure 3. Particulate matter carried a very significant fraction of all 13 compounds. This finding is consistent with previous studies reported by Day et al (1965), Hammond et al (1979), Hammond et al (1981), and Razote et al (2004).[10-12] Cai et al (2006) which showed that swine dust is a significant carrier of odor and odorous compounds.[13] All compounds in this study except CS_2 were found in swine PM by Cai et al (2006).[13] The presence of moisture in a closed plate-PM-air system can enhance gas-phase concentrations of odor causing semi-VOCs, often described as a "flooding out" effect.[21]

In the PM samples, abundance of specific VOCs decreased with the distance from the source from inside to outside to distant, with the exception of three compounds: hexanal, p-cresol, and skatole. Dimethyl disulfide, 3-methyl-butanal, octanal, acetic acid, and nonanal had larger abundance outside compared to inside location. This is likely due to differences in air velocities between inside and outside locations. Therefore the rate of adsorption to plates were likely different. Additionally, there was only a slight difference between the amounts of acetic acid present in the inside and distant samples.

Odor

Many odorants were present in each sample of which several were offensive. Butyric and isovaleric acids produced buttery and body odor notes. Other extremely strong, offensive odors which were quite characteristic for swine and were tentatively attributed to p-cresol and skatole. The plates carrying PM had much more odor. A comparison of the total odor measured can be found in Figure 4. The data utilized for comparison purpose are the sum of the products of odor intensity and odor duration collected with plates representing PM and no PM conditions. There was almost an order of magnitude increase in odor for plates with PM for the inside and outside location. The difference between PM/no-PM plate at a distant location was much less. In addition, the number of separate odor/aroma events was always greater by about a factor of 2 for plates with PM. Interestingly, there was also a positive correlation between sampling time and the amount of offensive odors carried on the rinsed plates, as shown in Figure 5. The offensive odor was chosen among all odor/aroma events with the following odor descriptor/tag: 'urinous,' 'barnyard,' 'body odor,' 'skunky,' and 'piggy.' The offensive odors carried by the rinsed plates for the swine barn increased in intensity with a longer sampling time. Additionally, the odor

tended to be the strongest at the inside location, followed by the outside location and then distant, with the exception of there being more odor present on the outside, 4 day sample than the inside 4 day sample.

The strongest and most offensive odors in the swine samples tended to come from butyric acid, isovaleric acid, p-cresol, and skatole. Out of the total odor area for the 7 day sample with swine PM, approximately 85% of the total odor area was contributed by these 4 compounds, suggesting that they play a large role in the ambient odor from swine facilities. Interestingly, odor from butyric and isovaleric acid was not detected at all in rinsed samples, while odor from p-cresol and skatole was much less intense. There are two possible explanations for this discrepancy. First, it is likely that the majority of these compounds are associated only with the PM themselves, not the ambient air. When the particles are physically removed via rinsing, they are present in much lower concentrations. Second, organic acids are water-soluble and could be simply rinsed off of the plate while other less water soluble compounds (p-cresol and skatole) remain on plates. In either case, by mechanically removing these key odorants through simple means, offensive odor is greatly reduced. Particulate matter has a great capacity to carry odor. This has significant implications for odor control. Reduction of PM should result in reduction of odor.

Another odorous compound in the swine samples tended to be dimethyl trisulfide (DMTS). This compound had an offensive, onion-like, almost characteristic swine smell. However, unlike the VFAs or p-cresol/skatole, the odor of DMTS was nearly as intense in the rinsed plates as the PM samples. This suggests that swine PM control would not likely affect the DMTS. Other strong odorants included hexanal (‘grassy’) and acetic acid (‘vinegar’), though these were neither as intense nor offensive as the C4-C5 VFAs and the phenolic/indolic compounds.

Identification of characteristic swine odorants

Multidimensional GC-MS-O analyses were used to further investigate the individual compounds responsible for characteristic odors. Conventional GC-MS-O or GC-O analyses allow for the approximate association of odors with the chemicals responsible for their existence. However, such analyses are somewhat limited as odor events can sometimes occur at retention times very

close to each other. In addition, air samples from livestock operations are very complex mixtures and it is very challenging to positively identify compounds, not to mention the assignment of the specific compound-odor link.

Multidimensional GC-MS-O is a good alternative to classic GC-O approach because it can improve the separation of chemicals and odor events.[21-23] In multidimensional chromatography, particular compounds eluting at specific retention times and carrying characteristic odors can be diverted and separated from the entire sample on a second column representing different phase selectivity. This process of switching between GC columns is called "heart-cutting". The result is a final signal in which significant compounds and odors are better separated and the potential of interferences from coeluting compounds (and therefore their odors and aromas) is minimized. For this investigation, a single sample, the Day 7 sample which was exposed to continuous barn exhaust air immediately outside the barn, was used to identify compounds with the characteristic swine odor.

In order to isolate and identify compounds with characteristic swine odor, the system was set to GC-FID-O mode with no heart-cutting. Comparison of the total ion chromatogram (TIC), FID signal, and the aromagram of headspace above the swine dust contaminated steel plate in a "screening" mode without heart-cutting is shown in Figure 6. In this mode, the entire air sample was separated on the pre-column only, and the panelist performed simultaneous olfactometry analysis at the sniff port. The entire air sample was separated, resulting in a chromatogram and aromagram that were very complex with many potentially coeluting peaks, not all of which are significant, odorous compounds. As seen in Figure 6, there are indeed many odor events (24) and multiple and coeluting peaks in the FID chromatogram. Not all of the FID peaks were associated with a particular odor event, nor were all odor events able to be specifically attributed to one particular compound from the TIC. A listing of odor events and their respective intensities and attributed compounds for the GC-FID-O mode can be found in Table 5.

Based upon samples taken in GC-FID-O mode, several retention times associated with characteristic odors were selected. 'Characteristic' odor was defined by each panelist smelling and memorizing the odor character from the pin sealing the storage jar before analysis. The

retention times selected were approximately the same among the three panelists (last column in Table 5). Each of the panelists identified the same five periods of retention times for heart-cutting, approximately 0.48-0.80, 3.45-4.10, 4.40-5.10, 9.90-13.55, and 15.40-18.3 min. After each of the panelists had analyzed the first sample in the GC-FID-O mode (Figure 6), pre-column heart-cut times were set and the second replicate sample was analyzed (Figure 7).

Comparison of the total ion chromatogram (TIC), FID signal, and the aromagram of headspace above the swine dust contaminated steel plate is presented in Figure 7. These profiles reflect a heart-cutting GC-MS-O mode focused only on specific swine odor compounds. During heart-cutting, only specific retention time regions with characteristic compounds are diverted away from the FID, as noted by the flat regions in the FID in Figure 7, and sent through a second column to the MS detector and to the sniff port. As many as 21 separate odors and aromas were identified. This was likely due to the improved multidimensional separations during which new compounds emerged. These compounds were coeluting and their odor was masked or blended when a regular GC-O mode was used.

All three panelists were very consistent in selecting p-cresol as a compound closely resembling the overall swine odor remaining on the steel plate. P-cresol was also consistently shown to have the greatest impact among all separated odorants (resulting in large peak #21 in Figure 7). The odor peak associated with p-cresol was the largest in terms of total odor area among each of the three panelists.

Average odor intensity (Part A) and total odor area (Part B) for p-cresol among the three panelists as well as for panelists three's additional samples is presented in Figure 8. The mean odor intensity caused by p-cresol was 60%. The standard deviation among the 3 panelist was 11% while the single panelist was very reproducible at the standard deviation equal to 1%. The former variation between the panelist responses was likely due to different sensitivities and their own relative scales of intensities developed while working with GC-O technology.

The total odor caused by p-cresol was much different for the single panelist compared with the mean of responses from 3 panelists. The single panelist analyzed the same headspace sample

after the 2 panelists. Closer inspection of the single ion chromatograms (107) for p-cresol revealed that the p-cresol was depleted from headspace with each SPME extraction. The rate of depletion was approximately 14% per one SPME extraction (R^2=0.88). This depletion of headspace concentration was consistent with SPME theory. Thus, the much lower response from the single panelist and significant variations observed in Figure 8 (Part B) were likely caused by decreasing concentration of p-cresol in the headspace above the steel plate. It is interesting however, that the apparent depletion of p-cresol did not have a significant effect on odor intensity caused by p-cresol (Figure 8, Part A) and perceived by three panelists. This could be possibly a reflection of the sigmoid curve nature of the human olfactory response.

Overall, there was some variation between each of the panelists as summarized in Table 6. In the analysis to determine heart-cutting times, the panelists recorded 24, 23, and 20 distinct odor events for panelists 1, 2, and 3, respectively. However, for the analysis of the samples when the multidimensional mode was used, panelists 1, 2, and 3 recorded 21, 23, and 8 odor events. Panelists 1 and 2 recorded a similar number of events, while panelist 3 recorded a number of odor events much smaller than the first two. Additionally, total odor area for all odor events was high for panelists 1 and 2, at 58,800 and 39,100, respectively, but low for panelist 3, at 8,300. Comparing the ratio of odor peak area vs. total number of odor events, values of 2,801, 1,699, and 1,039 were obtained for panelists 1, 2, and 3, respectively. These numbers average to 1846 with a standard deviation of 890 and relative standard deviation of 48.2%. Panelist 3 also replicated the multidimensional analysis two additional times. For the second and third samples, panelist 3 recorded a total of 10 and 7 odor events, a compared with the 8 from the first sample for a standard deviation of 2 and relative standard deviation of 18.3%. Total odor area was 21,351 and 10,322 as compared to 8,313. This discrepancy suggests that either the gases in the headspace are becoming more dilute as panelist 3 was the last to analyze the sample, or that panelist 3 was not as sensitive to the odor events and was not able to record all of them. More research is warranted to better estimate the variability between panelists.

Potential Causes of Error

The main potential sources of error are any background chemicals or odors that come from the storage and sampling. The steel plates were thoroughly washed and baked, but there still could

have been some background compounds that, for some reason, had not been rinsed clean. Furthermore, it is possible that some of the background compounds could have come from the washing process itself. The same contamination would affect the jars which were washed in the same manner.

Additionally, there was possible contamination from the air of the laboratory. Any chemicals present in the laboratory air would be in contact with the plates not only before they were wrapped in aluminum foil prior to sampling, but also after they had been placed in the jars for storage as these were filled with standard laboratory air. Any background chemicals in the lab air would then be in contact with the plates over several months as well as in contact with the SPME fibers during extraction. Many different chemicals are used in the laboratory to attempt to reproduce characteristic smells and could be the source for some of this contamination.

Perhaps the largest source of error is the rinsing of the plates subsequent to sampling. The results from the swine samples showed very clear trends in the strength of odors and ion peaks versus sampling location on those samples that had not been rinsed off. However, this trend was not very definite on those samples that had been rinsed, nor was it definite for sampling duration. In fact, the strengths of various peaks were seemingly random among the samples with individual compounds following different trends for various sampling locations and duration. While every effort was made to rinse the plates in the same manner, complete reproduction of the same rinsing methodology for plates rinsed at different times is not possible. The plates could have been rinsed for slightly different amounts of time or held under running water in a slightly different manner.

The effects of weather events (precipitation and wind direction) have likely influenced the amount of analytes adsorbed on plates. Temperature specifically could also play a role in the plate adsorption. For the week the plates were deployed, the mean temperature was 1 °C, with a maximum of 12 °C and minimum of -4 °C. These are outside temperatures and differ from the somewhat regulated temperature of a swine facility such as the one at which our plates were deployed. Differences in temperature could account for differences in samples taken inside and outside, as well as samples collected on different days. Yet, even relatively short exposure times

resulted in collections of detectable mass for several important odorants. Another possible source of uncertainty was the lack of control to the plate angles facing moving contaminated air. This could cause differences in loading rates of compounds to each plate. An improvement to this would be to hold all plates exposed at identical angle relative to the source. While no one of these variables by themselves would likely cause too large of a discrepancy, together they could combine to produce somewhat random results like the ones seen in this project.

In regards to the analysis of the plates using the SPME method, it is also possible that some compounds are essentially favored over others for extraction. Specifically, our findings indicate a lower VFA/p-cresol ratio than found in other works such as Hammond et al. (1979). It is likely that this discrepancy is a result of the Carboxen/PDMS fiber used preferentially extracting p-cresol over low molecular weight VFA's. As such, extraction would be biased towards high molecular weight compounds such as p-cresol as opposed to low molecular weight VFAs.

Furthermore, it is necessary to identify the recoveries for adsorption and desorption methods concerning the steel plates. It is possible that the plates become saturated at the surface with compounds. As such, it is possible that our data is biased in favor of certain compounds. However, this is related to the advantages of steel plates in that the odor is for the most part found at the surface. In materials such as polymers, which are more porous, odor penetrates deeper into the material over time. Thus, the steel plates retain more of the odor from the original sampling at the surface. More research is needed under controlled conditions on the tendency of the plates to preferentially absorb various compounds.

Overall Effectiveness of Plates for VOCs and Odor Collection

The plates were ultimately effective in collecting odors and gases from the ambient air in and surrounding livestock facilities. The compounds collected were able to be positively identified and agreed with previous compounds identified in livestock facility emissions. However, the plates had significantly more VOCs and odor when PM was not rinsed off. Plates that were covered in PM contained more odorants in larger amounts. Plates that had been rinsed did not contain significant odorous compounds such as butyric and isovaleric acids. Furthermore, plates that had been rinsed tended to have large discrepancies in result, likely due to inherent error in

the rinsing process. Using steel plates to sample ambient air showed how a large role PM plays in odor nuisance.

The plates are ultimately a good research tool for qualitative assessments of livestock gases and odor. The plates allow one to sample ambient air at various locations over a long sampling duration. The gases and odors collected on the plates can then be analyzed to investigate which compounds may be present as well as which ones seem to play a large role in producing the offensive odors emanating from that particular facility. Direct quantification of particular gases emitted is not possible with this methodology, however. It is better suited to identification and comparison between different sampling locations. Another possible application of plates is studies of PM settling and the studies of adsorption to and re-emission from building materials at livestock and poultry operations.

CONCLUSIONS

Several conclusions can be made:

1. Steel plates are capable of collecting VOCs and odorants from long term sampling of livestock operations.
2. Steel plates carried significantly more VOCs and odor when left not rinsed, as rinsing produced greater variability in results.
3. Steel plates were best used for analysis and qualitative comparison, not quantification
4. PM and other particulates have great potential significance in odor contribution
5. Butyric acid, isovaleric acid, p-cresol, and skatole play a large role in the odor from PM in ambient air at swine facilities
6. Dimethyl trisulfide plays a significant role in the odor in ambient air at swine facilities regardless of the presence of PM.
7. SPME-MDGC-MS-O analyses are very useful for the sampling, isolation, separation, and identification of important odorants in swine environments.
8. All three panelists in identified p-cresol as one of the key odorants causing the characteristic swine odor.

9. P-cresol was present on all plates even at the distant location without PM present. This underscores the potential for this compound to remain in environments exposed to air from livestock facilities for extended periods of time after the exposure.

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REFERENCES

1. National Research Council. *Air Emissions from Animal Feeding Operations: Current Knowledge, Future Needs*. The National Academies Press, Washington, DC, 2003.
2. Schaeffer, J.; Sampling, characterization and analysis of malodors. *Agriculture and Environment*. **1977**, *3*, 121-127.
3. Spoelstra, S.F. Origin of objectionable odorous components in piggery wastes and the possibility of applying indicator components for studying odour development. *Agriculture and Environment*. **1980**, *5*, 241-260.
4. Yasuhara A.; Fuwa, K.; Jimbu, M. Identification of odorous compounds in fresh and rotten swine manure. *Agric. Biol. Chem*. **1984**, *48*, 3001-3010.
5. O'Neal, D.H., Phillips, V.R. A review of the control of odour and nuisance from livestock buildings: part 3, properties of the odorous substances which have been identified in livestock wastes or in the air around them. *J. Agric. Engng. Res*. **1992**, *53*, 23-50.
6. Zahn, J.A.; Hatfield, J.L.; Laird, D.A.; Hart, T.T.; Do, Y.S.; DiSpirito, A.A. Functional classification of swine manure management systems based on effluent and gas emission characteristic. *J. Environ. Qual*. **2001,** *30*, 635-647.
7. Schiffman, S.S.; Bennett, J.L.; Raymer, J.H. Quantification of odors and odorants from swine operations in North Carolina. *Agricultural and Forest Meteorology*. **2001**, *108*, 213-240.
8. Koziel, J.A.; Lo, Y.C.; Wright, D.; Trabue, S.; Kerr, B. The use of SPME and multidimensional GC-MS-Olfactometry system for identification of key odorants from

swine manure. In *Proceedings of the 2005 AWMA Annual Meeting and Exhibition, Minneapolis, MN;* AW&MA, Pittsburgh, 2005. Paper #996.

9. Day, D.L.; Hensen, E.L.; Anderson, S. Gases and odors in confinement swine buildings. *Trans. ASAE*. **1965**, *8*, 118-121.
10. Hammond, E.G.; Fedler, C.; Smith, R.J. Analysis of particle-borne swine house odor. *Agric. Environ.* **1981**, *6*, 395-401.
11. Hammond, E.G.; Fedler, C.; Junk, G. Identification of dust-borne odors in swine confinement facilities. *Trans. ASAE.* **1979**, *22*, 1186-1189.
12. Razote, E.B.; Maghirang, R.G.; Seitz, L.M.; Jeon, J.J. Characterization of volatile organic compounds on airborne dust in a swine finishing barn. *Trans. ASAE.* **2004**, *47*, 1231-1238.
13. Cai L.; Koziel, J.A.; Lo, Y.C.; Hoff, S.J. Characterization of VOCs and odorants associated with swine barn particulate matter using SPME and gas chromatography-mass spectrometry-olfactometry. *J. Chromatogr. A.* **2006**. *1102*, 60-72.
14. ASTM. E697-91. Standard practice for determining odor and taste thresholds by force-choice concentration series method of limits. 2001. In *Annual Book of Standards*. Philadelphia, PA. American Society of Testing and Materials.
15. CEN. *Determination of odor intensity using dynamic serial dilution olfactometry*. Draft European Standard CEN/TC264. January 21, 1999.
16. Koziel, J.A.; Spinhirne, J.P.; Lloyd, J.; Parker, D.B.; Wright, D.; Kuhrt, F. Evaluation of sample recoveries of malodorous gases for odor bags, SPME, air sampling canisters, and sorbent tubes. *J. Air & Waste Manage Assoc.*, **2005**, *55*, 1147-1157.
17. Rabaud, N.; Ebeler, S.; Ashbaugh, L.; Floccinni, R. Characterization and quantification of odorous and non-odorous volatile organic compounds near a commercial dairy in California. *Atmos. Env*. **2003**, *37*, 933-940.
18. Willig, S.; Lacorn, M.; Claus, R. Development of a rapid and accurate method for the determination of key compounds of pig odor. *J. Chromatogr. A.* **2004**, *1038*, 11-18.
19. Trabue, S.L.; Scoggin, K.; Koziel, J.A. Relative humidity and its effect on the breakthrough volumes and analysis of volatile fatty acids on sorbent tubes. In *Proceedings of the joint AWMA and WEF International Conference on Animal*

Agriculture and Processing: Managing Environmental Impacts, St. Louis, MS; AW&MA: Pittsburgh, PA. 2005. Paper #05-A-AGR-4-AWMA.

20. Pelletier, F.; Marquis, A.; Godbout, S.; Jonkas, R.; Larouche, J.-P.; Masse, D.; Begue, P. Gas and odor emissions from swine building materials. *Trans. ASAE*. **2005**, *48*, 721-728.
21. Wright, D.W.; Nielsen, L.; Eaton, D.; Kuhrt, F.; Koziel, J.A.; Spinhirne, J.P.; Parker, D.B.. Multidimensional GC-MS-olfactometry for identification and prioritization of malodors from confined animal feeding operations. *J. Agric. Food Chem.* **2005**, *53*, 8663-8672.
22. Wright, D.W.; Mahler, K.O.; Ballard, L.B. The application of an expanded multidimensional GC system to complex fragrance evaluations. *J. Chrom. Sci.* **1986**, *24*, 60-65.
23. Wright, D.W. Application of multidimensional gas chromatography techniques to aroma analysis. In: Techniques for Analyzing Food Aroma (Ray Marsili, ed.). 1997. Marcel Dekker, Inc., NY, 113-141.
24. Wark, K.; Warner, C.F.; Davis, W.T. *Air Pollution: Its Origin and Control.* Third edition; Addison Wesley Longman, Inc.: 1998.
25. Koziel, J.A.; Pawliszyn, J. Air sampling and analysis of VOCs with solid phase microextraction. *J. Air & Waste Manage. Assoc*. **2001**, *51*, 173-184.
26. Davis, W.T. *Air Pollution Engineering Manual*. Eds.; John Wiley & Sons: New York, NY, 2000.

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Figure captions

Figure 1. Layout of sampling locations.

Figure 2. Comparison of selected compounds on steel plates exposed for 1, 4, and 7 days inside, outside, and at a distant location from a swine barn.

Figure 3. Swine PM as an odor carrier: Comparison of odorants in swine PM and air vs. air (no PM) collected for 7 days inside (part A), outside (part B), and distant from (part C) a swine barn in Iowa.

Figure 4. Swine PM as an odor carrier: comparison of the total odor (measured as the sum of odor intensity and odor duration for all odor/aroma events) collected on steel plates exposed for 7 days inside, outside, and at a distant location from a swine barn.

Figure 5. Total offensive odor area for steel plates exposed for 1, 3, and 7 days inside, outside, and distant from a swine barn. All plates were rinsed.

Figure 6. Separations on a pre-column in GC-FID-O mode: comparison of chromatogram (FID) and aromagram for the headspace of steel plates exposed to air at a swine barn. Description of odor is in Table 5.

Figure 7. Separations in MDGC-MS-O mode with heart-cutting between pre-column and analytical column: comparison of the FID chromatogram, total ion chromatogram and aromagram isolating only characteristic offensive odorants.

Figure 8. Comparison of the mean total Odor Area (product of odor intensity and odor duration) (Part A) and mean intensity (Part B) caused by p-cresol and evaluated by 3 panelists using MDGC-MS-O analyses. Error bars signify one standard deviation around the mean.

Table 1. Listing of selected past studies on swine odor, techniques used, and number of compounds identified.

Author	Year	Sample Preparation/Sampling	Analysis	Number of Compounds Identified
Schiffman et. al	2001	TD/solvent extraction	GC-MS, GC-FID, GC-FPD	331
Yasuhara et al	1984	Solvent extraction	GC-MS, GC-O	31
Willig et al	2004	SPE	GC-FID, HPLC-Fluorescence	12
Zahn et al	2001	Thermal desorption	GC-MS-sensory panel	22
Rabaud et al	2003	Thermal desorption	GC-MS	35
Hammond et al	1979	Solvent extraction	GC-FID	35 (in PM)
Hammond et al	1981	Solvent extraction	GC-FID	19 (in PM)

Table 2. Summary of swine plate sampling locations, dates, and weather events. All plates were deployed on March 4, 2005.

Plate Number	Sampling Location	Sampling Duration (Days)	Comments	Number of Rain/Snow Events
10	Inside	1	Rinsed	
11	Inside	4	Rinsed	
12	Inside	7	Rinsed	
13	Inside	7	Rinsed	
14	Inside	7	Rinsed	
15	Distant	1	Rinsed	
16	Distant	4	Rinsed	1
17	Distant	7	Rinsed	2
18	Distant	7	Rinsed	2
19	Distant	7	Rinsed	2
20	Distant	7	Not Rinsed	2
21	Distant	7	Not Rinsed*	2
22	Outside	1	Rinsed	
23	Outside	4	Rinsed	1
24	Outside	7	Rinsed	2
25	Outside	7	Rinsed	2
26	Outside	7	Rinsed	2
27	Inside	7	Not Rinsed	
28	Inside	7	Not Rinsed*	
40	Outside	7	Not Rinsed	2
41	Outside	7	Not Rinsed*	2

*Note: Analyzed at Microanalytics; Rain event on 3/6/05 & rain/snow event on 3/11/05

Table 3. Relative standard deviation among compounds in n = 3 identically treated plates exposed 7 days inside, outside, and at a distant location from a swine barn.

Compound Name	CAS Number	RSD (%) Inside	RSD (%) Outside	RSD (%) Distant
Carbon disulfide	75-15-0	7.5	56.5	24.1
3-Methyl-butanal	590-86-3	29.4	64.8	n/d
Diacetyl	431-03-8	14.7	16.8	n/d
Dimethyl disulfide	624-92-0	72.5	47.6	n/d
Octanal	124-13-0	56.7	44.0	n/d
Dimethyl trisulfide	3658-80-8	45.3	51.6	n/d
p-Cresol	106-44-5	40.1	61.7	25.76

Note: RSD is the ratio of relative standard deviation to the mean; n/d = not detected.

Table 4. Relative difference (%) of selected VOC's and odorants associated with samples with swine PM compared with samples with no PM collected with steel plates exposed for 7 days inside, outside, and at a distant location from a swine barn.

Name (Single Ion)	CAS	Inside (%)	Outside (%)	Distant (%)
Carbon disulfide (76)	75-15-0	14.9	34.1	45.7
Butanal, 3-methyl- (58)	590-86-3	100	93.0	
Diacetyl (86)	431-03-8	95.8	100	
Dimethyl disulfide (79)	624-92-0	99.4	93.0	
Hexanal (72)	66-25-1	97.3	98.9	26.3
Octanal (57)	124-13-0	79.9	91.3	
Dimethyl trisulfide (126)	3658-80-8	99.9	99.0	
Acetic acid (60)	64-19-7	99.1	98.4	36.6
Nonanal (57)	124-19-6	88.7	99.2	
Butyric acid (60)	107-92-6	100	100	
Isovaleric acid (60)	503-72-4	100	100	
p-Cresol (107)	106-44-5	98.3	99.5	58.1
Skatole (130)	83-34-1	100	100	
Average		90.3	92.8	41.7
Standard Deviation		23.4	17.9	13.5
Minimum		14.9	34.1	26.3
Maximum		100	100	58.1

Table 5. Summary of GC retention times, odor intensities, odor event start, odor duration, and specific regions selected for subsequent isolation with heart-cutting for swine odor sample shown in Figures 6 and 7.

#	Odor character tag	Odor I %	Odor start min	Odor D min	Odor area I×D×100	HC min
1	Fecal, sewer	30	0.70	0.06	179	HC 1
2	Sweet, buttery, acidic	50	0.99	0.20	998	
3	Sweet	31	1.32	0.07	216	
4	Acidic	30	1.43	0.12	359	
5	Grassy	40	1.66	0.07	279	
6	Plastic	31	2.27	0.07	216	
7	Winey, sweet, acidic, garlic, plastic	51	2.73	0.40	2,036	
8	Grassy, herbaceous, plastic	51	3.36	0.22	1,120	HC 2
9	Skunky, buttery, body odor, fatty acid	50	3.75	0.66	3,294	HC 3
10	Body odor, fatty acid	50	5.00	0.18	898	
11	Body odor, medicinal, fatty acid	40	5.24	0.40	1,597	
12	Plastic	31	5.99	0.16	495	
13	Body odor	10	6.65	0.12	119	
14	Soapy	7	7.52	0.03	20	
15	Fruity, burnt food	30	7.65	0.25	748	
16	Mushroom, earthy, moldy, musty	50	8.00	0.50	2,495	
17	Mushroom, earthy, moldy, musty	50	8.62	0.53	2,645	
18	Winey	7	9.29	0.03	20	
19	Burnt food	10	9.89	0.12	119	
20	Acidic, winey, body odor	10	10.34	0.16	159	
21	Barnyard, phenolic, medicinal, **characteristic**, naphthalenic, piggy, taco shell	91	10.52	1.80	16,352	HC 4
22	Buttery, barnyard, **characteristic**, body odor, burnt food, taco shell	31	12.69	0.93	2,878	
23	Taco shell, naphthalenic, cardboard, plastic	10	14.95	0.60	599	
24	Naphthalenic, phenolic, **characteristic**, piggy, barnyard	51	15.94	2.56	13,034	HC 5

Note: I = odor intensity, D = odor duration, HC = specific regions selected for subsequent isolation via heart-cutting

Table 6. Summary of odor analyses by panelists.

	Three Panelists			mean	St. dev.	RSD (%)
	1	**2**	**3**			
Odor events in GC-O mode	24	23	20	22.3	2.08	9.32
Odor events in MDGC-O mode	21	23	8	17.3	8.14	47.0
Total odor	58,800	39,100	8,300	35,400	25,500	71.9
	One Panelist			**mean**	**St. dev.**	**RSD (%)**
	3	**3**	**3**			
Odor events in MDGC-O mode	8	10	7	8.33	1.53	18.3
Total odor	8,300	21,400	10,300	13,300	7,000	52.7