Final Report

Development of a Standardized Method for Odor Quantification from Livestock Production Facilities: Final Report on Stages I and II

Project Number: 99-056

Participants in Stages I and II
Alan A. DiSpirito[1], James A. Zahn[1,3,4], , Young S. Do[1], Brian E. Brooks[2], Daniel W. Russell[2], Eric E. Cooper[2], and Jerry L. Hatfield[4]

Departments of Microbiology[1] and Psychology[2], Iowa State University, National Swine Center[3] and National Soil Tilth Laboratory, United States Department of Agriculture, Ames, IA 50011

ABSTRACT/SUMMARY

Anaerobic processing of livestock wastes results in the production of air pollutants including volatile organic compounds (VOCs), methane, hydrogen sulfide, ammonia, and odors. Quantification of odor and trace gases from animal production facilities have traditionally been addressed in separate, unrelated research efforts due to analytical difficulties associated with the measurement of low concentrations of analytes in air samples. As a result, there is currently a lack of information concerning the ambient air concentration range and chemical identity of odorant compounds released from stored animal manure. This lack of information has impeded research efforts focused on the development of emission abatement strategies and has necessitated the use of subjective, low-throughput odor measurement methods.

In this study, direct measurements of malodorous VOCs present in ambient air samples from 29 swine production facilities were used to develop a 19 component VOC odorant standard that was observed to mimic olfactory properties of swine manure. The emission profile for the standard VOC solution was optimized in a laboratory dynamic emission chamber to simulate VOC emission profiles of swine effluent. Following the emission optimization process, the dynamic emission chamber was modified to deliver air samples containing the VOC standard to a nose cone. Analyses employing either a human panel consisting of 14 subjects or gas chromatography were performed on the air stream from the emission chamber to assess human olfactory responses or odorant concentration, respectively. The ability of subjects to distinguish different air concentrations of the VOC standard was assessed by presenting six dilutions of the VOC standard to panelists. Concentration range was based on an average just detectable to intolerable range. Panelists were asked to compare odor intensity of each of the six air samples to a VOC reference standard of defined magnitude. Analysis of the responses using Fisher's LSD statistics showed that the subjects were sensitive to changes in air concentration of the VOC standard across dilutions differing by 17%. The effect of chemical synergisms and antagonisms on human olfactory response magnitudes was assessed by altering the concentration of individual components in the VOC standard over a 2-fold concentration range while maintaining the other 18 components of the VOC standard at a single air concentration. A statistically significant synergistic olfactory response was observed to occur when the air concentration of acetic acid or 3-methyl indole (skatole) was increased relative to the concentration of other VOC odorants in the standard. A statistically significant antagonistic olfactory response was observed when the air concentration of acetic acid, 3-methyl indole, isovaleric acid, isocapropic acid, and caprioc acid was increased relative to the other VOC odorants in the standard. In contrast, relative increases in the amount of 4-ethyl phenol, and indole tended to *decrease* subjects' ratings of the odor intensity of the mixture. The collective odorant responses for swine waste VOC were utilized to develop a prediction model to estimate human odor response magnitudes through measured air concentrations of "indicator" VOC odorants.

INTRODUCTION

Modern swine management practices have undergone extensive changes during the last two decades in an effort to improve animal production efficiency, to reduce animal mortality, and to provide safer, higher quality animal products (Barker et al., 1996). These improvements in production efficiency have transformed the infrastructure of the swine industry, allowing producers to effectively manage larger populations of animals on production sites. The recent expansion of concentrated animal feeding operations (CAFOS) throughout the United States has catalyzed an increased awareness by the general public and governmental agencies for the potential impacts of these facilities on water and air quality. Recent air quality studies have shown that CAFOS can adversely affect air quality through the release of odor (Jacobson et al., 1997a; Zahn et al., 1999), hydrogen sulfide (H_2S) (Jacobson et al., 1997b), ammonia (NH_3) (Asman, 1995), nitrous oxide (N_2O) (Eklund and LaCosse, 1995), methane (CH_4) (Safley et al., 1992), volatile organic compounds (VOCs) (Zahn et al., 1997; Zahn et al., 1999), particulate matter (VanWicklen, 1997), and bacterial pathogens (Cole et al., 1999).

Efforts to remediate odor from swine production facilities have been impeded by the lack of instruments capable of high-throughput odor measurements. The desire to develop high-throughput, inexpensive methods of odor quantification has been the impetus for several recent investigations that have focused on defining relationships between gas concentration of odorants emitted from animal manure and odor intensity measured by olfactory methods (Hobbs et al., 1995; Jacobson et al., 1997a; Jacobson et al., 1997b; Obrock-Hegel 1997; Pain et al., 1990). Obrock-Hegel (1997), found that nutritional manipulation of amino acid intake reduced NH_3, cresols, and indoles measured in air samples from production environments. However, no reduction in odor concentration was observed between control and treatment samples. Schulte et al. (1985) and Hobbs et al. (1995), linked high levels NH_3 to odor. Unfortunately, the latter authors noted that the relationship between NH_3 and odor could not be universally applied to all farms, especially when they differed in the type of manure management system utilized. The use of H_2S as a surrogate of livestock waste odor has also proven to be a formidable challenge. Jacobson et al., (1997a) evaluated odor and H_2S concentration in air from approximately 60 different pig, dairy, beef, and poultry manure storage units on farms in Minnesota. Low correlation was observed between H_2S and odor concentration for manure storages based on a species comparison and for production systems grouped according to manure management system type (pit, basin, and lagoon). The study further suggested the possibility that chemical odorants other than H_2S (i.e., VOCs) were responsible for swine odor. In support of this hypothesis, Powers et al., (1999) recently demonstrated that solution-phase concentrations several VOCs present in anaerobic digester effluent were positively correlated with odor intensity. However, solution-phase concentration of VOC did not predict odor intensities well enough to suggest that human panels should be eliminated. Data quality in the latter study was compromised by the fact that odor responses were correlated to solution-phase concentrations of odorants, rather than to direct measurements of odorants present in air samples. Previous studies have established the importance of using air-phase concentrations of odorants when performing correlations to odor concentration, since VOC volatilization rates are highly matrix-dependent (Hobbs et al., 1995; MacIntyre et al., 1995; Zahn et al., 1997). Problems associated matrix-dependent odorant volatilization were recently overcome by performing direct chromatographic analyses of air samples that were simultaneously evaluated for odor intensity by human panels (Zahn et al., 1999). By using this air-phase sample collection approach, it was shown that odor intensity from 29 swine production facilities correlated strongly ($r^2 = 0.88$) to the concentration of 19 volatile organic compounds present in ambient air samples. While this study provided evidence that direct multicomponent analysis of VOCs may be useful in monitoring livestock odor, several important details concerning fundamental properties of individual odorants and the behavior of these odorants in complex mixtures were not addressed in this study.

The aims of this study are similar to that of Zahn et al., (1999) in our desire to develop an instrument-based odor quantification method for CAFOS that is based on the air concentration of specific odorants. In addition to this aim, there is currently a need to define olfactory properties of odorant reference standards that were previously described by Zahn et al., (1999). The objectives of this study were: i) to validate the selection of odorants present in the reference standard by comparing the chemical profile to the chemical profile of stored swine manure samples, ii) to construct and validate an emission chamber for reproducible delivery of an air stream containing the indicator odorants to a absorbent tube and a nose cone for chemical and olfactory evaluation, respectively. iii) to define organoleptic properties of the odorant mixture at different air-phase concentrations. iv) to define synergistic and antagonistic responses between indicator odorants.

OBJECTIVES

The objectives of this proposal were:

1. Determine the antagonistic and synergistic effects of each in the swine odor mixture on the panel's response by:
    a. Vary the concentration each analyte individually.
    b. Vary the concentration of combinations of analytes in the mixture.
2. Create a multiple regression model, which would give a precise numerical value for the amount of smell at a particular site given an assay of the chemical composition in the atmosphere at the site.
3. Field tests the model

III. **Progress toward meeting objectives.**

All objectives have been meet and the material is published, in press and we are in the process of writing the final paper.

Publications in Referenced Journals

Zahn, J.A., J.L. Hatfield, Y.S. Do, and A.A. DiSpirito. 2001. Functional classification of swine waste management systems based on gas emission rates and solution-phase properties: The inadequaticy of animal numbers in the prediction of pollution potential. Journal of Environmental Quality. *in press March issue 2001.* (manuscript inclosed)

Zahn, J.A., A.A. DiSpirito, Y.S. Do, B.E. Brooks, E.E. Cooper, and J.L. Hatfield. 2001. Correlation of human olfactory responses to airborne concentrations of malodorous volatile organic compounds emitted from swine effluent. Journal of Environmental Quality. *in press March issue 2001.* (manuscript enclosed

Conference Proceedings

Zahn, J.A., J.L. Hatfield, Y.S. Do, and A.A. DiSpirito. 2000. Air Pollution from swine production facilities differing in waste management practice. *In.* Odors and VOC Emissions 2000. Water Environment Federation. .

Zahn, J.A., A.A. DiSpirito Y.S. Do, B. E. Brooks, D.W Russel, and E.E. Cooper. 2000. Correlation of human odor response magnitudes to air concentrations of malodorous volatile organic compounds associated with swine manure odor. *In.* Odors and VOC Emissions 2000. Water Environment Federation.

Published Abstracts

Zahn, J.A., A. A. DiSpirito, Y. S. Do, B. E. Brooks, and E. E. Cooper, and J. L. Hatfield, (2000), Correlation of Human Odor Response Magnitudes to Airborne Concentrations of Malodorous Volatile Organic Compounds Emitted From Stored Swine Manure, Abstracts of the American Society of Animal Science (Midwestern Section), (DesMoines, IA) (conference abstract)

Zahn, J.A., A. A. DiSpirito, Y. S. Do, and J. L. Hatfield, (2000), Air Pollution from Swine Production Facilities Differing in Waste Management Practice, Abstracts of the American Society of Animal Science (Midwestern Section), (DesMoines, IA).

METHODOLOGY/PROCEDURES

Composition of Odorant Solutions

Sensory responses were measured for solutions containing 19 volatile organic compounds that were previously correlated to odor from commercial swine production facilities (Zahn et al., 1999). The chemical composition of synthetic swine odor Z2 was optimized in a laboratory dynamic flux chamber to mimic emission parameters for VOCs emitted from manure collected from a high-odor, Type 1 swine manure management system. The synthetic swine odor solution Z2 (Zahn and DiSpirito, 1999), consisted of: 0.05 mM dimethyl disulfide, 8 mM acetic acid, 3.5 mM propionic acid, 0.5 mM isobutyric acid, 0.4 mM 2-butanol, 1.4 mM butyric acid, 0.2 mM isovaleric acid, 0.5 mM valeric acid, 0.1 mM isocaproic acid, 0.2 mM caproic acid, 0.2 mM heptanoic acid, 0.1 mM indole, 0.15 mM 3-methyl indole, 0.2 mM 4-methyl phenol, 0.12 mM 4-ethyl phenol, 0.15 mM phenol, 0.1 mM benzyl alcohol, 0.1 mM 2-amino acetophenone, 0.1 mM butylated hydroxytoluene, and 8 mM ammonium acetate. Pure compounds (Aldrich Chemical Co., Milwaukee WI) were dissolved in warm (45° C) double distilled water (ddH$_2$O) while stirring and the solution pH was frequently adjusted to pH 6.8 with 2 M potassium hydroxide.

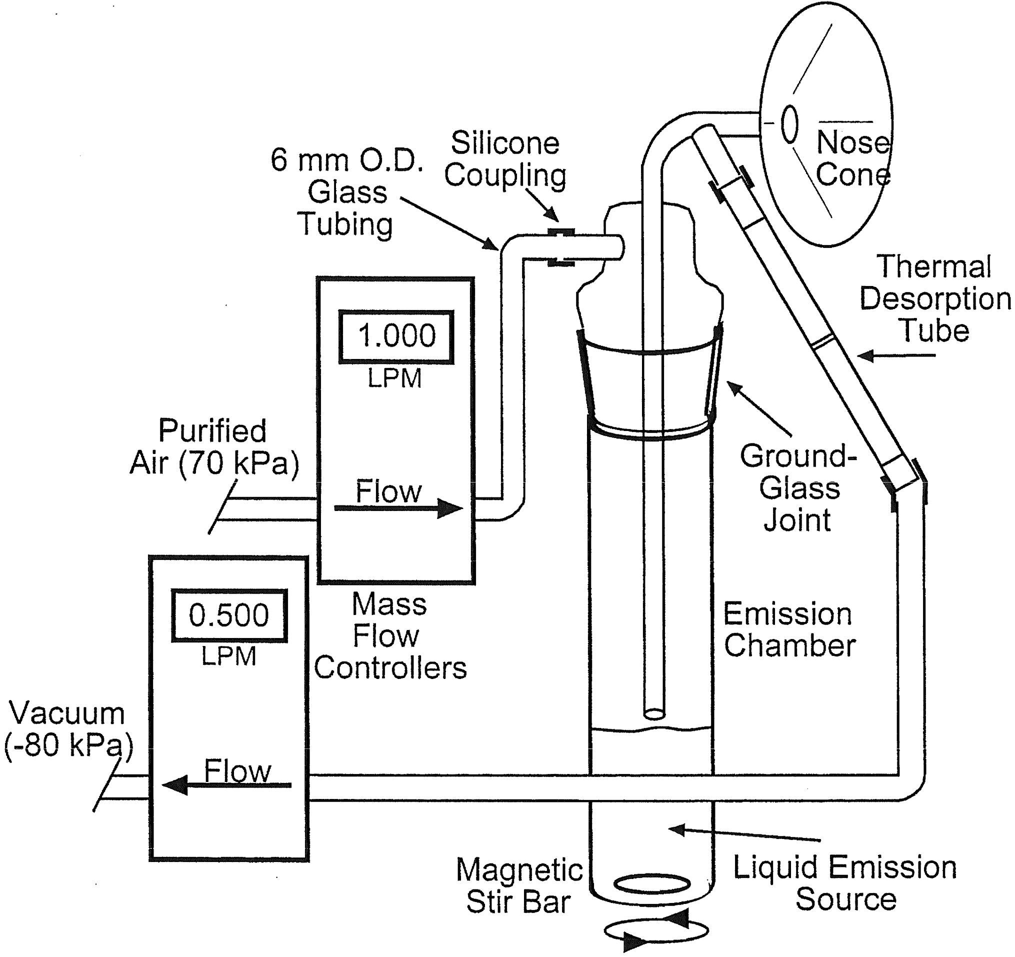
The reference stimulus solution was produced by diluting synthetic swine odor solution Z2 in an equal volume of ddH$_2$O. Odorant solutions were formulated within one hour of human evaluation to reduce variation due to loss of the odorants through volatilization or chemical decomposition and were maintained at 21.0 ± 1.1°C during all procedures. Two series of experimental stimuli were formulated for olfactory studies: First, the effect of odorant concentration on olfactory responses was evaluated by preparing by 6 dilutions (83%, 67%, 50%, 33%, 17%, 1%) of synthetic swine odor solution Z2 in ddH$_2$O. Second, the effect of synergistic or antagonistic interactions between odorants was investigated by doubling the concentration of individual odorants present in synthetic swine odor Z2, while maintaining the remaining 18 odorants at concentrations equivalent to synthetic swine odor Z2. The latter odorant preparations were diluted over the same concentration range (100%, 83%, 67%, 50%, 33%, 17%, 1%) used in the first series of experimental stimuli trials.

Emission Chamber Design and Operational Parameters

Olfactory and chemical quantification of VOC odorants were performed on the gas stream emitted from the dynamic emission chamber shown in figure 1. Compressed air was purified by passage over activated carbon and then was introduced to the dynamic emission chamber at a height of 10 cm above the odorant solution. The flow of clean air was maintained at 1000 $\mathrm{mL}\bullet\mathrm{min}^{-1}$ (±1.2%) using a thermal mass flow controller (series 810, Sierra Instruments, Inc., Monterey, CA). The flow of air through the chamber proceeded downward towards the surface of the odorant solution and then exited the emission chamber through a glass transfer tube that was positioned 1 cm from the surface of the odorant solution. The odorant-containg gas was forced up the transfer tube to a nose cone and sampling tee for olfactory and chemical analyses, respectively. The sampling tee was positioned at the base of the nose cone to eliminate potential discrepancies between olfactory and chemical measurements due to non-equivalent flow paths.

Odorant solutions (50 mL) and a single 1.5 cm magnetic stir bar were introduced into the chamber through a ground-glass joint at the top of the chamber. The chamber was then closed and fixed on a magnetic stir plate inside a cabinet (3.0 m^3) equipped with an exhaust fan (exhaust rate = 3.1 $\mathrm{m}^3 \bullet \mathrm{min}^{-1}$). Upon start-up of the dynamic emission chamber, the initial five minutes (~5 liters of odorant-containg gas) of operation were dedicated to equilibrating the flow path to odorants present in the gas stream. During this equilibration period the exhaust fan was operated to remove odorants from the cabinet. After the equilibration period, the fan was shut off and the air stream was sampled by human panelists or by chemical methods. Chemical and human olfactory analyses were conducted separately in order to minimize potential interferences with human olfactory evaluations. Olfactory evaluations of odorant air streams were conducted using full air flow through the dynamic emission chamber (1000 $\mathrm{mL}\bullet\mathrm{min}^{-1}$). The exhaust fan was operated for 1 minute after each evaluation to remove residual odorants from the sampling area and air temperature in the evaluation area was maintained at 21.0 ± 1.1° C during measurements. Comparisons between the reference stimulus and experimental stimuli were performed by placing a second dynamic emission chamber in the evaluation cabinet at a distance of 0.35 m from the reference stimulus. The second chamber is referred to as the "experimental stimulus".

FIGURE 1. Design of the dynamic emission chamber.



Volatile organic compounds present in the air stream were trapped on adsorbent resins at the sampling tee, using a flow rate of 950 mL•min^{-1}. The adsorbent resins consisted of a multibed combination of Tenax TA and Carboxen-569 as previously described by Zahn et al., (1997). Compounds captured on the adsorbent tubes were transferred to a gas chromatograph, following the thermal desorption process, and were detected by flame ionization or by a mass selective detector as previously described by Zahn et al. (1997).

Scale Development and Sensory Panel Design

Development of a scale to measure the effects of odorant concentration was completed using Steven's magnitude estimation technique with fourteen human panelists (Stevens, 1957, 1961, 1962). Subjects were presented with an odorant air stream from an emission chamber containing the reference stimulus solution and were instructed that the stimulus had an intensity value of 100 (arbitrary) odor intensity units. Panelists were then instructed to sample an air stream from a second chamber (experimental sample) and to score the intensity of the odor relative to the reference stimulus. For example, if the subject perceived that the intensity of an experimental sample was half that of the reference stimulus, then a value of 50 was reported for the experimental sample. If the subject perceived that the odor was 75% more intense than the reference stimulus then a value of 175 was reported for the experimental sample. Odor intensity scores were reported between a range of 0 and 200 relative odor intensity units.

Magnitude estimation studies have shown that the perceived magnitude of a stimulus is a power function of the intensity of the stimulus (Stevens, 1957, 1961, 1962). The mathematical relationship between perceived magnitude and physical intensity of the stimulus (Steven's Law) is:

$$P = k^{*}I^{b} \text{ where:}$$

P = the experimentally-defined perceived magnitude of a stimulus; k = a stimulus-dependent constant that represents the intercept of the line function; b = a stimulus-dependent constant that represents the slope of the line function; I = the actual physical intensity of the stimulus.

The magnitude estimation technique was used with two different panels of 14 human subjects. The panel ranged in age from 18 to 40 years and was composed of an equal number of male and female subjects to minimize gender bias. In the first stage of the study, subjects were presented with synthetic swine odor solution Z2 and five dilutions of the solution (100%, 83%, 67%, 50%, 33%, 17%, 1%) as described in the "Composition of Odorant Solutions" section. The solutions were place in emission chambers with encrypted labels and were randomly positioned in the experimental stimulus position throughout the study. Individuals on the panel were instructed to score the physical intensity of each experimental stimulus relative to the reference stimulus. In subsequent stages of the study, the panel was presented with 18 different experimental stimuli, differing only in the concentration of a single odorant. The concentration of a single odorant in the solution was doubled from the original concentration value, while other odorants (the remaining 18) present in the solution were unchanged. Solutions were again diluted over a concentration range from 100% to 1%, and then placed in emission chambers for presentation to the panel. Based on the results from experiments doubling the concentration of single odorant, three double odorant solutions were tested. In these studies the concentrations of 4-ethyl phenol + *p*-cresol, acetic acid + heptanoic acid, and isovaleric acid + phenol were doubledfrom the original concentration value, while other odorants (the remaining 18) present in the solution were unchanged. Solutions were again diluted over a concentration range from 100% to 1%, and then placed in emission chambers for presentation to the panel.

The order in which the first 14 subjects sampled the odorants was balanced using a Latin Square to reduce sampling bias. Panelists evaluated each experimental stimulus twice during individual sessions. Each subject would compare the experimental stimulus to the reference stimulus in one serial order, and then would be presented the same samples for a second trial in a different serial order. Thus, the effects of the presentation order could be randomized in order to reduce sampling bias. Panelists were allowed to evaluate odor stimuli as many times as they wished before reporting the stimulus score to the panel operator. Individual sampling sessions for the duplicate analysis of 6 experimental stimuli were completed in 15 minutes for individual panel members and were performed on two separate days during the same week.

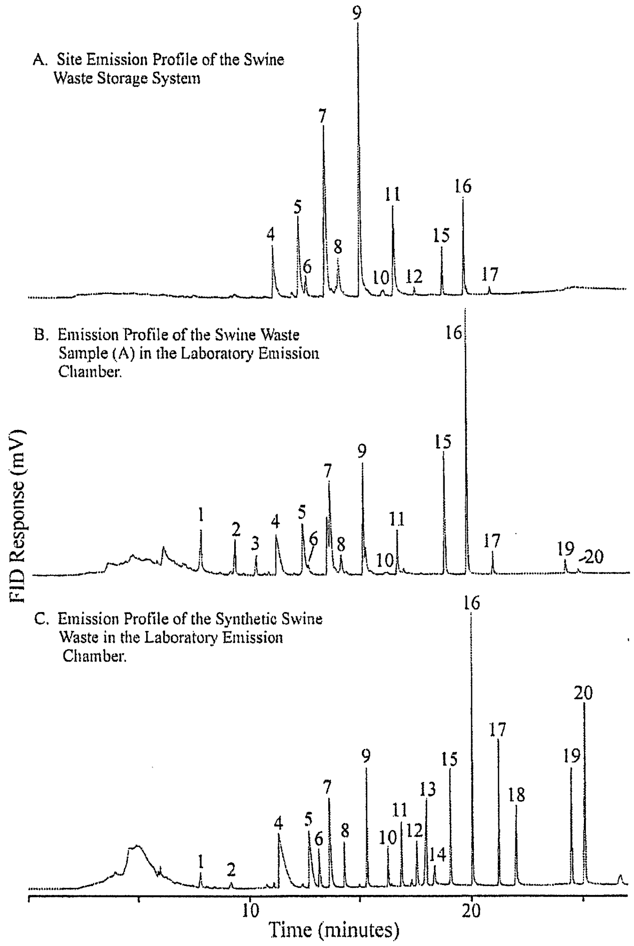
RESULTS AND DISCUSSION

Development of Synthetic Swine Odor Z2

Synthetic swine odor Z2 consists of a buffered mixture of volatile organic compounds in an aqueous solution. The constituents of this solution were selected based on the qualitative analysis of ambient air samples (n = 328) collected from 29 swine production facilities located in Iowa, North Carolina, and Oklahoma (Zahn et al., 1997; Zahn et al., 1999). The concentration of compounds in the solution was determined empirically by comparing emission profiles of swine manure samples collected from the 29 sites to the emission profiles from mixtures of pure odorants using the dynamic emission chamber. A series of chromatograms collected for one comparison is shown in Fig. 2. The identity and properties of compounds separated in chromatograms are described in Table 1. Typical ambient air concentrations for compounds present in the synthetic swine odor solution ranged from approximately equal to the odor threshold to almost 4000-fold above the odor threshold in the case of 3-methyl indole (Table 1). In addition to validating the synthetic swine odor solution by chemical emission parameters, qualitative odor characteristics of the solution were determined for odor solution Z2 and for 6 dilutions of this solution. Individually, few of the compounds had a distinct manure odor character. However, the collective odorant properties of VOCs present in the synthetic swine odor solutions were found to simulate olfactory properties of swine manure odor (Table 2).

Over 200 volatile organic compounds have been identified from solid and liquid swine manure, however, few of these laboratory studies have confirmed the presence and concentration of these compounds in ambient air samples near swine production facilities (Mackie et al., 1999). In addition to the constituents of synthetic swine odor Z2, a number of other odiferous compounds, such as amine and sulfide-containing compounds, have been associated with swine manure odor based on studies that have detected these compounds in the solution-phase of manure (Yasuhara et al., 1984). However, hydrogen sulfide, sulfide and amine-containing compounds are often not detectable in ambient air samples from swine production facilities (Zahn et al., 1997; Zahn et al., 1999). It has been well established that sulfides and amines are inherently unstable in oxidized atmospheres due to their high chemical reactivity. Sulfides are weak monoprotic and polyprotic (H_2S) acids that are highly reactive under aerobic conditions and neutral pH. Ammonia and amines, on the other hand, are weak bases that play a major role in neutralization of sulfur dioxide and nitrogen oxides in the atmosphere (Harper and Sharpe, 1996). Acid/base neutralization of air pollutants has been shown to produce salts that contribute to chemically-generated particulate matter in the atmosphere. While there is currently little direct evidence to explain the absence of these compounds in ambient air samples, the presence of high concentrations of disulfides such as dimethyl disulfide (the oxidation product from two molecules of methyl mercaptan) and dimethyl trisulfide (the oxidation product from hydrogen sulfide and two methyl mercaptan) provides indirect evidence that free sulfides are readily oxidized in the atmosphere or during sample collection and analysis procedures. In contrast, VOCs in synthetic swine odor Z2 are more chemically-stable than sulfides and amines-containing compounds and have high atmospheric transport coefficients (Zahn et al., 1997). These compounds are therefore, ideal candidates for the synthetic swine odor solution.

FIGURE 2. Chromatographic profiles of organic compounds present in A) ambient air samples from a swine production facility, B) swine manure slurry in an emission chamber, and C) synthetic swine odor Z2. Peak numbers refer to the compounds listed in table 1.



A. Site Emission Profile of the Swine Waste Storage System

B. Emission Profile of the Swine Waste Sample (A) in the Laboratory Emission Chamber.

C. Emission Profile of the Synthetic Swine Waste in the Laboratory Emission Chamber.

TABLE 1. Odor characteristics, olfactory thresholds, and recommended exposure limits for volatile organic compounds identified from air samples at swine production facilities.

Organic Compound and Peak Identification Number	Typical Air Conc. (mg/m^3)†	Ref.	Odor Characteristic	Odor Threshold (mg/m^3)‡	Recommended TWA Limits (mg/m^3)
Hydrogen sulfide	0.050	1	Rotten eggs	0.140	14
Ammonia	3.70	1	Sharp, pungent	0.027-2.2	18
1. Dimethyl disulfide	0.017	1	Putrid, decayed vegetables	0.0011-0.61	-
2. 2-Butanol	0.019	1	Alcohol	0.11	305
3. Dimethyl trisulfide	0.013	1	Nauseating	0.0072-0.023	-
4. Acetic acid	0.520	2	Pungent	0.1-2.5	25
5. Propionic acid	2.150	2	Fecal	0.0025	30
6. Isobutyric acid	0.580	2	Fecal	0.00072	-
7. Butyric acid	1.170	2	Fecal, stench	0.00025	-
8. Isovaleric acid	0.098	1	Fecal	0.00017	-
9. n-Valeric acid	0.360	1	Fecal	0.00026	-
10. Isocaproic acid	0.010	1	Stench	0.0020	-
11. n-Caproic acid	0.740	2	Fecal	0.0020	-
12. Heptanoic acid	0.008	1	Pungent	0.0028	-
13. Benzyl alcohol	1.900	2	Alcohol	nd	-
14. Phenol	1.360	2	Aromatic	0.23-0.38	19
15. 4-Methyl phenol	4.230	2	Fecal	0.0021-0.009	22
16. 4-Ethyl phenol	1.040	2	Pungent	0.0035-0.010	25
17. 2-Amino acetophenone	1.090	2	Fruity, ammonia	nd	-
18. Indole	0.002	1	Fecal	0.0019	
19. Hexadecanoic acid	0.009	1	Pungent	nd	-
20. 3-Methyl indole	0.002	1	Fecal, nauseating	0.0000005-0.0064	-

† Typical ambient air concentration at outdoor emission source.

‡ Milligrams of substance per cubic meter of air.

nd = not determined.

§ The time-weighted average concentration for a normal 8-hour workday and a 40 hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

References: 1 = Zahn, et al., 2000. 2 = Zahn, et al., 1997.

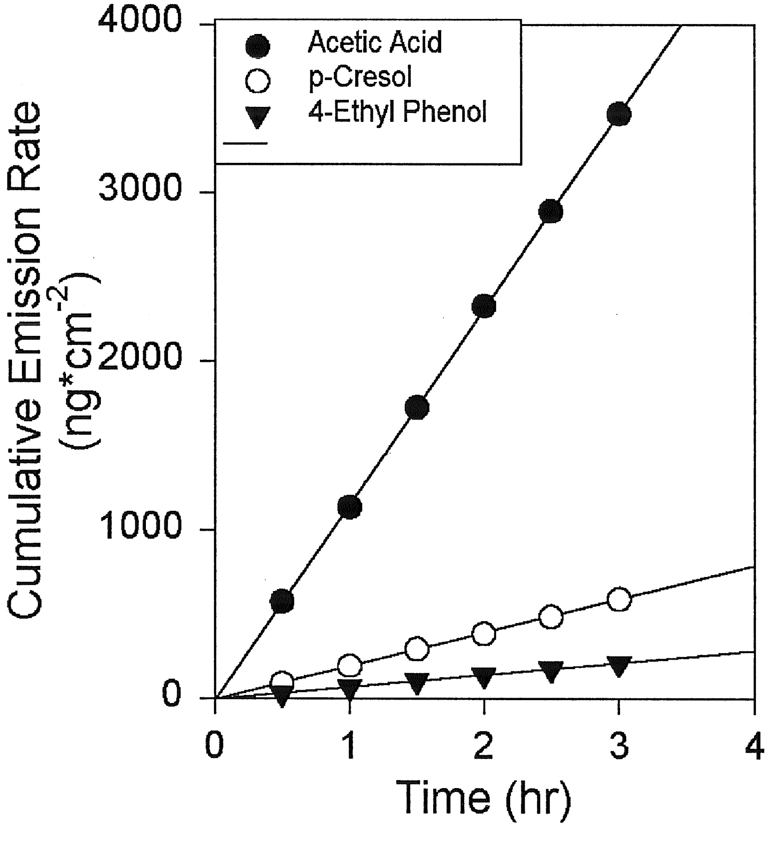
TABLE 2. Odorant qualities associated with synthetic swine odor solutions. Odorant concentrations are reported as a percent of synthetic swine odor Z2.

1%	16%	32%	50%
Barely detectable Nothing Noticeable Barely present Moderate Sweet-smelling Very mild Slightly unpleasant Mildly unpleasant	Stinky Sweeter Not all that unpleasant Mild Somewhat bothersome Dense Obvious odor Pungent	Mildly Smelly Moderate Gross Feces-like	Unpleasant Wet socks Foot odor Slightly bothersome Rotting garbage
67%	**83%**	**100%**	
Smelly Pungent Sweet Bothersome Powerful Really bad	Strong Very unpleasant Annoying Acidic Bothersome Garbage	Very bad Strong Powerful Headache Very unpleasant Ammonia Potent Sickening Very acidic Dizzying Very bothersome Astringent	

Operational Parameters of the Dynamic Emission Chamber

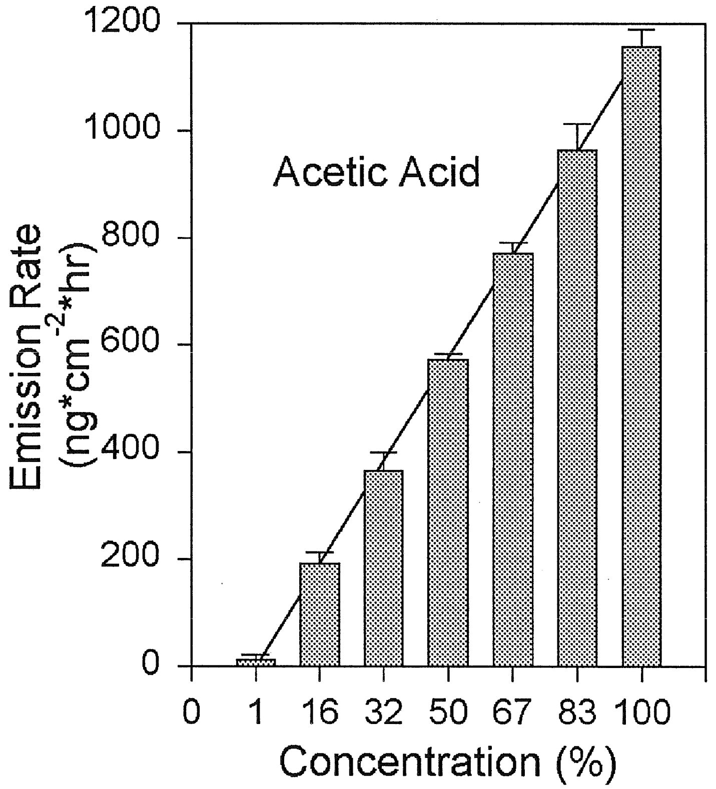
The ability to maintain a constant emission rate of VOCs at the olfactory sampling port during the course of experiments was considered a critical element in the success of the study. Therefore emission rate studies were conducted on the effluent from the dynamic emission chamber to determine: 1) if the emission rate of VOCs release from the dynamic emission chamber was constant over a typical sampling time period and 2) if emission rate of VOCs was proportional to the concentration of VOCs present in the liquid-phase of the emission source. The emission rate of 19 VOCs present in synthetic swine odor Z2 were measured by trapping the airborne analytes on adsorption tubes and by analyzing concentration changes in the liquid emission source. Adsorption samples were collected over a 3 hour period in 0.5 hour intervals from air emitted from the dynamic emission chamber. The cumulative emission rates of acetic acid, p-cresol, and 4-ethyl phenol over the 3 hour sampling period are shown in Fig. 3. The linear shape of the fitted line ($r^2 > 0.97$) shows that the emission rate for each VOC remained nearly constant during the sampling period. Analysis of the air concentration of the other 16 compounds, present in the effluent from the chamber, showed that the emission rate of these compounds also remained nearly constant over the 3 hour collection period. The concentration of VOCs present in liquid-phase of the emitting source was reduced 0.3% to 5.1% over the 3 hour collection period. Compounds such as dimethyl disulfide, which had a relatively low source concentration and high volatility showed the most noticeable changes in concentration over the sample period (5.1%), while compounds with lower volatility (4-ethyl phenol, 1.1%) or high source concentration (acetic acid, 0.3%), exhibited less change in solution concentration over the sampling period. Comparison of the total amount of VOCs recovered by adsorption tubes to the losses of analytes measured in the solution phase, showed that between 94% to 99% of the VOCs emitted from the solution were recovered.

FIGURE 3. The emission rate of VOCs present in synthetic swine odor Z2 from the dynamic emission chamber.



The effect of the solution concentration of VOCs on the emission rate of these compounds was tested for the seven VOC concentrations used in olfactometric trials by trapping analytes present in the emission stream on adsorbent resins. Solution concentration of acetic acid was found to be proportional to the emission rate of acetic acid over the concentration range tested (Fig. 4). The relationship between solution concentration and emission rate of all other VOCs present in synthetic swine odor solutions was observed to be similar to the emission behavior exhibited by acetic acid.

FIGURE 4. The effect of the solution concentration on the emission rate of acetic acid.



Panel and Scale Development

Three olfactometric trials (n = 504) were conducted on the group of 7 experimental stimuli representing synthetic swine odor Z2 and dilutions of this solution using two separate human panels of 14 individuals in each panel. The mean perceived magnitude of stimuli (P) and the physical intensity of stimuli (I) for individual trials were analyzed to determine fit to Stevens' Law (see Methodology section for equation). The best fit equation for these samples and for samples containing a 2-fold higher concentration of individual analytes is shown in Table 3. Analysis of variance for each of the odorant series shows that the data conform well to Stevens' Law and that variance in these measurements was minimal.

Several points should be noted in the analysis of Table 3. First, the value of b (the power to which I is raised) provides a measure of the slope of the best fitting curve. Higher values of b indicate greater slope meaning that mixtures with a high b value (i.e., standard + butyric acid, b = 0.432) were more affected by concentration changes than mixtures with a low b value, such as standard + heptanoic acid (b = 0.283). Also of interest is the fact that the values of b range from 0.265 to 0.432 with a mean of 0.333. Different senses can vary widely in their b values. For example, for judging the brightness of a light, the b value is approximately 0.3, while for judging the strength of electric shock, the b value is approximately 3.5. Previous olfactory research conducted on evaluating the odor intensity of coffee and heptane has reported b values near 0.5 (Stevens, 1961, 1970, 1975). The results of this study show that synthetic swine odor has values of b that are comparable to the studies of other odorants.

Also of interest were the extremely high values of r^2 that were obtained for analysis of variance. Analysis of variance showed that Stevens' Law could explain, on average, 97% of the variation in the subjects' estimates of odor intensity. This result provides evidence that the VOC delivery system produces highly reproducible olfactory stimuli.

TABLE 3. Fitting equation for the perceived odor intensity of synthetic swine odor solutions (standard) and for odorant solutions containing a two-fold concentration of individual odorants.

Odorant	**Equation**	**Measured variance (r^2)**
Standard	$P = 36.60\ I^{0.265}$	0.921
Standard + valeric acid	$P = 21.92\ I^{0.413}$	0.994
Standard + butyric acid	$P = 19.09\ I^{0.432}$	0.959
Standard + heptanoic acid	$P = 38.20\ I^{0.283}$	0.974
Standard + acetic acid	$P = 40.79\ I^{0.300}$	0.983
Standard + isobutyric acid	$P = 27.21\ I^{0.344}$	0.985
Standard + p-cresol	$P = 32.34\ I^{0.307}$	0.997
Standard + 4-ethyl phenol	$P = 27.42\ I^{0.310}$	0.985
Standard + 3-methyl indole	$P = 25.32\ I^{0.371}$	0.952
Standard + phenol	$P = 32.33\ I^{0.304}$	0.943
Standard + benzyl alcohol		
Standard + isocaproic acid		
Standard + caproic acid		
Standard + indole		
Standard + propionic acid		
Standard + isobutyric acid		
Standard + 2-butanol		
Standard + 4-ethyl phenol + p-cresol		
Standard + acetic acid + heptanoic acid		
Standard + isovaleric acid + phenol		

TABLE 4. Mean perceived odor intensity scores for synthetic swine odor solutions and the effect of individual odorants on the intensity score.

Odorant	Mean rating	Standard error
Standard	94.60	4.9
Standard + valeric acid	97.61	5.9
Standard + butyric acid	94.71	5.7
Standard + heptanoic acid	104.68	5.4
Standard + acetic acid	119.51	6.1
Standard + isobutyric acid	94.39	5.6
Standard + p-cresol	97.40	4.9
Standard + 4-ethyl phenol	83.26	4.9
Standard + 3-methyl indole	99.34	6.5
Standard + phenol	95.94	5.1
Standard + benzyl alcohol		
Standard + isocaproic acid		
Standard + caproic acid		
Standard + indole		
Standard + propionic acid		
Standard + isobutyric acid		
Standard + 2-butanol		
Standard + 4-ethyl phenol + p-cresol		
Standard + acetic acid + heptanoic acid		
Standard + isovaleric acid + phenol		

A Within Subjects Factorial Analysis of Variance (ANOVA) was used to determine the effects of odorant concentration on the mean perceived odor intensity scores. Two factors were included in the ANOVA: 1) The effect of odorant concentration on olfactory responses over 7 odorant concentrations (100%, 83%, 67%, 50%, 33%, 17%, 1%), and 2) the effect of synergistic or antagonistic interactions between 9 odorants present in synthetic swine odor Z2. The analysis yielded a reliable main effect due to concentration of odorants ($F(5, 65) = 142.35$, $p < 0.0001$), a reliable main effect due to synergistic/antagonistic interactions between odorants ($F(9, 117) = 3.58$, $p < 0.001$), and a reliable interaction between concentration and synergistic/antagonistic interactions between odorants ($F(45, 585) = 3.128$, $p < 0.0001$). Subsequent analysis of the main effects showed that several of the chemical mixtures produced reliably greater mean odor intensity ratings than others. The mean rating for each of the solutions and standard error are shown in Table 4.

Analysis of data for determining synergistic/antagonistic interactions between 9 odorants present in synthetic swine odor Z2 was completed using Fisher's LSD statistic. The value of Fisher's LSD for odorant interactions was 13.52 odor intensity units, meaning that any of the mean ratings differing by more than 13.52 are reliably different. Odorant solutions containing a 2-fold higher concentration of acetic acid gave mean perceived odor intensity scores that were statistically higher than the standard, while solutions containing 2-fold higher concentrations of 4-ethyl phenol gave statistically lower odor intensity scores than the standard (Table 4). Other treatments in this series were found to be statistical equivalent.

The concentration of odorant solutions evaluated in this study were found to elicit a strong effect on mean perceived odor intensity scores. The value of Fisher's LSD statistic for concentration data was 9.59 odor intensity units (Table 5). As such, the 1% concentration produced statistically lower mean perceived odor intensity scores than the other 5 concentrations evaluated. The 17% concentration produced odor intensity scores that were statistically lower than the 34%, 67%, 83% and 100% concentrations. This pattern of statistical significance was observed for all subsequent odorant concentrations. Thus, the human panel was clearly sensitive to changes in concentration across all odorant concentrations used in the study.

TABLE 5. Mean perceived odor intensity scores for synthetic swine odor solutions differing in stimulus concentration.

Stimulus concentration (%)	Mean score	Standard error
1	30.64	2.08
17	73.14	2.98
34	96.64	2.79
67	114.91	2.85
83	130.99	3.11
100	142.55	3.60

Multiple regression analysis was performed on odorant concentration data sets and on data sets used for determining synergistic/antagonistic interactions in an attempt to predict the panel perceived odor intensity scores based on the concentration stimulus. The mean perceived odor intensity scores reported by panelists were used as the dependent (predicted) variable for these analyses. There was a strong correlation ($r^2 = 87.6$) observed between predicted and authentic values for mean perceived odor intensity scores. The quality of the model was further corroborated by the high level of statistical significance for the analysis ($F(9,51) = 40.14$, $p < 0.0001$). Table 6 shows the regression coefficients for each of the odorants included in the model.

TABLE 6. Correlation between intensity value and chemical composition for synthetic swine odor Z2 and the effect of individual odorants on mean perceived odor intensity.

Odorant	**Coefficient (ppm)**	**t**	**p**
Standard Mixture	46.971	13.800	<0.001
Acetic acid	0.058	4.390	<0.001
Butanoic acid	0.063	1.220	0.230
Caprioc acid	0.781	3.301	0.025
p-Cresol	0.193	0.670	0.507
4-Ethyl Phenol	-0.962	-2.320	0.024
Heptanoic acid	0.326	1.069	0.290
Indole	-1.492	-2.260	0.028
Isobutyric acid	0.237	0.193	1.317
Isocaproic acid	1.523	2.307	0.025
Isovaleric acid	0.690	2.346	0.023
3 Methyl Indole	0.687	2.160	0.035
4- Methyl Phenol	0.228	0.634	0.528
Phenol	0.086	0.190	0.851
Propionic acid	0.027	0.888	0.379
Valeric acid	0.196	1.590	0.119

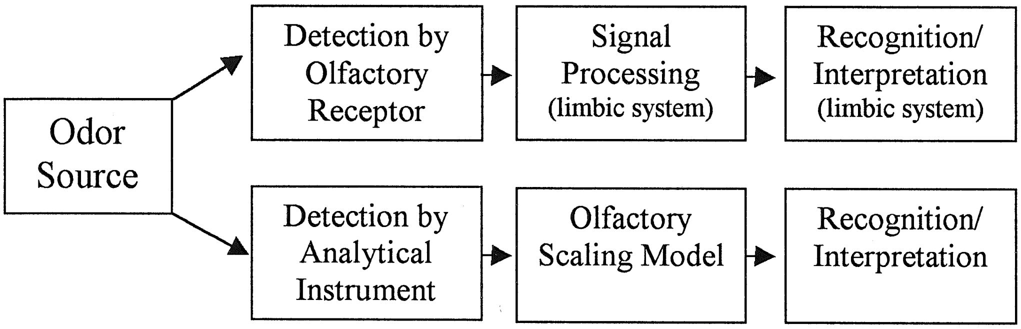
The key points to note about the above table are that five of the chemical mixtures had a statistically significant affect (i.e., $p < 0.05$) on subject's intensity ratings. Relative increases in the amount of acetic acid, 3-methyl indole, isovaleric acid, isocapropic acid, and caprioc acid tended to *increase* subjects' ratings of the odor intensity of the mixture.

In contrast, relative increases in the amount of 4-ethyl phenol, and indole tended to *decrease* subjects' ratings of the odor intensity of the mixture. No other chemicals appeared to have a statistically significant effect on subjects' intensity ratings.

CONCLUSIONS

The release of odor from animal production facilities represents a significant problem that threatens sustainability of modern animal agriculture. Efforts to regulate or remediate odor from swine production facilities have been impeded by the lack of instruments capable of high-throughput odor measurements. The results of this study show that direct multicomponent analysis of VOCs present in ambient air near animal production facilities may be applied towards estimating perceived odor intensity. This instrument-based odor quantification approach would consist of 1) collecting ambient air samples from an animal production facility, 2) determining the concentration of specific odorants present in the air sample by gas chromatography, and finally, 3) processing the concentration data by an olfactory scaling model in order to estimate the perceived odor intensity (Fig. 5). This instrument-based odor quantification system has been successfully applied to the quantification of odor emitted from 29 swine manure management systems in Iowa, Oklahoma, and North Carolina (Zahn et al., 2000). The methods provided an inexpensive means to rapidly and accurately detect swine manure management systems that emitted high amounts odor.

FIGURE 5. Odor quantification by chemical and olfactory methods.



STATUS OF RESEARCH

All but one of the objectives listed both state 1 and 2 of this proposal have been meet. In addition all field and laboratory experiments have been completed. The sole objective involves the conversion equation, i.e equation to convert chemical data into human response is not complete. The graduate student working on this project is on vacation. This is why tables 3 and 4 are incomplete. I have the raw data (see table 5) but should consult with the student before calculating these final number. The constants are necessary to complete the equation. We would like to use the remaining funds in Stage 2 of this proposal to purchase a statistical package and for salaries to complete the equation. To date this research as resulted in four paper accepted and two in the preparation stages, one patent field and one to be submitted upon completion of the conversion equation (see following section).

Publications and Patents Resulting from the Research on Stages 1 and 2 of this Proposal

Zahn, J.A., and DiSpirito, A.A. 1999. Composition and use of a swine odor standard in quantitation of swine odors. *Patent Pending*, United States Patent and Trademark Office. Washington, DC.

Zahn, J.A., J.L. Hatfield, Y.S. Do, and A.A. DiSpirito. 2000. Functional classification of swine waste management systems based on gas emission rates and solution-phase properties: The inadequaticy of animal numbers in the prediction of pollution potential. Journal of Environmental Quality. *in press.*

Zahn, J.A., A.A. DiSpirito, Y.S. Do, B.E. Brooks, E.E. Cooper, and J.L. Hatfield. 2000. Correlation of human olfactory responses to airborne concentrations of malodorous volatile organic compounds emitted from swine effluent. Journal of Environmental Quality. *in press.*

Zahn, J.A., J.L. Hatfield, Y.S. Do, and A.A. DiSpirito. 2000. Air Pollution from swine production facilities differing in waste management practice. *In.* Odors and VOC Emissions 2000. Water Environment Federation. *in press.*

Zahn, J.A., A.A. DiSpirito Y.S. Do, B. E. Brooks, D.W Russel, and E.E. Cooper. 2000. Correlation of human odor response magnitudes to air concentrations of malodorous volatile organic compounds associated with swine manure odor. *In.* Odors and VOC Emissions 2000. Water Environment Federation. *in press.*

REFERENCES

Asman, W.A.H. 1995. Ammonia and ammonium in the atmosphere: Present knowledge and recommendations for further research. *In* G.J. Heij and J.W. Erisman (Eds). Acid Rain Research: Do We Have Enough Answers? Proceedings of a Speciality Conference. ‘s-Hertogenbosch, Netherlands, 10-12 October 1994. Elsevier Science B.V., Amsterdam, Netherlands. pp 55-70.

Barker, J., S. Curtis, O. Hogsett, and F. Humenik. 1996. Safety in swine production systems. North Carolina cooperative extension service. Pub. no. PIH-104.

Cain, W.S. R. Wijk, C. Lulejian, F. Schiet, and lai-Chu See. 1998. Odor identification: preceptual and semantic dimensions. Chem. Senses. 23:309-326.

Cole, D.J., V.R. Hill, F.J. Humenik, and M.D. Sobsey. 1999. Health, safety, and environmental concerns of farm animal waste. Occupational medicine: Sate of the art reviews. 14(2):423-448.

Degel, J. and Koster, E.P. 1998. Implicit memory for odors: A possible method for observation. Perceptual and motor skills. 86:943-952.

DiSpirito, A.A. and Zahn, J.A. 1998 Device for quantitation of odors from liquid livestock wastes. United States Pat. No. 5,766,551. United State Patent and Trademark Office. Washington, DC.

DiSpirito, A. A., Y.S. Do, C.L. Krema, J. Emerson, and Zahn, J. A.. 1995. Methods to monitor microbial populations and odors from livestock wastes, *In* Proceedings of the international livestock odor conference. pp. 80-85. Iowa State University College of Agriculture. Ames, IA.

Eklund, B. and LaCosse, J. 1995. Field measurements of greenhouse gas emissions from the wastewater treatment systems at two farms. EPA contract No. 68-D-0031. Work assignment 66. U.S. EPA. Office of research and development. Washington, DC.

Giusquiani, P.L., L. Concezzi, M. Businelli, and A. Macchioni. 1998. Fate of pig liquid fraction in calcareous soil: Agricultural and envirionmental implications. J. Environ. Qual. 27:364-371.

Harper, L.A., and Sharpe, R.R. 1997. Climate and water effects on gaseous ammonia emissions from a swine lagoon. pp. 223-229. *in* L.M. Risse (ed.) Proceedings of the southwestern sustainable animal waste management workshop. Feb. 11-13. Tifton, GA. Univ. of Georgia publication No. ENG97-001.

Hill, D.T. and Bolte, J.P. 1989. Digester stress as related to isobutyric and isovaleric acids. Biological Wastes 28:33-37.

Hobbs, P.J., T.H. Misselbrook, and B.F. Pain. 1995. Assessment of odours from livestock wastes by a photoionization detector, an electronic nose, olfactometry and gas chromatography-mass spectrometry. J. Agric. Engng. Res. 60:137-144.

Jacobson, L.D., C. Radman, D. Schmidt, and R. Nicalai. 1997(a). Odor measurements from manure storages on minnesota pig farms. Proceedings of TLES. pp. 93-100. ASAE. May 29-31. Blominton, MN.

Jacobson, L.D., C.J. Clanton, C. Radman, D. Schmidt, R. Nicalai, and K.A. Janni. 1997(b). Comparsion of hydrogen sulfide and odor emissions from animal manure storages. pp. 404-412. *In* J.A.M. Voermans and G.J. Monteny (eds.) Proceedings of the international symposium on animal and odor control from animal production facilities. Oct. 6-10. Vinkeloord, Netherlands. ISBN:90-9011059-3.

Liden, E., S. Nordin, L. Hogman, A. Ulander, F. Deniz, and A.G. Gunnarsson. 1998. Assessment of odor annoyance and its relationship to stimulus concentration and odor intensity. Chem. Senses. 23:113-117.

Livermore, A. and D.G. Laing. 1998. The influence of chemical complexity on the perception of multicomponent odor mixtures. Perception and psychophysics. 60(4):650-661.

MacIntyre, S., R. Wanninkhof, and J.P. Chanton. 1995. Trace gas exchange across the air-water interface in freshwater and coastal marine environments. pp 52-97. *In* P.A.

Mackie, R.I., P.G. Stroot, and V.H. Varel. 1998. Biochemical identification and biological origin of key odor components in livestock waste. J. Anim. Sci. 76:1331-1342.

Miner, J.R. 1982. Controlling odors from livestock production facilities. pp. 30-35. In R.J. Smith (ed.) Research results in manure digestion, runoff, refeeding, odors. North central regional research publication no. 284. Ames, IA.

Miner, J.R. 1995. An executive summary: A review on the literature on the nature and control of odors from pork production facilities. National Pork Producers Council. Des Moines, IA.

Miner, J.R. 1999. Alternatives to minimize the environmental impact of large swine production units. J. Anim. Sci. 77:440-444.

Obrock-Hegel, CE. 1997. The effects of reducing dietary crude protein concentration on odor in swine facilities. MS Thesis. University of Nebraska. Lincoln, NE.

Oleszkiewicz, J.A., and Sharma, V.K. 1990. Stimulation and inhibition of anaerobic processes by heavy metals: A review. Biological Wastes 31:45-67.

Pain, B.F., V.R. Phillips, C.R. Clarkson, T.M. Misselbrook, Y.J. Rees, and J.W. Farrent. 1990. Odor and ammonia emissions following spreading of aerobically-treated pig slurry on grassland. Biological Wastes. 34:149-160.

Plog, B.A. 1988. Fundamentals of industrial hygiene. pp. 770-783. National Safety Council. Chicago, IL.

Powers, W.J., H.H. Van Horn, A.C. Wilkie, C.J. Wilcox, and R.A. Nordstedt. 1999. Effects of anaerobic digestion and additives to effluent or cattle feed on odor and odorant concentration. J. Anim. Sci. 77:1412-1421.

Safley, Jr. L.M., M.E. Casanda, J.W. Woodbury, and K.F. Roos. 1992. Global methane emissions from livestock and poultry manure. United States Environmental Protection Agency. Washington, DC.

Schiffman, H.R. 1982. Sensation and perception: An integrated approach. New York. John Wiley.

Schiffman, S.S., E.A. Sattely Miller, M.S. Suggs, and B.G. Graham. 1995. The effect of environmental odors emanating from commercial swine operations on the mood of nearby residents. Brain Research Bulletin 37(4):369-375.

Schulte, D.D., D.A. Kottwitz, and C.B. Gilbertson. 1985. Nitrogen content of scraped swine manure. pp. 321-328. *In* Proceedings of the fifth international symposium on agricultural waste. ASAE. St. Joseph, MI.

Sharpe, R.R., and Harper, L.A. 1998. Ammonia and nitrous oxide emissions from sprinkler irrigation applications of swine effluent. J. Environ. Qual. 26:1703-1706.

Sharpe, R.R., and Harper, L.A. 1997. Atmospheric methane emissions from a swine lagoon. pp. 237-241. *In* L.M. Risse (ed.) Proceedings of the southwestern sustainable animal waste management workshop. Feb. 11-13. Tifton, GA. Univ. of Georgia Publication No. ENG97-001.

Stevens, S.S. 1957. On the psychophysical law. Psychol. Rev. 64:153-181.

Stevens, S.S. 1961. Science. 133:80-86.

Stevens, S.S. 1962. The surprising simplicity of sensory metric. Am. Psychol. 17:29-39.

Stevens, S.S. 1970. Science. 170:1043-1050.

Stevens, S.S. 1975. Psychophysics: Introduction to its perceptual, neural, and social aspects. New York. John Wiley.

Thu, K., K. Donham, R. Ziegenhorn, S.J. Reynolds, P.S. Thorne, P. Subramanian, W. Whitten, and J. Stookesberry. 1997. A control study of health and quality of life of life of residents living in the vicinity of large scale swine production facilities. J. Agric. Health and Safety. 3(1):13-26.

Turk, A. and Hyman, A.M. 1991. Odor measurement and control. pp. 842-881. *In* G.D. Clayton and F.L. Clayton (eds.) Patty's industrial hygiene and toxicology. John Wiley and Sons, Inc., New York.

U.S. Environmental Protection Agency. 1979. Methods for chemical analysis of water and wastes. (U.S. EPA Rep. 600/4-79-020). U.S. EPA, EMSL, Cincinnati, OH.

VanWicklen, G.L. 1997. Air quality in confinement animal facilities. pp. 231-236. *In* L.M. Risse (ed.) Proceedings of the southwestern sustainable animal waste management workshop. Feb. 11-13. Tifton, GA. Univ. of Georgia Publication No. ENG97-001.

Yasuhara, A., K. Fuwa, and M. Jimbu. 1984. Identification of odorous compounds in fresh and rotten swine manure. Agric. Biol. Chem. 48(12):3001-3010.

Zahn, J.A., J.L. Hatfield, Y.S. Do, A.A. DiSpirito, D.A. Laird, and R.L. Pfeiffer. 1997. Characterization of volatile organic emissions and wastes from a swine production facility. J. Environ. Qual. 26(6):1687-1696.

Zahn, J.A.. 1997. Swine odor and emissions from pork production. pp. 20-122 , *In* Kelly McGuire (ed.) Envirionmental assurance program. National Pork Producers Council. Des Moines, IA.

Zahn, J.A., and DiSpirito, A.A. 1999. Composition and use of a swine odor standard in quantitation of swine odors. *Patent Pending*, United States Patent and Trademark Office. Washington, DC.

Zahn, J.A., J.L. Hatfield, Y.S. Do, and A.A. DiSpirito. 2000. Functional classification of swine waste management systems based on gas emission rates and solution-phase properties: The inadequaticy of animal numbers in the prediction of pollution potential. Journal of Environmental Quality. *in press.*

Zahn, J.A., A.A. DiSpirito, Y.S. Do, B.E. Brooks, E.E. Cooper, and J.L. Hatfield. 2000. Correlation of human olfactory responses to airborne concentrations of malodorous volatile organic compounds emitted from swine effluent. Journal of Environmental Quality. *in press.*

Zahn, J.A., J.L. Hatfield, Y.S. Do, and A.A. DiSpirito. 2000. Air Pollution from swine production facilities differing in waste management practice. *In.* Odors and VOC Emissions 2000. Water Environment Federation. *in press.*

Zahn, J.A., A.A. DiSpirito Y.S. Do, B. E. Brooks, D.W Russel, and E.E. Cooper. 2000. Correlation of human odor response magnitudes to air concentrations of malodorous volatile organic compounds associated with swine manure odor. *In.* Odors and VOC Emissions 2000. Water Environment Federation. *in press.*