Simulation of Hydrogen Sulfide Emission from Deep-Pit Manure Storage During Agitation

H. Lin, W. Liu, J. Gan, Y. Wang, B. Hu

Abstract. *Human and animal exposure to hydrogen sulfide (H_2S) in animal barns has long been a serious issue due to the acute and chronic toxicity of H_2S. The H_2S concentration in the room air of deep-pit swine barns is usually within hundreds of parts per billion by volume; however, it can sharply increase to hundreds and even thousands of parts per million (ppm) during manure agitation and pump-out. To explore the sudden release and concentration distribution of H_2S, this study collected and analyzed samples from varying depths of a normal non-foaming barn and a foaming barn and then mathematically simulated the H_2S concentrations and emissions in the pit headspace and room air for both barns during pit agitation. Simulations were conducted for six ventilation scenarios, or six different combinations of pit fan and wall fan ventilation rates. The simulation results suggested that pit ventilation was more effective than wall ventilation in decreasing H_2S concentration in room air where pigs may be housed during agitation. A minimal pit ventilation rate of 40 cfm per pig was necessary to lower the peak concentration in room air to less than the permissible exposure limit of 20 ppm. The simulation results also indicated that gas bubble release during agitation accounted for the main part (81%) of H_2S emission in the foaming barn, and expedited molecular diffusion contributed the main part (70.2%) of H_2S emission in the non-foaming barn. The disturbed air-manure interface during agitation induced a pH decrease and therefore increased the apparent overall mass transfer coefficient of H_2S, resulting in a substantially increased mass transfer rate and concentration. The immediately dangerous to life or health (IDLH) concentration of 100 ppm may be reached during pit agitation if pit fan ventilation is not fully provided, and the duration of the exceedance could be more than 30 min. The results provide empirical data for future simulation of spatial and temporal H_2S distribution and are beneficial for developing methods to control H_2S below hazardous levels so that the health and safety of workers can be better secured.*

Keywords. *Agricultural safety, Deep-pit storage, Hydrogen sulfide concentration, Sulfide distribution, Swine manure.*

Hydrogen sulfide (H_2S) is a toxic and hazardous gas (Ballerino-Regan and Longmire, 2010). The National Institute for Occupational Safety and Health (NIOSH) defines an H_2S concentration of 100 parts per million by volume (or ppm) as the immediately dangerous to life or health (IDLH) concentration, and 10 ppm for 10 min is the recommended exposure limit (REL). The Occupational Safety and Health Administration (OSHA) enforces an acceptable ceiling concentration of 20 ppm as a permissible exposure limit (PEL) in 29 CFR 1910.1000, table Z-2 (OSHA, 2017). H_2S is generated in typical swine manure storage units either from sulfate by sulfate-reducing bacteria or by microbial mineralization of proteins and sulfur-containing amino acids (Zhu, 2000). The gas is then gradually released from the air-liquid interface and emitted to the aerial environment through pit and/or wall (sidewall or tunnel) ventilation or through natural ventilation. A typical distribution of mechanical ventilation fans in a deep-pit pig finishing barn was provided by Jacobson et al. (2005).

Many manure storage systems are in use in animal housing, including deep-pit storage, pull-plug systems, pit recharge systems, flushing systems, and scraper systems (Spellman and Whiting, 2007). In the upper midwestern U.S., including Iowa, Minnesota, and Illinois, the major pig producing states (USDA, 2014), deep-pit storage is the most commonly used manure storage system, especially for grow/finish barns. Deep-pit systems with greater depth are also used in the cattle and dairy industries. Although emission of H_2S has been reported for all types of indoor swine manure storage (Chénard et al., 2003; Heber et al., 2006; Hoff et al., 2006; Liu et al., 2014; Zhao et al., 2005), deep-pit systems need more attention because of their wide installation and potentially higher emission rates and higher concentrations. For example, a meta-analysis study (Liu et al., 2014) for finishing pigs showed that deep-pit barns emitted 1.019 kg H_2S year^{-1} per animal unit (AU), followed by re-

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charge pits (0.525 kg H_2S year^{-1} AU^{-1}), drain pits (or pull-plug systems, 0.137 kg H_2S year^{-1} AU^{-1}), dry manure handling barns (0.121 kg H_2S year^{-1} AU^{-1}), and hoop barns (0.078 kg H_2S year^{-1} AU^{-1}). The average concentrations and emissions calculated from the data summarized in another study showed that deep pits had an average concentration of 353 ppb and emission of 2.1 kg H_2S year^{-1} AU^{-1}, as compared to shallow pits with 304 ppb and 1.0 kg H_2S year^{-1} AU^{-1} (Rumsey et al., 2014).

Despite many H_2S emission studies assessing the environmental footprint of the pig industry, limited studies have evaluated H_2S concentrations in manure storage. The real-time H_2S concentration distribution in barns during manure pit disturbance is largely unknown. Emission studies have mostly considered H_2S as an odor source and air contaminant (Blunden et al., 2008b), but it would be equally, if not more, important to study H_2S concentration and the resultant toxicity. "Mysterious" burst releases of H_2S were found to occur randomly during routine operation, although the concentrations hardly exceeded several ppm during routine management of a barn (Ni et al., 2000a, 2000b, 2001). H_2S concentration and human/animal exposure can become seriously risky when manure is disturbed, which can cause H_2S concentrations to spike by several thousand fold (Blanes-Vidal et al., 2012; Patni and Clarke, 1991). Excessive H_2S exposure can lead to acute toxicity and even fatalities of farm workers and animals (Douphrate et al., 2013; Park et al., 2016). Human exposure to H_2S in industrial settings, such as oil and gas industries, paper mills, refineries, and meat packing plants, has long been an issue (Jacobson et al., 2003). This issue is also severe in swine barns in midwestern U.S. states (Beaver and Field, 2007; Hallam et al., 2012). In addition to the fatal accidents recorded in the literature, several anecdotal accidents involving H_2S toxicity in deep-pit swine and dairy operations have been reported in recent years in Ohio, Wisconsin, and Iowa (Alowairdi, 2016; Bullvine, 2015; Farm and Dairy, 2016; Leonard, 2015; Mueller, 2016; Rodgers and Eller, 2015).

Researchers have found that disturbances such as manure addition and agitation can suddenly release entrapped gas bubbles and thereby increase the H_2S emission in bench-scale simulated manure storage (Ni et al., 2009). A similar mechanism would explain the high H_2S emissions during manure pump-out. However, until the current study, no single study has related the underlying manure characteristics with H_2S concentrations and emissions during manure pump-out. The partitioning of gas emissions between pit and wall ventilation further complicates H_2S concentration predictions. By mathematical simulation based on sampled manure characteristics, this study aimed to quantify the H_2S release during deep-pit agitation so that the dangers of H_2S release during manure disturbance can be recognized. We sampled manure from two deep-pit barns (one foaming and one non-foaming) in Minnesota to determine the distribution of total sulfide, pH, gas, and solids along the depth of a pit. We then estimated the fraction or partitioning of H_2S emissions into pit ventilation with an artificial neural network (ANN) based on literature observations, and then predicted H_2S concentrations for six different ventilation scenarios. The obtained results are essential for assessing the mortality and morbidity risks of working inside animal barns during agitation and for developing methods to control H_2S concentrations below hazardous levels.

MATERIALS AND METHODS

SIMULATED MANURE STORAGE TEST

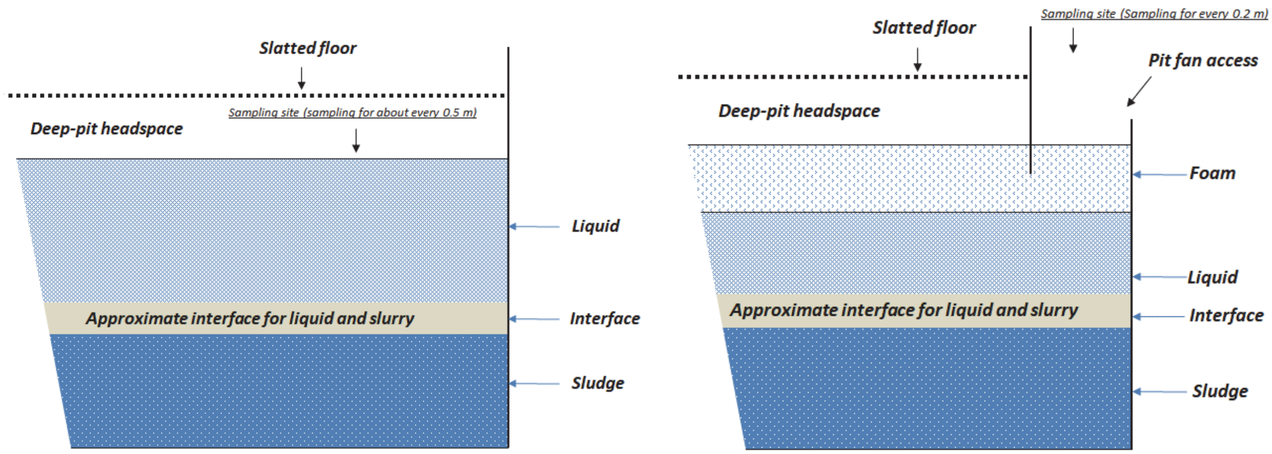
A laboratory manure storage test was performed for preliminarily assessment of manure characteristics at varying depths. A 5 in. (0.13 m) diameter polycarbonate column was filled with fresh swine manure collected from the concrete floor of a swine barn at the Swine Research Facility of the University of Minnesota, where the pigs were fed a corn-soybean diet. The total height of the column was 2.4 m. The manure was allowed to stratify through natural sedimentation for 7 days, and then manure samples were collected at 0.25 m depth increments using a vacuum pump with a hose penetrating to the desired depth. Each manure sample was subjected to anaerobic degradation for 45 days in a 100 mL serum bottle. The gas volume was quantified, and the composition was analyzed using gas chromatography. The manure samples were also analyzed for manure characteristics, including total solids, total sulfide, and pH.

DEEP-PIT MANURE SAMPLING

Two field sampling events were conducted for manure characterization on 3 November 2015 and 15 April 2016, respectively. The configuration of the deep-pit systems and manure handling characteristics are shown in figure 1. The first pit is in a research barn with a relatively small number of pigs; the second pit is in a typical commercial barn with 2400 pigs. Both barns use a deep-pit configuration and housed growing-finishing pigs that were predominately fed a corn-soybean diet. Further information on the barns is listed in table 1. Sampling in barn 1 was performed with a peristaltic pump equipped with PVC tubing. For the liquid layer, manure was pumped through the tubing to a plastic transfer pipette, where the volume of gas and liquid was recorded. For slurry samples, manure was drawn into PVC tubing, which was then sealed. The slurry in the tubing was gradually settled at one end, and therefore the volume of gas and slurry was measured by the corresponding length of tubing occupied by either gas or slurry. Manure sampling in barn 2 was performed with a vacuum pump, with the inlet placed at the designated depth. Samples were transported to the lab and stored in a -18°C walk-in freezer before analysis. Specifically, barn 2 was a foaming barn, i.e., a barn with a thick layer of foam that developed and was retained during manure storage. Foam was collected and fully filled in 5 gal (19 L) pails. After a frost and defrost cycle, the liquid in the foam settled to the bottom of the pails and was collected for volume measurement and characterization.

GAS COMPOSITION MEASUREMENTS

Biogas composition was quantified for H_2S, methane, carbon dioxide, oxygen, hydrogen, and nitrogen gas using a gas chromatograph (CP-4900 Micro-GC, Varian Inc., Palo Alto, Cal.) equipped with two columns of molecular sieve 5A and Porapak Q. Detailed protocols are available in a pre-



(a) (b)

Figure 1. Deep-pit sampling sites of (a) barn 1 (non-foaming) and (b) barn 2 (foaming).

Table 1. Information on the sampled barns.

	Barn 1	Barn 2
Sampling date	3 November 2015	15 April 2016
Pit condition	Non-foaming	Foaming
Location	Morris, Minn.	Pelican Rapids, Minn.
Sampling site	Under slatted floor	At pit fan access
Animal type	Growing-finishing pigs	Growing-finishing pigs
Approximate number of animals	120	2400
Feed type	Corn-soybean	Corn-soybean and 8% to 10% DDGS
Manure depth	2.2 m	2.2 to 2.4 m
Average pit temperature	17.7°C ±0.8°C	17.8°C ±0.4°C

vious article (Lin et al., 2016). The four-point GC calibration had coefficients of determination of 0.9969 for H_2S (10 to 250 ppm), methane (30% to 70%), carbon dioxide (10% to 60%), and hydrogen gas (1% to 15%), 0.9968 for oxygen gas (1% to 4%), and 0.9969 for nitrogen gas (4% to 15%). The GC lower limit of detection for H_2S was 20.8 ppm, calculated according to IUPCA's recommendation with a factor of 3 multiplied by the estimated standard deviation of measurement (Currie, 1999). The H_2S concentration was measured with RAE tubes (0.1 to 6 ppm, ±5%, PKSafety, Alameda, Cal.) when the concentration was not detectable by GC.

Manure Characteristics

Manure samples were analyzed for relevant characteristics based on standard methods (APHA, 1998). Total solids were quantified by overnight drying in oven at 105°C (Standard Method 2540-B), and volatile solids (VS) were quantified by ashing samples in a muffle furnace at 550°C (Standard Method 2540-C). Kinematic viscosity of manure was measured with glass capillary viscometers at 20°C. Total sulfide concentration in 10-fold diluted samples was determined with ion-selective glass electrodes (Cole Parmer, Chicago, Ill.) according to Standard Method 4500-G. Sulfide standards were prepared on the day of analysis from sulfide stock solution, and the calibration curves had $R^2 > 0.9989$. Sulfide stock solution was prepared from sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, Sigma Aldrich, St. Louis, Mo.) dissolved in sulfide anti-oxidation buffer. The final sulfide concentrations in the stock solution were determined weekly for quality control by $PbCl_2O_8$ solution (Sigma Aldrich, St. Louis, Mo.) titration terminated at the point at which the ISE reading experienced a sharp increase.

Statistical Analysis

One-way analysis of variance (ANOVA) was performed at a significance level of 0.05 when comparisons were required. Significance of manure depth in the pit over manure characteristics was assessed using p-values obtained by F-tests for the slope of the corresponding linear model with or without log transformation.

Simulation of H_2S Release at Quiescent and Agitated Conditions

Table 2 lists the variables and constants related to development of the model for simulating H_2S emissions. The goal was to estimate the H_2S concentration and emission at the pit and wall (or tunnel) fan exhausts for different barn ventilation scenarios based on sampled manure characteristics. The H_2S concentrations at the pit and wall fan exhausts were equivalent to the concentrations in the pit headspace and barn air, where animals or humans can be potentially exposed to the gas (i.e., the animal-occupied and human-occupied zones). Briefly, the first category of simulation assumed that the manure storage was quiescent, i.e., the condition during routine operation of the barns, without pump-out or agitation. Under quiescent storage conditions, it was assumed that the interface emission of H_2S is dictated by molecular diffusion from the liquid/gas interface, and the interface is not disturbed by external forces. The second category of simulation assumed that the manure pit was agitated during manure pump-out, so ebullition of entrapped manure gas bubbles or foam occurred, and the manure surface was disturbed. For both simulation categories, six ventilation scenarios were assessed. A detailed protocol of the emission simulation is described in the following sections.

Table 2. Parameters used in simulation.

Symbol	Definition	Units
A	Manure pit surface area of a 2000-head twin-barn	m^2
α and β	Empirical parameters determining manure gas release rate	-
C_p	H_2S concentration in pit fan exhaust, i.e., in pit headspace	ppm
C_w	H_2S concentration in wall fan exhaust, i.e., in barn air on average	ppm
d_i	Thickness of the *i*th manure layer	m
E_p	Average H_2S emission rate from pit fan exhaust	mg s^{-1}
E_w	Average H_2S emission rate from wall (or tunnel) fan exhaust	mg s^{-1}
f_i	Volumetric gas ratio of *i*th layer of manure	-
H_2S_{air}	Overall H_2S concentration in barn air at a specific time	ppm
$H_2S_{air,d}$	Ideal H_2S concentration in fan exhaust	ppm
$[H_2S]_l$	Concentration of dissolved H_2S in a manure sample	mM
$[H_2S^-]$	Concentration of bisulfide in a manure sample	mM
I	Total emission rate of H_2S diffused from manure surface	mg s^{-1}
$I_{bub.avg}$	Average emission rate of H_2S from bubble breakdown	mg s^{-1}
J	Flux of H_2S diffusion across air-liquid interface	mg m^{-2} s^{-1}
K_H	Henry's law constant for H_2S	M atm^{-1}
K_{OL}	Overall diffusion rate of H_2S across air-liquid interface	m s^{-1}
L	Length of manure pit of a 2000-head twin-barn	m
m_{ent}	Amount of H_2S gas entrapped in manure gas bubbles	m^3
$P_{H_2S,i}$	Equilibrium partial pressure of H_2S	ppm
$P_{H_2S\ in\ air,avg,r}$	Average exhaust H_2S concentration contributed by gas bubble release	ppm
$P_{H_2S\ in\ air,avg}$	Average exhaust H_2S concentration	ppm
$P_{H_2S\ in\ air,peak}$	Peak H_2S concentration during manure pump-out	ppm
$P_{H_2S\ in\ air,r}$	Exhaust H_2S concentration at a specific time contributed by gas bubble release	ppm
$P_{H_2S\ in\ bub,avg}$	Average H_2S concentration in manure gas	ppm
pK_a	Acid dissociation constant of H_2S	-
pH	pH value of a manure sample	-
Q_p	Pit fan ventilation rate	m^3 s^{-1}
Q_r	Manure gas release rate	m^3 s^{-1}
Q_v	Total ventilation rate for twin-barn	m^3 s^{-1}
Q_w	Wall (or tunnel) fan ventilation rate	m^3 s^{-1}
R_e	Fraction of H_2S emission from pit fan exhaust	-
[S]	Concentration of total sulfide in a manure sample	mM
T	Temperature of a manure sample	K
T_r	Duration of gas bubble ebullition from manure pit due to agitation	h
V_{barn}	Volume of air space in barn	m^3
V_{ent}	Total volume of entrapped gas in pit	m^3
W	Width of manure pit of a 2000-head twin-barn	m

Quiescent Manure Storage

Under the quiescent manure storage scenario, i.e., typical operation without pump-out events, it is assumed that the emission of H_2S is dictated by molecular diffusion from the liquid/gas interface, and the interface is not disturbed by external forces. It is also assumed that the decrease in total sulfide concentration in the manure is negligible due to the short period under consideration and the ongoing biogenic process in the aging manure. The concentration of H_2S ($H_2S_{air,d}$, ppm) in the barn air through diffusion can be calculated with the following equations:

$$[S] = [H_2S]_1 + [HS^-] \tag{1}$$

$$pH = pK_a + \log_{10}\frac{[HS^-]}{[H_2S]_1} \tag{2}$$

$$J = 34000 \times K_{OL} \times [H_2S]_1 \tag{3}$$

$$I = J \times A \tag{4}$$

$$A = L \times W \tag{5}$$

$$H_2S_{air,d} = 1000 \times 0.707 \times \frac{I}{Q_v} \tag{6}$$

where

[S] = total concentration of sulfide species in manure (mM)

$[H_2S]_1$ = H_2S concentration in aqueous phase (mM)

$[HS^-]$ = bisulfide concentration in aqueous phase (mM)

pK_a = dissociation constant (approx. 7.0) of H_2S in water

J = flux of H_2S diffusion (mg m^{-2} s^{-1})

K_{OL} = overall diffusion rate of H_2S (6.6×10^{-8} m s^{-1}) (Rumsey and Aneja, 2014)

A = pit manure surface area (m^2)

L = length of typical 2000-pig deep-pit twin-barn

W = typical width of barn

I = total emission rate of H_2S diffused from manure surface in the pit (mg s^{-1})

Q_v = total ventilation rate for the twin-barn (m^3 s^{-1})

0.707 = unit conversion factor for $H_2S_{air,d}$ from μg L^{-1} to ppm by volume.

Note that the dissociation of bisulfide to sulfide is negligible in this study due to the near-neutral pH of the manure samples.

Agitated Manure with Bubble Release

Under the scenario of manure pump-out, i.e., when the manure needs to be stirred, equations 1 to 6 were applicable except for adopting a different H_2S overall diffusion rate of 5.23×10^{-6} m s^{-1} (Santos et al., 2012). The volumetric gas ratio (f_i) of the *i*th layer of manure is calculated using the following equation:

$$f_i = \frac{\text{Gas volume}}{\text{Gas volume} + \text{Liquid or slurry volume}} \tag{7}$$

Under this scenario, the release of entrapped gas from the manure contributes to H_2S burst release. The entrapped gas bubbles are under equilibrium with the surrounding manure characteristics. The equilibrium concentration of H_2S in gas bubbles entrapped in the *i*th layer of manure, or equivalently, the equilibrium partial pressure of H_2S ($P_{H_2S,i}$, ppm), is calculated from the measured total sulfide, temperature, and pH:

$$P_{H_2S,i} = 1000 \times \frac{[H_2S]_l}{K_H} \tag{8}$$

$$K_H = 0.1 \times e^{2100 \times \left(\frac{1}{T} - \frac{1}{298.13}\right)} \tag{9}$$

where K_H is the Henry's law constant for H_2S (M atm^{-1}), and T is the temperature (K). The total amount of H_2S gas entrapped in manure gas bubbles (m_{ent}) can be calculated as follows:

$$m_{ent} = \sum_{i=1}^{n} \left(f_i \times d_i \times A \times P_{H_2S,i} \right) \tag{10}$$

where d_i is the thickness of the ith manure layer.

The total volume of entrapped gas (V_{ent}) and the average H_2S concentration ($P_{H_2S\ in\ bub,avg}$, ppm) in manure gas can be calculated as follows:

$$V_{ent} = \sum_{i=1}^{n} \left(f_i \times d_i \times A \right) \tag{11}$$

$$P_{H_2S\,in\,bub,\,avg} = \frac{m_{ent}}{V_{ent}} \tag{12}$$

Assuming that there are three to four pit fans and four to five wall (sidewall or tunnel) fans in one pit, there will be six to eight pit fans and eight to ten wall (or tunnel) fans in a twin-barn housing 2000 pigs (Hoff et al., 2006). With two manure pumps simultaneously working at pump-out accesses in each pit, the manure pump-out for one pit can usually be done within an 8 h day (Hoff et al., 2006). Based on previously monitored data (Patni and Clarke, 2003; Swestka, 2010), it is reasonable to assume that gas bubble release mainly occurs in the first 2 h (T_r) of the continuous agitation, and the gas bubble release rate decreases to zero thereafter. Therefore, the average H_2S emission rate due to gas bubble release, and the average exhaust H_2S concentration contributed by gas bubble release, can be estimated using the following equations:

$$I_{bub,\,avg} = \frac{m_{ent}}{T_r} \tag{13}$$

$$P_{H_2S\,in\,air,\,avg,\,r} = \frac{m_{ent}}{\left(V_{ent} + V_{barn} + Q_v \times T_r\right)} \tag{14}$$

where $I_{bub,avg}$ is the average emission rate of H_2S from bubble breakdown, T_r is the duration of bubble breakdown in agitation (h), $P_{H_2S\ in\ air,avg,r}$ is the average exhaust H_2S concentration contributed by gas bubble release, and V_{barn} is the volume of air space in the barn. The average exhaust H_2S concentration, contributed by both diffusion and gas bubble release, is as follows:

$$P_{H_2S\,in\,air,\,avg} = P_{H_2S\,in\,air,\,avg,\,r} + H_2S_{air,\,d} \tag{15}$$

It is assumed that the manure gas release rate (Q_r) is proportional to agitation time before time T_r:

$$Q_r = \alpha - \beta t \tag{16}$$

Parameters α and β can be determined with the following integral, with the boundary condition $\alpha - \beta T_r = 0$:

$$V_{ent} = \int_0^{T_r} Q_r\, dt \tag{17}$$

During agitation and pump-out, it is assumed that the volume change of barn air is negligible compared with the high ventilation rate, the emitted manure gas is immediately well mixed with the environment, and the H_2S concentration is homogeneously distributed in the manure gas bubbles. Therefore, the H_2S mass balance gives the following equation:

$$dP_{H_2S\,in\,air,\,r} V_{barn} = P_{H_2S\,in\,bub,\,avg} Q_r\, dt - P_{H_2S\,in\,air,\,r} Q_v\, dt \tag{18}$$

where $P_{H_2S\ in\ air,r}$ is the real-time exhaust H_2S concentration contributed by gas bubble release. The differential form of the above equation gives the following first-order linear ordinary differential equation, and the solution to this equation for $P_{H_2S\ in\ air,r}$ predicts the peak H_2S concentration in the barn air caused by manure gas bubble ebullition:

$$V_{barn} \frac{dP_{H_2S\,in\,air,\,r}}{dt} + Q_v P_{H_2S\,in\,air,\,r} = P_{H_2S\,in\,bub,\,avg} Q_r \tag{19}$$

MATLAB ODE solvers can be used to solve the above equations with the boundary condition $P_{H_2S\ in\ air,r}$ (t = 0) = 0 ppm. The overall H_2S concentration (H_2S_{air}) in the barn air is the sum of the two release mechanisms:

$$H_2S_{air} = P_{H_2S\,in\,air,\,r} + H_2S_{air,d} \tag{20}$$

The peak H_2S concentration ($P_{H_2S\ in\ air,peak}$) can be obtained by solving the following equation:

$$\frac{dP_{H_2S\,in\,air,\,r}}{dt} = 0 \tag{21}$$

PARTITIONING OF H_2S EMISSION AND ESTIMATION

Air exchange occurs between the room air and pit headspace air across the slatted floor, and this mass transfer affects the concentration distribution and emission ratio of pollutants from pit and wall (or tunnel) ventilation. However, no direct observations of the upward or downward flow rates were made for the slatted floor of animal barns (Zong et al., 2014), and calculations based on observations of pollutant concentrations and exhaust airflow rates (Janni et al., 2009), assuming either two-zone or three-zone configurations, yielded either a very high air exchange rate across the slatted floor or an unacceptably wide range of values, indicating that average data collected over weeks may not provide practical estimates of the pit-room air exchange rate. Alternatively, it can be assumed that partitioning of emissions into pit and wall ventilation is directly related to the ventilation pattern but not to pollutant concentrations (Ye et al., 2009). The pit emission fraction (R_e, %) is defined as follows:

$$R_e = 100 \times \frac{E_p}{E_w + E_p} \quad (22)$$

where the pit emission rate (E_p, mg s^{-1}) and wall emission rate (E_w, mg s^{-1}) are defined as follows:

$$E_p = 1.417 \times C_p Q_p \quad (23)$$

$$E_w = 1.417 \times C_w Q_w \quad (24)$$

where 1.417 is a factor for unit conversion, C_p and C_w are the H_2S concentrations (ppm) in the pit fan (or pit headspace air) and wall fan (or room air) exhaust at time *t*, respectively, and Q_p and Q_w are the pit and wall ventilation rates (m^3 s^{-1}), respectively. The air and H_2S mass balances at time *t* require:

$$Q_p + Q_w = Q_v \quad (25)$$

$$H_2S_{air} \times \left(Q_p + Q_w\right) = 1.417 \times \left(C_w Q_w + C_p Q_p\right) \quad (26)$$

where Q_v (m^3 s^{-1}) is the overall ventilation rate of pit and wall fans. When a maximum of six to eight fans are working simultaneously at full capacity in one room of a twin-barn, the overall ventilation rate can reach the full capacity of about 47.2 m^3 s^{-1}, or equivalently 170,000 m^3 h^{-1} or 100 cubic feet per minute (cfm) per pig (Jacobson et al., 2005, 2011). It was assumed that the maximum pit ventilation rate is 40 cfm per pig and the maximum wall ventilation rate is 60 cfm per pig. To evaluate the effect of ventilation rate, six ventilation scenarios were evaluated. Four of the scenarios were as follows: low pit ventilation and low wall ventilation (10 and 10 cfm per pig, respectively), low pit ventilation and high wall ventilation (10 and 60 cfm per pig, respectively), high pit ventilation and low wall ventilation (40 and 10 cfm per pig, respectively), and high pit ventilation and high wall ventilation (40 and 60 cfm per pig, respectively). Two additional scenarios were evaluated: using only the wall fans (60 cfm per pig, R_e = 0%) or only the pit fans (40 cfm per pig, R_e = 100%). For the first four scenarios, once the ventilation rates were set, R_e was estimated from an empirical dataset using an ANN. Solving equations 23 to 26 yielded the H_2S concentrations in the pit and wall fan exhaust at time *t*, or equivalently, the H_2S concentration in the pit headspace and room air, respectively.

To estimate the partitioning phenomenon, an ANN was used to calibrate the pit/wall ventilation rates and pit emission fraction (R_e). The training dataset, including 61 data points, was collected from previous ventilation studies focusing on pollutant partitioning, and the ventilation rate was converted to cfm per pig (Jacobson et al., 2005; Janni et al., 2009). The ANN was constructed with two input nodes (pit/wall ventilation rates), one hidden layer with two nodes, and one output node. ANN training and prediction were performed using the free tool JustNN (Neural Planner Software, Cheshire, U.K.). Learning was stopped when the average error was less than 0.01, and validation was stopped when all errors were within 10%. Prediction of R_e was made according to the designated ventilation rate for each scenario. The estimated pit emission fractions for the four above-mentioned scenarios were 76.2%, 20%, 96%, and 82.7%, respectively.

Results and Discussion

Manure and Gas Characteristics in Simulated Storage

Manure samples collected from the 2.4 m column after one week of sedimentation varied substantially in total solids, especially the bottom layer (fig. 2a). The samples had decreasing sulfide concentrations with depth (fig. 2b), and pH was substantially dependent on depth (fig. 2c). Therefore, the upper layers of manure served as a more substantial sulfide reservoir. After 45 days of anaerobic storage, the manure gas yield (more than 96% carbon dioxide) ranged from 35.6 mL g^{-1} added VS for the bottom layer to 77.3 mL g^{-1} added VS for the top layer. The lower layers of manure generated more gas but the gas contained less H_2S (figs. 2d and 2e). The simulated storage experiment indicated that the top layer of manure had a higher tendency for H_2S emission because of its higher sulfide and H_2S concentrations.

Sulfide and H_2S Distribution

Profiles of pH, a critical parameter that determines the H_2S concentration in the gas phase, are shown in figure 3. In all of the plots, p-values for the significance of depth for manure characteristics were calculated for liquid and slurry manure, excluding the foaming layer in the foaming barn (barn 2). The pH in barn 1 (fig. 3a) was between 6.79 and 7.44, and depth (distance from the upper surface of the manure in pit) contributed significantly to the pH decrease. The critical point of pH change was at the interface of the liquid and slurry layers (dashed line). The foaming barn was sampled at two sites: fan 3 (figs. 3c and 3d) and fan 4 (figs. 3e and 3f). For both sites, the pH of the foaming layer deviated from the pH of liquid and slurry manure: 7.45 ±0.02 vs. 7.74 ±0.05 for fan 3 and 7.54 ±0.03 vs. 7.82 ±0.09 for fan 4 (figs. 3c and 3e). The bottom layers of manure in barns 1 and 2 were slightly acidified. This observation was consistent with Swestka (2010), who observed that recirculation of bottom manure to the top may decrease pH and therefore sharply increase H_2S emission.

The total sulfide concentrations in each layer of the manure pits are also shown in figure 3. Sulfide concentration was higher in liquid layers than in slurry in the non-foaming pit of barn 1 (fig. 3b), and the sulfide concentration significantly decreased with depth, following a pattern similar to the simulated storage experiment (fig. 2b). In the foaming barn (barn 2), the foam had higher sulfide content than the liquid and slurry at both fans 3 and 4. A similar profile, i.e., decreasing sulfide content with the increasing depth, was identified as in the foaming barn (fig. 3d). The cause of the sulfide concentration gradient is not clear. However, the simulated storage experiment confirmed that the liquid portion of manure has greater capacity to generate sulfide. It is also possible that micro-bubble floatation during manure storage brings gaseous H_2S to the upper layers of liquid manure, and then H_2S is dissolved back into the manure, creating a con-

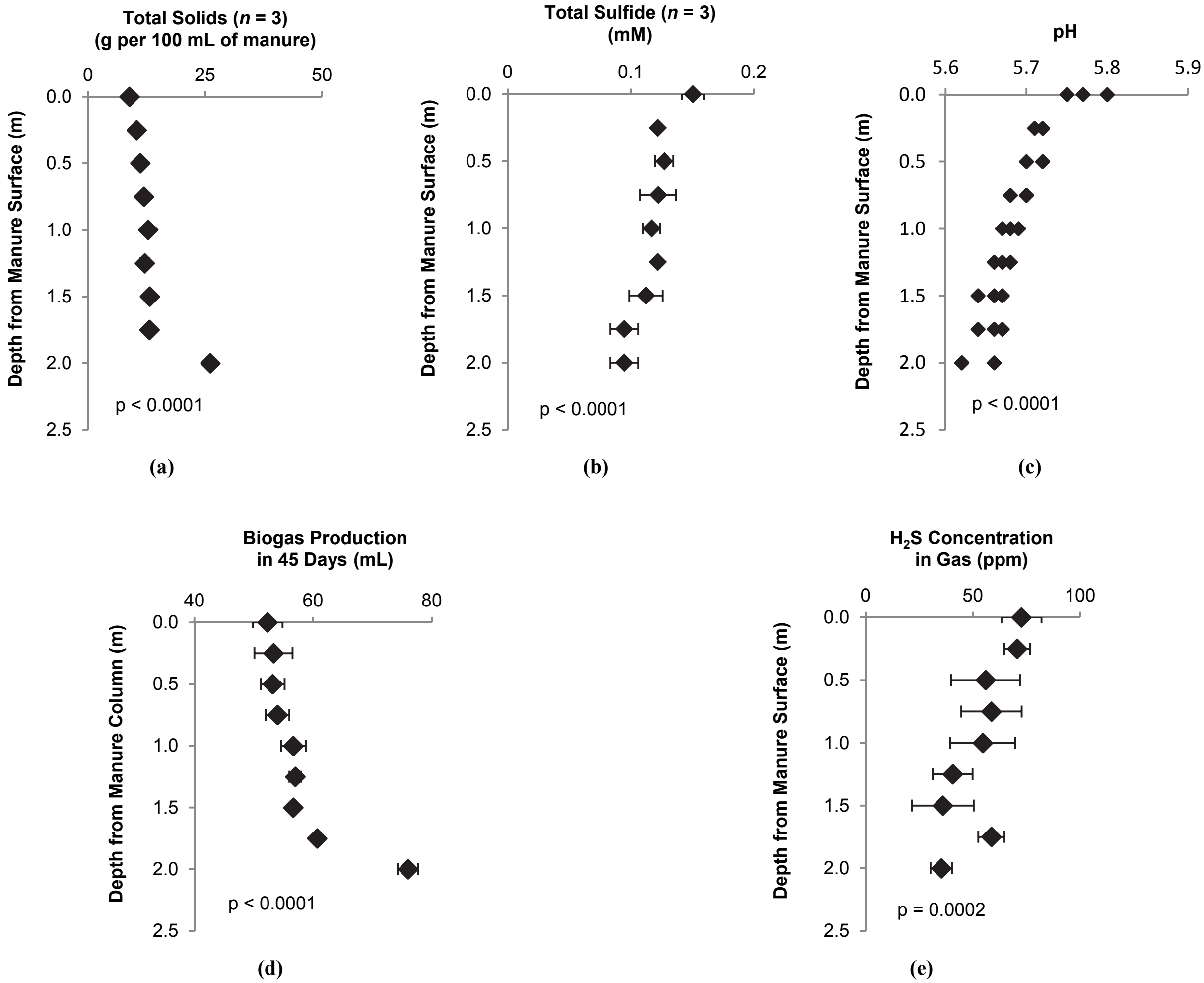


Figure 2. (a) Total solids, (b) total sulfide, and (c) pH distribution in manure of different depths after 7-day sedimentation, and (d) biogas production and (e) H_2S concentration.

centration gradient with depth. It was also found that the sulfide content differed substantially in manure samples from the two sites: 3.12 ±1.05 mM and 0.14 ±0.38 mM for fans 3 and 4, respectively, indicating an inconsistency in the horizontal profile of sulfide content. However, the foam layers had closer sulfide concentrations of 6.28 and 1.24 mM (or 201 and 40 mg L^{-1}, equivalently), respectively. The sulfide concentration at fan 3 was closer to previous tests that reported average concentrations of 202 mg L^{-1} (Martin, 2003) and 138 mg L^{-1} (Trabue et al., 2016) for deep-pit manure. This value was therefore considered typical and was used in the simulation study.

Gas and Total Solids Distribution

Manure from the non-foaming barn (barn 1) had a volumetric gas proportion of 6% at 0.1 m, 3.2% at 0.2 m, and 0.9% at 0.7 m (fig. 4a). The gas ratios increased to 17.7%, 41.1%, and 53.7% at depths of 1.2, 1.7, and 2.2 m, respectively, under the corresponding pressures induced by depth. The liquid to slurry transition occurred at roughly 1.2 m (dashed line), at which point the gas ratio suddenly increased. The results indicate that manure slurry entrapped a significant amount of gas, but the reason for this gas entrapment is not known. A high proportion of gas bubbles in solids or liquid (or void fraction), e.g., between 40% and 50%, was observed in sediment (Flury et al., 2015) and sludge (Van Kessel and Van Kesteren, 2002). Barn 2 had a foam thickness of 0.55 m and manure thickness of 1.66 m (1.05 m of liquid and 0.61 m of slurry; fig. 4b). The foaming layer consisted mainly of gas, i.e., 91% of the volume was occupied by gas. The sampling protocol for this barn did not allow us to assess the gas proportions in the liquid or slurry layers, but visual inspection of the manure at lower layers did not reveal substantial gas bubbles after samples were lifted to ground level. Further experimental confirmation will be necessary to rule out the existence of a large amount of gas bubble entrapment in lower layers. For barns 1 and 2, the interface between liquid and slurry manure was roughly at depths of 1.1 m and 1.5 to 1.6 m, respectively, and total solids were distributed more homogeneously in barn 2 (figs. 4c and 4d).

In barn 1, the manure density slightly increased with depth, and the kinematic viscosity increased by two orders of magnitude as the depth increased to 1.7 m (fig. 5). Kinematic viscosity represents the thickness of a fluid, i.e., the level of internal friction when there is relative movement between different layers of a fluid. Highly viscous manure could possibly entrap gas bubbles so that even the buoyant

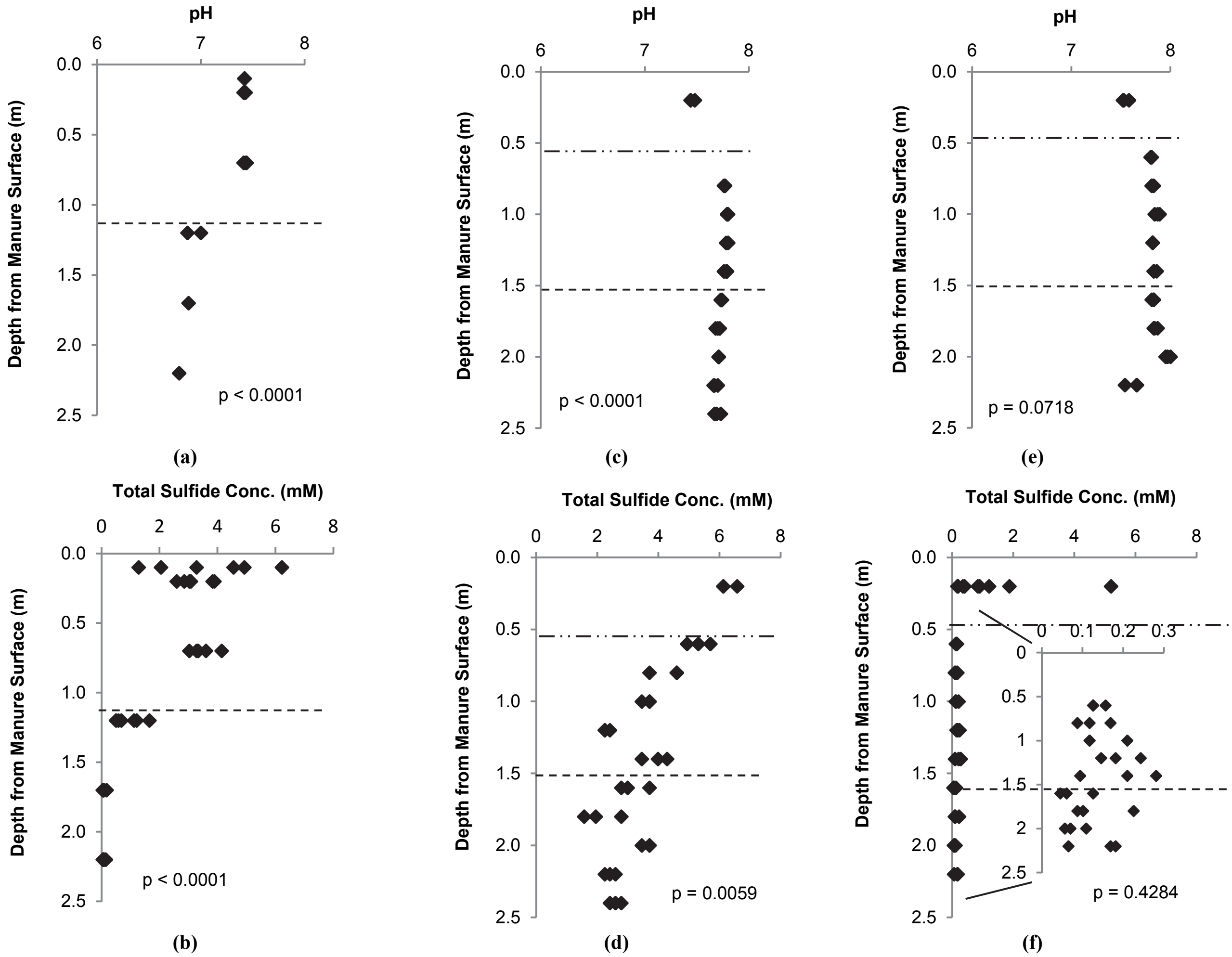


Figure 3. Values of pH and total sulfide concentrations in manure samples of (a and b) barn 1, (c and d) fan 3 of barn 2, and (e and f) fan 4 of barn 2. Dashed lines indicate the interface between liquid and slurry manure, and dashed-dotted lines indicate the interface between foam and liquid manure in the foaming barn.

force is not sufficient to overcome the static friction. Analysis indicated a linear relationship between total solids content and manure density, and between total solids content and the log transformation of kinematic viscosity. The bottom layer of manure at barn 1 had total solids of 17.3 g per 100 mL sample, and barn 2 had total solids of 9.3 g per 100 mL (fan 3 samples). By extrapolating the regression model of $\log_{10}$(kinematic viscosity) = 0.1766(total solids) + 0.0874, the predicted kinematic viscosities of the two samples were 1389 and 54 $mm^2\ s^{-1}$, respectively, indicating a 26-fold higher capacity of the manure sludge to entrap gas bubbles in barn 1 than in barn 2. The fluidity of manure, as indicated by the total solids content, probably explains the retention of gas bubbles in manure, and the entrapped gas bubbles may have an important influence on H_2S emissions to the barn air. The foaming layer entraps gas by a mechanism different from the change in manure viscosity, i.e., the decreased surface tension due to potential surfactants and stabilizers (Jacobson et al., 2013). The large amounts of gas entrapped in manure slurry and foam can play an important role in H_2S emissions during manure agitation and are critical in the simulation of emissions.

H_2S Concentrations in Headspace and Room Air

The simulation results based on sampled manure characteristics predicted H_2S concentrations for six different ventilation scenarios of pit ventilation and wall ventilation at different airflow rates. For barn 2, the manure characteristics at fan 3 were considered typical, as the sulfide concentration was comparable to values reported in the literature (Martin, 2003; Trabue et al., 2016). The simulation factors for the swine barn and manure pit are listed in table 3. The 1000-head swine barn is commonly used in the midwestern U.S. swine industry (Hoff et al., 2006; Jacobson et al., 2005).

If H_2S was emitted to the air only by molecular diffusion, and the manure surface was quiescent, then the concentration was low and did not exceed any exposure limit, e.g., 10 ppm (table 4). In each barn, a lower total ventilation rate resulted in a higher H_2S concentration due to a lower dilution effect. Meanwhile, the pit headspace concentration was always higher than, or at least equal to, the corresponding room air concentration. Barn 2 generated a slightly higher concentration due to higher dissolved H_2S concentrations at the surface of the manure. The highest concentration was expected to occur in barn 2 at the lowest overall ventilation rate, corresponding to a pit headspace concentration of

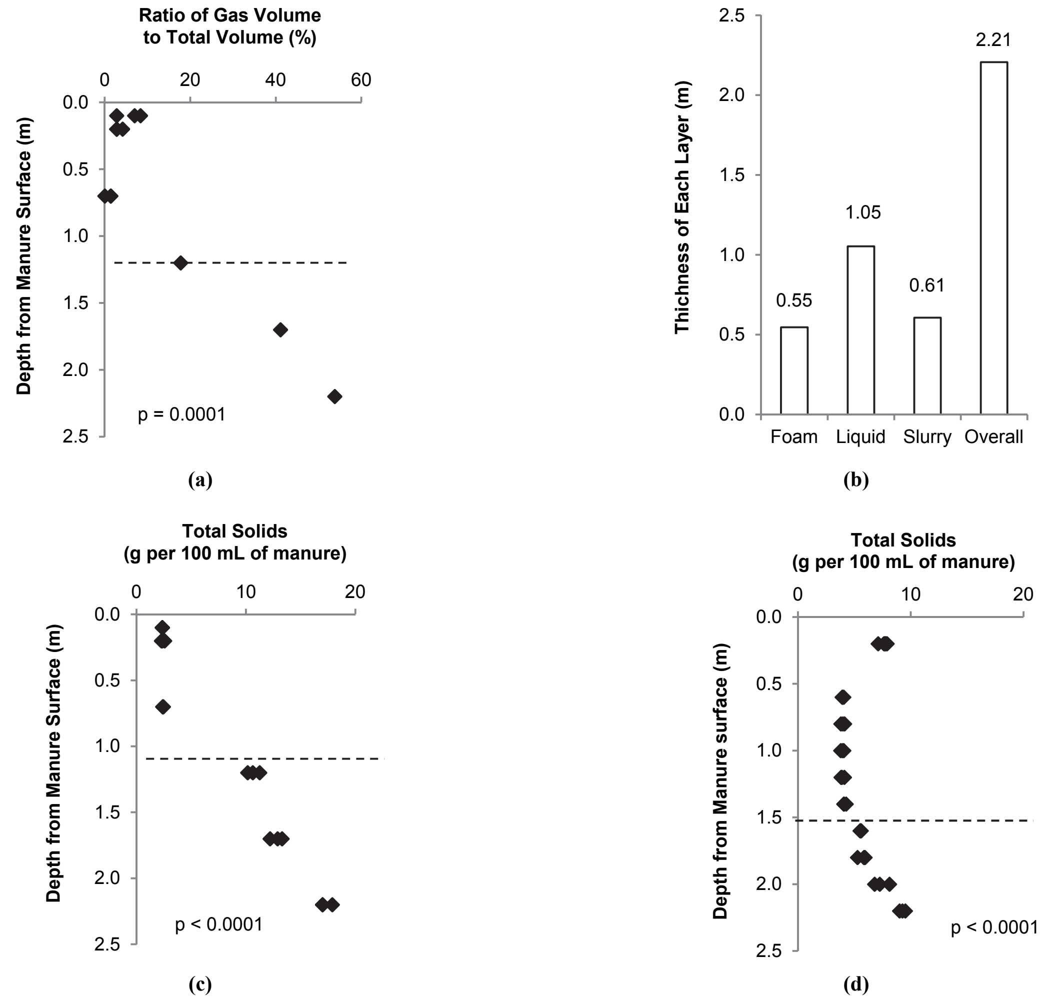


Figure 4. (a) Gas ratio in barn 1, (b) thickness of each layer in barn 2, and total solids contents of (c) barn 1 and (d) barn 2.

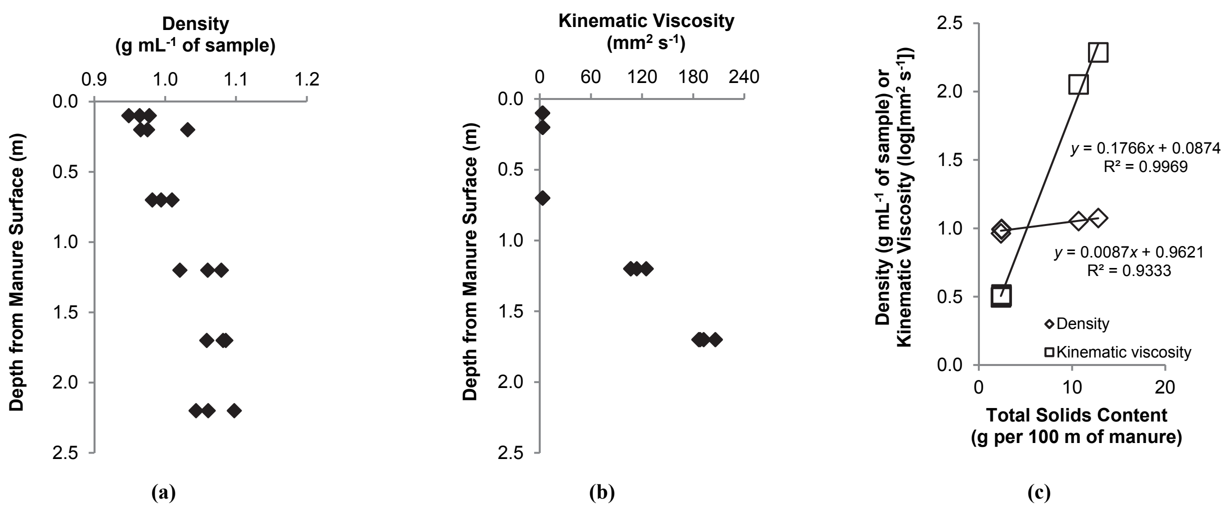


Figure 5. (a) Density, (b) kinematic viscosity, and (c) relationship to total solids content of manure from barn 1.

0.21 ppm, while the room air concentration was 0.10 ppm. The assumption of solely diffusional emission under quiescent conditions was therefore most likely insufficient, as most observations during manure agitation well exceeded these concentrations (Patni and Clarke, 1991; Swestka, 2010), indicating that molecular diffusion was not the primary source of H_2S emission during manure agitation and contributed only part of the H_2S emissions.

However, when pit agitation disturbed the quiescent manure surface and released manure gas from entrapped bubbles or foam, the H_2S concentration behaved very differently compared to the quiescent condition (table 4). Again, the

Table 3. Barn and pit factors used in mathematical simulation.

	Value		Units
Barn factors			
Pigs in a typical swine barn	1000		Head
Manure excreted per pig	4.54		L pig^{-1} d^{-1}
Manure produced per barn	4536		L $barn^{-1}$ d^{-1}
Total volume of manure	1656		m^3 $barn^{-1}$ $year^{-1}$
Deep-pit width	12.5		m
Deep-pit length	60		m
Deep-pit depth	2.50		m
Average height of barn	3.90		m
Pit surface area	750		m^2
Wall fan ventilation rate	102,000		m^3 h^{-1}
Pit fan ventilation rate	68,000		m^3 h^{-1}
Air volume inside barn	2,930		m^3 $barn^{-1}$
Pit factors	Barn 1	Barn 2 (fan 3)	Units
Foaming	No	Yes	-
Gas trapped in manure	0.51	0.53	m^3 m^{-2} floor
Total gas trapped in manure	383	398	m^3
Average equilibrium H_2S concentration in bubbles	714	13,479	ppm

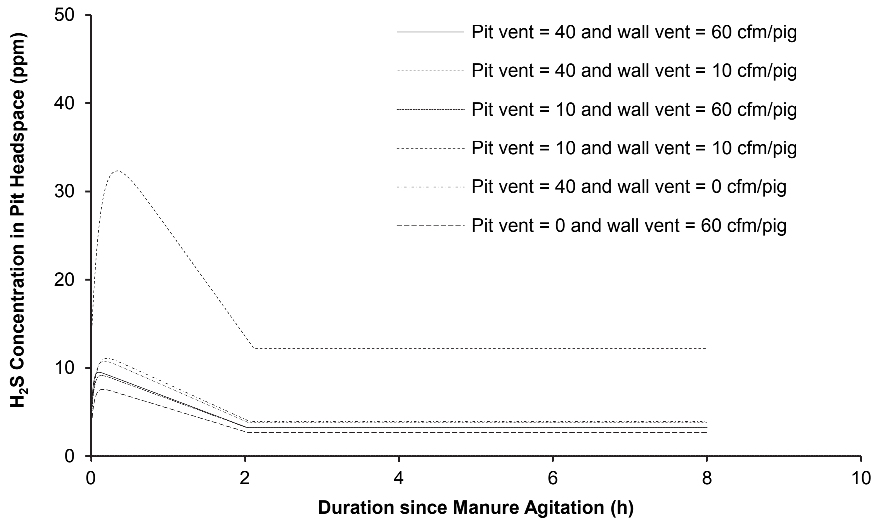
overall H_2S concentration in the ventilation exhaust gas was proportional to the ventilation rate for both barns. When pit and wall ventilation were both set at low rates (e.g., a total of 20 cfm per pig), barn 1 had an average overall concentration of 55.7 ppm, and the corresponding pit headspace and room air concentrations were 84.9 and 26.5 ppm, respectively. Those concentrations exceeded the REL time-weighted average of 10 ppm and the PEL of 20 ppm, and the headspace concentration was close to the IDLH concentration of 100 ppm. Pit ventilation seemed more effective in reducing H_2S concentration in the room air, where animals might be located during an agitation event. For example, when barn 2 was ventilated at 70 cfm per pig (10 and 60 cfm per pig for pit and wall ventilation, respectively) and 50 cfm per pig (40 and 10 cfm per pig for pit and wall ventilation, respectively), the first ventilation scenario yielded a lower average H_2S concentration in the room air due to the higher ventilation rate. However, the second scenario had much lower concentrations in the room air (14.9 vs. 4.45 ppm). The peak H_2S concentration was generally 4.5 to 5.5 times the corresponding average concentration in pit or wall fan exhaust air, and in many cases it exceeded the 10 ppm limit in barn 1 and the 100 ppm limit in barn 2. Extremely high peak concentrations in the pit headspace and room air (421 and 131 ppm, respectively) were found for the lowest ventilation scenario of 10 cfm per pig for both pit and wall ventilation. The second highest peak in room air (102 ppm) occurred when no pit ventilation was provided, although the highest wall ventilation was assumed. The results indicate that a higher pit ventilation rate is recommended for reducing H_2S concentration in room air, and a pit ventilation rate of 40 cfm per pig is necessary to guarantee that the peak concentration in room air is lower than the PEL of 20 ppm for barn 2 (table 4). The pit headspace or the pit fan exhaust had consistently higher concentrations than the room air, so animals and workers who are not directly exposed to the pit fan exhaust can avoid potential overexposure.

Time profiles of H_2S concentration are shown in figures 6 and 7 for the different ventilation scenarios, locations, and manure conditions in barns 1 and 2, respectively. Again, barn 2 generated higher concentration than barn 1 when other conditions were the same, and pit fan ventilation was necessary and effective in decreasing H_2S concentration in the room air. Peaks occurred between 6 and 20 min after agitation started, depending on the overall ventilation rate, indicating that the early stage of agitation during manure pump-out was more dangerous than the subsequent time. The local transient concentration in the animal-occupied zone (AOZ) or human-occupied zone (HOZ) may therefore exceed the IDLH limit, although its precise distribution was not achievable with the method used in this study. If the re-

Table 4. Predicted average and peak H_2S concentrations in the pit headspace and room air.[a]

		Q_p (cfm pig^{-1})	Q_w (cfm pig^{-1})	Total Ventilation Rate (cfm pig^{-1})	Average Conc. in Emission (ppm)	Average C_p (ppm)	Average C_w (ppm)	Peak C_p (ppm)	Peak C_w (ppm)
Quiescent	Barn 1	0	60	60	0.06	0.06	0.06	(Values are the same as the corresponding average concentrations)	
		40	0	40	0.09	0.09	0.00		
		10	10	20	0.18	0.28	0.09		
		10	60	70	0.05	0.07	0.05		
		40	10	50	0.07	0.09	0.01		
		40	60	100	0.04	0.08	0.01		
	Barn 2	0	60	60	0.07	0.07	0.07		
		40	0	40	0.11	0.11	0.00		
		10	10	20	0.21	0.32	0.10		
		10	60	70	0.06	0.08	0.06		
		40	10	50	0.08	0.10	0.02		
		40	60	100	0.04	0.09	0.01		
Agitated	Barn 1	0	60	60	3.29	3.29	3.29	7.59	7.59
		40	0	40	4.94	4.94	NA	11.1	0.00
		10	10	20	9.88	15.1	4.70	32.3	10.1
		10	60	70	2.82	3.95	2.63	9.15	6.10
		40	10	50	3.95	4.74	0.79	10.8	1.79
		40	60	100	1.98	4.08	0.57	9.51	1.33
	Barn 2	0	60	60	18.6	18.7	18.6	102	102
		40	0	40	27.8	27.8	NA	148	0.00
		10	10	20	55.7	84.9	26.5	421	131
		10	60	70	15.9	22.3	14.9	123	82
		40	10	50	22.3	26.7	4.45	145	24
		40	60	100	11.1	23.0	3.21	129	18

[a] Q_p = pit ventilation rate, Q_w = wall ventilation rate, C_p = H_2S concentration in pit-ventilated air, and C_w = H_2S concentration in wall-ventilated air.



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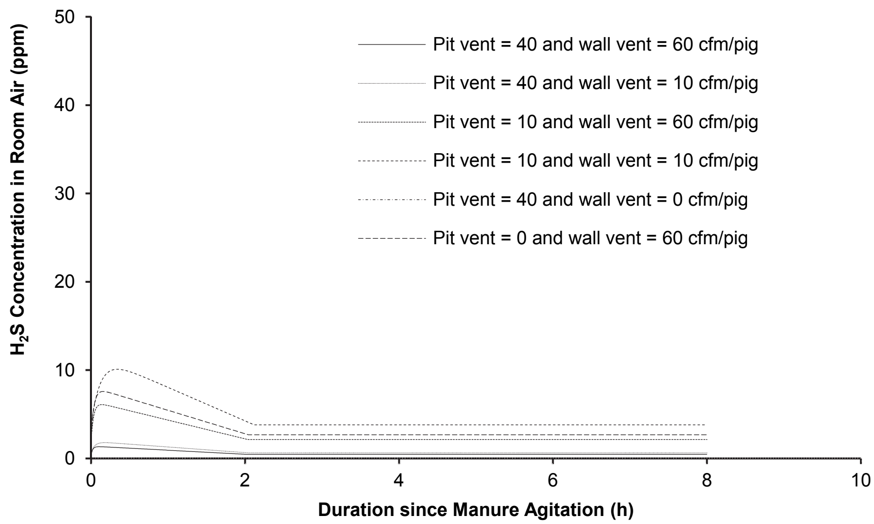


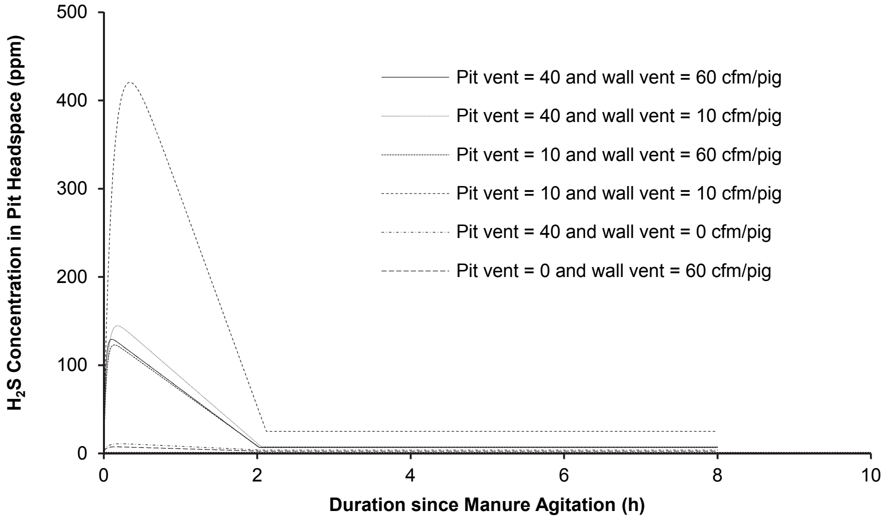
(b)

Figure 6. Predicted H_2S concentrations during manure agitation based on characteristics of barn 1: (a) headspace and (b) room air.

leased gas is not well mixed with the barn air and inlet air, the local and transient H_2S concentrations may be fatal to exposed animals or workers inside the barn during manure agitation. For barn 2 (the foaming barn), when low pit ventilation was provided, the peak concentration in room air exceeded the IDLH limit of 100 ppm between 6 and 44 min. Strict precautions must be taken for manure handling in this type of barn, and animals and workers should be vacated during manure pump-out.

Animal housing researchers recommend wearing suitable personal protective equipment (PPE), including protective clothing, a full-face respirator with H_2S-adsorbent filters, and a portable H_2S sensor with acoustic and light alarms, when approaching manure pump-out accesses, even during regular operation. They also recommend sampling manure as gently as possible to avoid disturbing the manure. When analyzing manure gas composition, full ventilation should be turned on, and gas samples should only be released inside well-functioning fume hoods that are subjected to annual inspection by the facilities management of a research institute.

Previous studies have identified a wide range of peak H_2S concentrations during manure agitation (table 5). The peak concentrations commonly exceeded the IDLH limit of 100 ppm (Patni and Clarke, 1991, 2003; Swestka, 2010), and some studies detected concentrations greater than 1000 ppm in room air when no pit ventilation was provided (Patni and Clarke, 2003). Researchers at Iowa State University monitored H_2S concentrations during manure subsurface and surface agitation, and concentrations greater than 100 ppm were frequently observed during surface agitation (Swestka, 2010). The same study concluded that the H_2S distribution was not predictable but could be affected by the aggressiveness of agitation, manure splashing on the crust or supporting columns during surface agitation, the distance to the agitation source, and the airflow pattern (Swestka, 2010). Shallow-pit systems are not exempt from massive H_2S release. Activities such emptying in-barn manure, power-washing,



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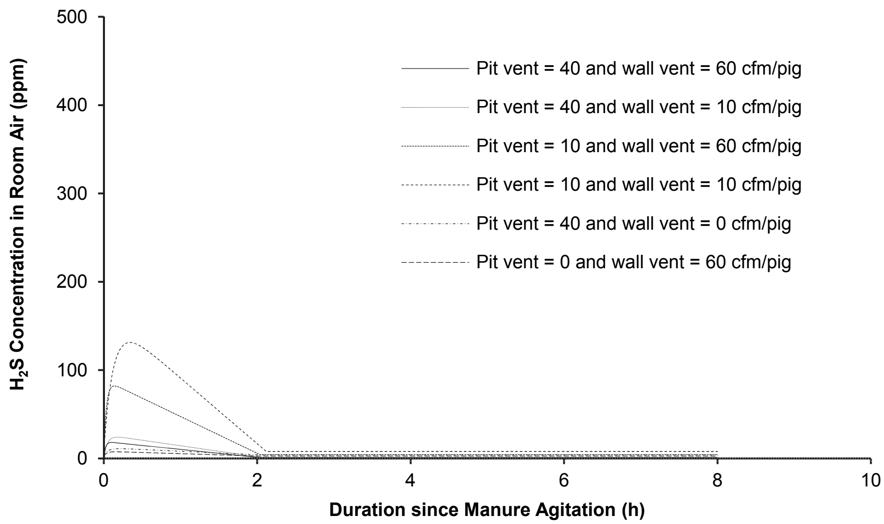


(b)

Figure 7. Predicted H_2S concentrations during manure agitation based on characteristics of barn 2: (a) pit headspace and (b) room air.

Table 5. Observed H_2S concentration in manure storage under disturbance.

Air Sampling Location	Type of Animal House	Type of Agitation	H_2S Concentration (ppm)	Reference
Tunnel fan	Swine barn	Pit agitation and pumping	16, peak	Hoff et al., 2006
Pit fan	Swine barn	Pit agitation and pumping	36, peak	Hoff et al., 2006
Floor level	Dairy barn	Pit agitation and pumping	70, peak	Patni and Clarke, 1991
Pit exhaust air	Swine barn	Pit agitation and pumping	110, peak	Patni and Clarke, 1991
Center and 1.0 m above floor	Swine barn	Surface agitation	>100, peak	Patni and Clarke, 1991
Pit exhaust air	Swine barn	Air blown to bottom of manure pit	>200, peak	Patni and Clarke, 1991
Pit exhaust air	Swine barn	Air blown to bottom of manure pit	>200, peak	Patni and Clarke, 1991
Pit exhaust air	Swine barn	Surface agitation and pit fan	>365, peak	Patni and Clarke, 2003
Barn air	Swine barn	No pit fan	1300, peak	Patni and Clarke, 2003
Barn air	Swine barn	No pit fan	1100, average	Patni and Clarke, 2003
0.1 m above floor	Swine barn	Surface agitation	>500, peak	Swestka, 2010
1.5 m above floor	Swine barn	Surface agitation	146, peak	Swestka, 2010
0.1 m above floor	Swine barn	Subsurface agitation	>500, peak	Swestka, 2010
1.5 m above floor	Swine barn	Subsurface agitation	74, peak	Swestka, 2010
Storage headspace	Simulated storage	Slurry mixing for 2 min	>50, average	Blanes-Vidal et al., 2012

and emptying outdoor manure storages may release high concentrations of H_2S in shallow-pit systems (Chénard et al., 2003). In particular, pulling plugs for emptying in-barn manure storages can result in H_2S levels as high as 1000 ppm. These high levels can last for as long as half an hour. High levels of H_2S are a common problem during plug-pulling events (Chénard et al., 2003). Among 119 plug-pulling events in several barns, 29% of the events produced H_2S levels exceeding 100 ppm in the barn air, and the highest H_2S level could be widely distributed at many locations in barn, not necessarily near the drain. Gas bubble release was the primary H_2S source during those events (Ni et al., 2001). Those studies, along with the results of this study, emphasize the danger to animals or humans present in swine barns when manure pits are disturbed.

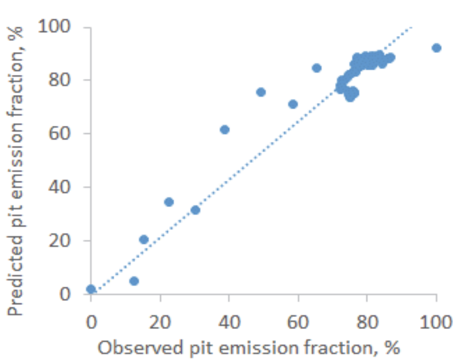
H_2S Emission from Pit and Wall Fans

An ANN model for predicting the partitioning of H_2S into pit and wall ventilation fan exhaust was established based on the summarized literature data (Jacobson et al., 2005; Janni et al., 2009). Most of the training examples were clustered around a pit emission fraction between 70% and 90% due to the ventilation configuration of the barns being studied (fig. 8a). However, the data covered a wide range of pit emission fractions. The correlation between prediction and experiment was 0.9545. From the contour of the regression model (fig. 8b), it can be seen that pit ventilation rate (Q_p) was the dominant factor in determining the pit emission fraction. When Q_p exceeded 10 cfm per pig, the fraction of pit emission was greater than 50%, even though the wall ventilation rate (Q_w) was 3 times higher (30 cfm per pig). The partitioning model indicates that, under normal operation, pit ventilation treatment will remove the majority of emissions and can perform better and be more economical than wall ventilation treatment. For example, installing bio-filters at the pit fan outlet will decrease H_2S emissions from deep-pit barns even through a 3-fold lower airflow rate is being treated.

When the manure surface was quiescent, the overall H_2S emission rate from barns 1 and 2 was 3.24 and 3.69 μg m^{-2} s^{-1}, respectively (table 6). These values were within the range of average emission rates that have been frequently observed for swine barns and pig waste lagoons under normal operation (Hoff et al., 2006; Lim et al., 2003; Ni et al., 2001). When the manure was agitated and homogenized during pump-out, the emission rates increased substantially from 3.24 to 174 μg m^{-2} s^{-1} (54-fold) for barn 1 and from 3.69 to 981 μg m^{-2} s^{-1} (266-fold) for barn 2. This phenomenon has been reported in many previous studies, as shown in table 7. For example, for a simulated manure storage, Ni et al. (2001) reported that the emission rate increased from 1.13 to 82.6 μg m^{-2} s^{-1} (71-fold). Another simulated manure storage showed an increase from 2.99 to 474 μg m^{-2} s^{-1} (159-fold) (Blanes-Vidal et al., 2012). In addition to these simulation studies, a field study reported an increase from 7.11 to 483 μg m^{-2} s^{-1} (68-fold) (Hoff et al., 2006).

It was previously proposed that bubble release may contribute to this abrupt emission rate increase. Several theoretical and empirical models have been developed and validated with varying accuracies for quantifying H_2S emissions from wastewater storages, including swine waste lagoons (Blunden et al., 2008a; Carrera-Chapela et al., 2016; Matos et al., 2016; Rumsey and Aneja, 2014). However, those models focused on modeling the overall mass transfer coefficient for H_2S with the environmental conditions (table 8), and none of those H_2S emission models included the gas bubble release process, which could be substantial. The manure sample observations in this study, as well as the simulation results, generally support the theory proposed by Ni et al. (2009). For the foaming barn (barn 2), the total H_2S emission during the pump-out event was 21.2 kg (table 7), and 81% of the emission was due to the release of gas bubbles from the manure and foam.

For the non-foaming barn (barn 1), the total H_2S emission during the 8 h pump-out event was 3.8 kg (table 7), and 70.2% of the emission was attributed to the expedited diffusional mass transfer from manure to air. Therefore, the pH change at the air-manure interface under agitation can be considered the second reason for the expedited emission rate, and this change requires adoption of a higher overall mass transfer coefficient for H_2S. Previously, several assumptions have been made to correlate the mass transfer co-



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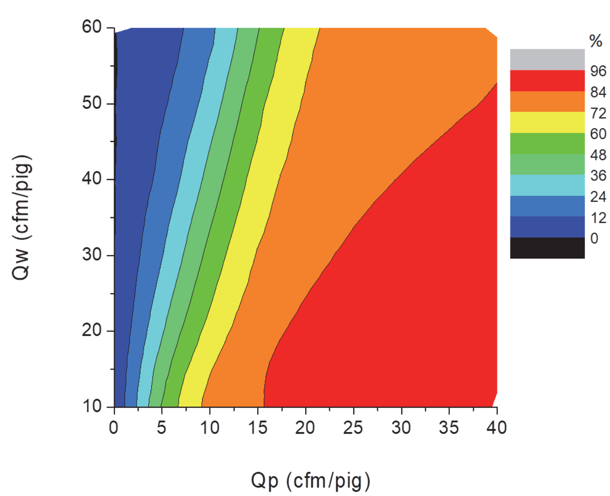

(b)

Figure 8. (a) ANN prediction of fraction of H_2S emission from pit fans, and (b) contour of predicted fraction of H_2S emission from pit fans at different ventilation conditions.

Table 6. Predicted H_2S emissions at different ventilation configurations.

		Ventilation Rate (cfm per pig)			Total Emission of H_2S in 8 h	Fraction of Pit Emission	H_2S Emission Rate ($\mu g\ m^{-2}\ s^{-1}$)		
		Q_p	Q_w	Total	(kg)	(%)	Overall	Pit Fans	Wall Fans
Quiescent	Barn 1	0	60	60	0.07	0	3.24	0.00	3.24
		40	0	40		100	3.24	3.24	0.00
		10	10	20		76	3.24	2.47	0.77
		10	60	70		20	3.24	0.65	2.59
		40	10	50		96	3.24	3.11	0.13
		40	60	100		82	3.24	2.68	0.56
	Barn 2	0	60	60	0.08	0	3.69	0.00	3.69
		40	0	40		100	3.69	3.69	0.00
		10	10	20		76	3.69	2.81	0.88
		10	60	70		20	3.69	0.74	2.95
		40	10	50		96	3.69	3.54	0.15
		40	60	100		82	3.69	3.05	0.64
Agitated	Barn 1	0	60	60	3.8	0	174	0	174
		40	0	40		100	174	174	0
		10	10	20		76	174	133	41
		10	60	70		20	174	35	139
		40	10	50		96	174	167	7
		40	60	100		82	174	144	30
	Barn 2	0	60	60	21.2	0	981	0	981
		40	0	40		100	981	981	0
		10	10	20		76	981	748	233
		10	60	70		20	981	196	785
		40	10	50		96	981	942	39
		40	60	100		82	981	811	170

Table 7. Values of H_2S flux in literature of simulated storage, lagoon emission, and barn emission studies.

Experimental or Simulation Setting	H_2S Flux ($\mu\ m^{-2}\ s^{-1}$)	Agitation	Note	Reference
Simulated manure storage	1.00E+00	No	Averaged from tests	Dai et al., 2015
Pig barn emission	3.75E+00	No	Test in a barn in 2002	Hoff et al., 2006
Pig barn emission	7.11E+00	No	Test in a barn in 2002	Hoff et al., 2006
Pig barn emission	7.86E+00	No	Test in a barn in 2003	Hoff et al., 2006
Pig barn emission	2.03E+01	No	Test in a barn in 2003	Hoff et al., 2006
Simulated manure storage	1.13E+00	No	Day 35 of manure storage	Ni et al., 2001
Simulated manure storage	4.12E+00	No	Day 41 of manure storage	Ni et al., 2001
Pig waste lagoon emission	2.25E-02	No	Average of four experiments	Rumsey and Aneja, 2014
Pig waste lagoon emission	2.54E-02	No	Average of four experiments	Blunden and Aneja, 2008
Pig waste lagoon emission	1.22E+01	No	Average of three-month data	Zahn et al., 2001
Pig waste lagoon emission	5.70E+00	No	Average	Lim et al., 2003
Simulated manure storage	2.99E+00	No	Averaged from days 37 and 46	Blanes-Vidal et al., 2012
Pig barn emission	4.31E+00	No	One year average	Blunden et al., 2008b
Pig barn emission	3.24E+00	No	Quiescent condition	This study
Pig barn emission	3.69E+00	No	Quiescent condition	This study
Pig barn emission	3.86E+02	Yes	Test in a barn in 2002	Hoff et al., 2006
Pig barn emission	4.83E+02	Yes	Test in a barn in 2002	Hoff et al., 2006
Pig barn emission	4.60E+02	Yes	Test in a barn in 2003	Hoff et al., 2006
Pig barn emission	3.68E+02	Yes	Test in a barn in 2003	Hoff et al., 2006
Simulated manure storage	8.26E+01	Yes	Day 35 of manure storage	Ni et al., 2001
Simulated manure storage	1.03E+02	Yes	Day 41 of manure storage	Ni et al., 2001
Simulated manure storage	4.74E+02	Yes	Averaged from days 37 and 46	Blanes-Vidal et al., 2012
Simulated manure storage	6.10E+02	Yes	Maximum emission	Blanes-Vidal et al., 2012
Pig barn emission	1.74E+02	Yes	Agitated condition	This study
Pig barn emission	9.81E+02	Yes	Agitated condition	This study

efficient to environmental conditions. For example, a constant overall mass transfer coefficient, a linear increase in overall mass transfer coefficient with air velocity in the Gostelow model (Gostelow et al., 2001), and a power-function increase of overall mass transfer coefficient with air velocity in TOXCHEM+ have been assumed in different modeling approaches (Santos et al., 2012). An empirical correlation between the overall mass transfer coefficient and environmental conditions was experimentally developed for water and manure in a convective emission chamber (Arogo et al., 1999). A similar methodology based on wind tunnel testing was used to measure the overall mass transfer coefficient for developing an emission model for wastewater, but the coefficient values differed by two orders of magnitude (Santos et al., 2012), and the smaller values were corroborated with the data used in other emission models (Blunden, 2006).

Following that study, a relationship between the overall mass transfer coefficient and corresponding environmental parameters was obtained by multiple linear regression, and an empirical emission model was developed with good agreement with observations from a manure storage lagoon (Rumsey and Aneja, 2014). The model slightly overestimated emission flux, and the authors attributed the differ-

Table 8. Overall mass transfer coefficient of H_2S available in literature of experimental or modeling studies.

Experimental or Simulation Setting	Coefficient ($m\ s^{-1}$)	Chemical	Note	Reference
Pig manure storage	1.80E-04	$[H_2S(L)]$	Prediction at 20°C air and manure temperatures and 0.1 $m\ s^{-1}$ air velocity	Arogo et al., 1999
Pig waste lagoon	8.84E-08	$[H_2S(L)]$	Averaged from three experimental conditions	Blunden et al., 2008a
Pig waste lagoon	1.99E-06	$[H_2S(L)]$	Predicted from mass transport model neglecting chemical reactions	Blunden et al., 2008a
Pig waste lagoon	1.17E-05	$[H_2S(L)]$	Predicted from mass transport model with chemical reactions but constant pH	Blunden et al., 2008a
Pig waste lagoon	1.21E-05	$[H_2S(L)]$	Predicted from mass transport model with chemical reactions and pH gradient	Blunden et al., 2008a
Pig waste lagoon	1.43E-08	Total $[S^{2-}]$	Predicted from model including surface pH adjustment	Blanes-Vidal et al., 2009
Pig waste lagoon	1.11E-08	Total $[S^{2-}]$	Experimental data	Blanes-Vidal et al., 2009
Wastewater lagoon	5.23E-06	$[H_2S(L)]$	A constant in WATER9	Santos et al., 2012
Wastewater lagoon	2.08E-06	$[H_2S(L)]$	Averaged from experimental data of low friction velocity	Santos et al., 2012
Wastewater lagoon	5.97E-06	$[H_2S(L)]$	Predicted for low friction velocity based on TOXCHEM+	Santos et al., 2012
Wastewater lagoon	1.70E-05	$[H_2S(L)]$	Predicted for low friction velocity based on Gostelow model	Gostelow et al., 2001; Santos et al., 2012
Pig waste lagoon	6.60E-08	$[H_2S(L)]$	Averaged from four experimental durations	Rumsey and Aneja, 2014

ence partially to the deviation in surface pH and bulk pH in the manure storage. This novel observation about surface pH and its disruption is critical and must be considered in H_2S emissions from animal barns. A similar trend was observed in studies using two-film theory to simulate emissions (Blunden et al., 2008a), and a correction of the interface pH based on buffer components seemed to effectively address the overestimation (Blanes-Vidal et al., 2009). As mentioned (table 8), values of the overall mass transfer coefficient vary considerably in the literature, i.e., from 1.11×10^{-8} to 1.80×10^{-4} $m\ s^{-1}$ for dissolved H_2S concentrations. More appropriate coefficient values might be deduced from deep-pit emission studies, given the inclusion of the corresponding sulfide concentrations and pH values. However, these data are not yet accessible in animal barn emission studies.

Therefore, two very different values of mass transfer coefficient were found in the literature: 5.23×10^{-6} $m\ s^{-1}$ was adopted in the WATER9 model and many wastewater lagoon emission studies where the liquid was running or the surface was constantly disrupted, or where the simulated waste was at extremely low pH (table 8), and 1.11×10^{-8} to 6.60×10^{-8} $m\ s^{-1}$ (calculated from data provided in the corresponding studies) was recently found to be more suitable for swine lagoon emission studies. To reflect this research progress, two scenarios must be distinguished according to the air-liquid interface condition. When the air-liquid interface is quiescent, it is appropriate to adopt the most recent value of about 6.60×10^{-8} $m\ s^{-1}$ as observed at common temperatures (Rumsey and Aneja, 2014), corrected from previous results (Santos et al., 2012), and corroborated by a similar data range in a swine lagoon study (Blanes-Vidal et al., 2009). Note that this value was observed at a wind speed range of 1.45 to 2.76 $m\ s^{-1}$, corresponding to a friction velocity of 0.038 to 0.077 $m\ s^{-1}$, which is considered a low friction velocity and quiescent conditions, e.g., <0.3 $m\ s^{-1}$ (Santos et al., 2012). This friction velocity range is compatible with the airflow range in the pit headspace and room space regardless of barn ventilation conditions. When the air-liquid interface is disrupted, e.g., when the manure is agitated, a value of 5.23×10^{-6} $m\ s^{-1}$ would be more appropriate. For future barn emission modeling based on mass transfer coefficients, it is recommended to select between the two coefficients by carefully evaluating the stability of the air-liquid interface.

CONCLUSION

This study collected and analyzed manure samples from foaming and non-foaming deep-pit swine barns. It was found that a sulfide reservoir was located in the top layers of the deep-pit manure and in the foam. The foaming and non-foaming barns had different gas reservoir locations: the former was in the foam, and the latter was in the bottom sludge layer. The distribution of manure characteristics varied substantially, not only vertically but also horizontally. This study then evaluated H_2S concentrations and emissions in the pit headspace and room air for six different ventilation scenarios when the manure pit was agitated for pump-out and land application. An artificial neural network predicted the fraction of H_2S emitted in the pit fan exhaust, and pit ventilation released a dominant amount of H_2S when the pit and wall ventilations were comparable. The simulation of agitated manure suggested that pit ventilation was more effective than wall ventilation in decreasing H_2S concentration in the room air, where animals may be located. A minimal pit ventilation rate of 40 cfm per pig was necessary to lower the peak concentration in the room air to less than the permissible exposure limit of 20 ppm.

The simulation results also indicated that gas bubble release during manure agitation accounted for the main part of H_2S release for the foaming barn, and the expedited diffusion over mass transfer was considered the main emission mechanism for the non-foaming barn. For both the foaming and non-foaming barns, the air-manure interface was disturbed during agitation and induced a decrease in pH, thereby increasing the apparent overall mass transfer coefficient of H_2S and resulting in a substantially increased mass transfer rate and H_2S concentration. For the foaming barn, the IDLH exposure limit may be reached for up to 40 min in the room air when full ventilation is not provided. This study simulated the spatial and temporal distributions of H_2S during a manure pump-out event. The results can help with the design of emission treatment systems and secure the health and safety of workers and animals under possible H_2S exposure.

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REFERENCES

Alowairdi, L. (2016). Teenager killed in farm accident in Clark County (14 Sept. 2016). Eau Claire, WI: WEAU 143 News. Retrieved from http://www.weau.com/content/news/Teenager-killed-in-farm-accident-in-Clark-County-393467341.html

APHA. (1998). *Standard methods for the examination of water and wastewater*. Washington, DC: American Public Health Association.

Arogo, J., Zhang, R. H., Riskowski, G. L., & Day, D. L. (1999). Mass transfer coefficient for hydrogen sulfide emission from aqueous solutions and liquid swine manure. *Trans. ASAE, 42*(5), 1455-1462. https://doi.org/10.13031/2013.13309

Ballerino-Regan, D., & Longmire, A. W. (2010). Hydrogen sulfide exposure as a cause of sudden occupational death. *Arch. Pathol. Lab. Med., 134*(8), 1105.

Beaver, R. L., & Field, W. E. (2007). Summary of documented fatalities in livestock manure storage and handling facilities: 1975-2004. *J. Agromed., 12*(2), 3-23. https://doi.org/10.1300/J096v12n02_02

Blanes-Vidal, V., Guardia, M., Dai, X.-R., & Nadimi, E. S. (2012). Emissions of NH_3, CO_2, and H_2S during swine wastewater management: Characterization of transient emissions after air-liquid interface disturbances. *Atmos. Environ., 54*, 408-418. https://doi.org/10.1016/j.atmosenv.2012.02.046

Blanes-Vidal, V., Sommer, S. G., & Nadimi, E. S. (2009). Modeling surface pH and emissions of hydrogen sulfide, ammonia, acetic acid, and carbon dioxide from a pig waste lagoon. *Biosyst. Eng., 104*(4), 510-521. https://doi.org/10.1016/j.biosystemseng.2009.09.008

Blunden, J. (2006). Measurement, analysis, and modeling of hydrogen sulfide emissions from a swine facility in North Carolina. Raleigh, NC: North Carolina State University, Department of Marine, Earth, and Atmospheric Sciences.

Blunden, J., & Aneja, V. P. (2008). Characterizing ammonia and hydrogen sulfide emissions from a swine waste treatment lagoon in North Carolina. *Atmos. Environ., 42*(14), 3277-3290. https://doi.org/10.1016/j.atmosenv.2007.02.026

Blunden, J., Aneja, V. P., & Overton, J. H. (2008a). Modeling hydrogen sulfide emissions across the gas-liquid interface of an anaerobic swine waste treatment storage system. *Atmos. Environ., 42*(22), 5602-5611. https://doi.org/10.1016/j.atmosenv.2008.03.016

Blunden, J., Aneja, V. P., & Westerman, P. W. (2008b). Measurement and analysis of ammonia and hydrogen sulfide emissions from a mechanically ventilated swine confinement building in North Carolina. *Atmos. Environ., 42*(14), 3315-3331. https://doi.org/10.1016/j.atmosenv.2007.06.040

Bullvine. (2015). Wisconsin father and son died after falling into a manure pit at their family farm (17 July 2015). Hamilton, Ontario, Canada: The Bullvine. Retrieved from http://www.thebullvine.com/news/wisconsin-father-and-son-died-after-falling-into-a-manure-pit-at-their-family-farm/

Carrera-Chapela, F., Donoso-Bravoc, A., Gonzaleza, J. A., & Ruiz-Filippib, G. (2016). Air emissions from a sludge thickener: Dynamic data for air quality models. *Chem. Eng. Trans., 54*, 151-156. https://doi.org/10.3303/CET1654026

Chénard, L., Lemay, S. P., & Laguë, C. (2003). Hydrogen sulfide assessment in shallow-pit swine housing and outside manure storage. *J. Agric. Saf. Health, 9*(4), 285-302. https://doi.org/10.13031/2013.15458

Currie, L. A. (1999). Detection and quantification limits: Origins and historical overview. *Anal. Chim. Acta, 391*(2), 127-134. https://doi.org/10.1016/S0003-2670(99)00105-1

Dai, X.-R., Saha, C. K., Ni, J.-Q., Heber, A. J., Blanes-Vidal, V., & Dunn, J. L. (2015). Characteristics of pollutant gas releases from swine, dairy, beef, and layer manure, and municipal wastewater. *Water Res., 76*, 110-119. https://doi.org/10.1016/j.watres.2015.02.050

Douphrate, D. I., Stallones, L., Lunner Kolstrup, C., Nonnenmann, M. W., Pinzke, S., Hagevoort, G. R., ... Xue, L. (2013). Work-related injuries and fatalities on dairy farm operations: A global perspective. *J. Agromed., 18*(3), 256-264. https://doi.org/10.1080/1059924X.2013.796904

Farm and Dairy. (2016). OSHA: Ohio farm worker killed by manure gas (6 April 2016). Salem, OH: Farm and Dairy. Retrieved from https://www.farmanddairy.com/news/osha-ohio-farm-worker-killed-by-manure-gas/328366.html

Flury, S., Glud, R. N., Premke, K., & McGinnis, D. F. (2015). Effect of sediment gas voids and ebullition on benthic solute exchange. *Environ. Sci. Tech., 49*(17), 10413-10420. https://doi.org/10.1021/acs.est.5b01967

Gostelow, P., Parsons, S. A., & Cobb, J. (2001). Development of an odorant emission model for sewage treatment works. *Water Sci. Tech., 44*(9), 181-188. https://doi.org/10.2166/wst.2001.0535

Hallam, D. M., Liao, J., & Choi, K. (2012). Manure pit injuries: Rare, deadly, and preventable. *J. Emerg. Trauma Shock, 5*(3), 253. https://doi.org/10.4103/0974-2700.99702

Heber, A. J., Ni, J.-Q., Lim, T. T., Tao, P.-C., Schmidt, A. M., Koziel, J. A., ... Jacobson, L. D. (2006). Quality-assured measurements of animal building emissions: Gas concentrations. *J. Air Waste Mgmt. Assoc., 56*(10), 1472-1483. https://doi.org/10.1080/10473289.2006.10465680

Hoff, S. J., Bundy, D. S., Nelson, M. A., Zelle, B. C., Jacobson, L. D., Heber, A. J., ... Beasley, D. B. (2006). Emissions of ammonia, hydrogen sulfide, and odor before, during, and after slurry removal from a deep-pit swine finisher. *J. Air Waste Mgmt. Assoc., 56*(5), 581-590. https://doi.org/10.1080/10473289.2006.10464472

Jacobson, L. D., Bicudo, J. R., Schmidt, D. R., Wood-Gay, S., Gates, R. S., & Hoff, S. J. (2003). Air emissions from animal production buildings. *Proc. 11th Intl. Congress ISAH* (pp. 23-27). International Society for Animal Husbandry.

Jacobson, L. D., Hu, B., Yan, M., & Akdeniz, N. (2013). The potential causes of manure pit foaming in pig finishing barns. ASABE Paper No. 131620730. St. Joseph, MI: ASABE. http://dx.doi.org/10.13031/aim.20131620730

Jacobson, L. D., Janni, K. A., Hetchler, B. P., & Schmidt, D. R. (2005). Partitioning of ammonia and hydrogen sulfide emissions into pit and wall exhaust fractions for a deep-pit pig finishing barn. ASAE Paper No. 054035. St. Joseph, MI: ASAE. https://doi.org/10.13031/2013.19834

Jacobson, L. D., Schmidt, D. R., Lazarus, W. F., & Koehler, R.

(2011). Reducing the environmental footprint of pig finishing barns. ASABE Paper No. 1110589. St. Joseph, MI: ASABE.

Janni, K. A., Jacobson, L. D., & Hetchler, B. P. (2009). Three-zone model of ammonia and hydrogen sulfide in a deep-pit swine finishing barn. *Proc. 8th Intl. Livestock Environment Symp.* (p. 229-235). St. Joseph, MI: ASABE.

Leonard, B. (2015). Over 1,000 hogs die in confinement pit gas accident near Tracy (3 Nov. 2015). Knoxville, IA: KNIA/KRLS News. Retrieved from http://kniakrls.com/2015/11/over-1000-hogs-die-in-confinement-pit-gas-accident-near-tracy/

Lim, T.-T., Heber, A. J., Ni, J.-Q., Sutton, A. L., & Shao, P. (2003). Odor and gas release from anaerobic treatment lagoons for swine manure. *J. Environ. Qual., 32*(2), 406-416. https://doi.org/10.2134/jeq2003.4060

Lin, H., Williams, N., King, A., & Hu, B. (2016). Electrochemical sulfide removal by low-cost electrode materials in anaerobic digestion. *Chem. Eng. J., 297*, 180-192. https://doi.org/10.1016/j.cej.2016.03.086

Liu, Z., Powers, W., Murphy, J., & Maghirang, R. (2014). Ammonia and hydrogen sulfide emissions from swine production facilities in North America: A meta-analysis. *J. Animal Sci., 92*(4), 1656-1665. https://doi.org/10.2527/jas.2013-7160

Martin, J. H. (2003). A characterization of transformations occurring as swine manure accumulates in deep pits. Boston, MA: Eastern Research Group, Inc.

Matos, R. V., Matias, N., Ferreira, F., & Matos, J. S. (2016). Dynamic modeling of hydrogen sulfide within enclosed environments in biosolids recovery facilities. *Water Environ. Res., 88*(12), 2209-2218. https://doi.org/10.2175/106143016X14798353399179

Mueller, C. (2016). Coroner: Farmer died of gas poisoning (14 Sept. 2014). Appleton, WI: Stevens Point Journal. Retrieved from http://www.stevenspointjournal.com/story/news/2016/09/14/coroner-farmer-died-gas-poisoning/90365328/?hootPostID=116e126a90c5dabc8fb7604e6d681d17

Ni, J. Q., Heber, A. J., Sutton, A. L., & Kelly, D. T. (2009). Mechanisms of gas releases from swine wastes. *Trans. ASABE, 52*(6), 2013-2025. https://doi.org/10.13031/2013.29203

Ni, J.-Q., Heber, A. J., Diehl, C. A., & Lim, T. T. (2000a). SE-structures and environment: Ammonia, hydrogen sulfide, and carbon dioxide release from pig manure in under-floor deep pits. *J. Agric. Eng. Res., 77*(1), 53-66. https://doi.org/10.1006/jaer.2000.0561

Ni, J.-Q., Heber, A. J., Diehl, C. A., Lim, T. T., Duggirala, R. K., & Haymore, B. L. (2000b). Burst releases of hydrogen sulfide in mechanically ventilated swine buildings. *Proc. Water Environ. Fed., 2000*(3), 564-574. https://doi.org/10.2175/193864700785302971

Ni, J.-Q., Heber, A. J., Kelly, D. T., & Sutton, A. L. (2001). Mechanism of gas release from liquid swine wastes. ASAE Paper No. 014091. St. Joseph, MI: ASAE. https://doi.org/10.13031/2013.15699

OSHA. (2017). 29 CFR 1910.1000, Table Z-2: Toxic and hazardous substances. Washington, DC: Occupational Safety and Health Administration.

Park, J., Kang, T., Jin, S., Heo, Y., Kim, K., Lee, K., ... Yoon, C. (2016). Asphyxiation incidents by hydrogen sulfide at manure storage facilities of swine livestock farms in Korea. *J. Agromed., 21*(2), 144-148. https://doi.org/10.1080/1059924X.2016.1141735

Patni, N. K., & Clarke, S. P. (1991). Transient hazardous conditions in animal buildings due to manure gas released during slurry mixing. *Appl. Eng. Agric., 7*(4), 478-484. https://doi.org/10.13031/2013.26249

Patni, N. K., & Clarke, S. P. (2003). Gaseous emissions in swine barns and during slurry mixing in sub-floor pits. ASABE Paper No. 034081. St. Joseph, MI: ASAE.

Rodgers, G., & Eller, D. (2015). Iowa father, son die from manure pit fumes (28 July 2015). Des Moines, IA: Des Moines Register. Retrieved from https://www.desmoinesregister.com/story/money/agriculture/2015/07/28/iowa-father-son-die-manure-pit-fumes/30809037/

Rumsey, I. C., & Aneja, V. P. (2014). Measurement and modeling of hydrogen sulfide lagoon emissions from a swine concentrated animal feeding operation. *Environ. Sci. Tech., 48*(3), 1609-1617. https://doi.org/10.1021/es403716w

Rumsey, I. C., Aneja, V. P., & Lonneman, W. A. (2014). Characterizing reduced sulfur compounds emissions from a swine concentrated animal feeding operation. *Atmos. Environ., 94*, 458-466. https://doi.org/10.1016/j.atmosenv.2014.05.041

Santos, J. M., Kreim, V., Guillot, J.-M., Reis, N. C., de Sá, L. M., & Horan, N. J. (2012). An experimental determination of the H_2S overall mass transfer coefficient from quiescent surfaces at wastewater treatment plants. *Atmos. Environ., 60*, 18-24. https://doi.org/10.1016/j.atmosenv.2012.06.014

Spellman, F. R., & Whiting, N. E. (2007). *Environmental management of concentrated animal feeding operations (CAFOs).* Boca Raton, FL: CRC Press.

Swestka, R. J. (2010). Hydrogen sulfide spatial distribution and exposure in deep-pit swine housing. MS thesis. Ames, IA: Iowa State University, Department of Agricultural Engineering.

Trabue, S. L., Kerr, B. J., Bearson, B. L., Hur, M., Parkin, T., Wurtele, E. S., & Ziemer, C. J. (2016). Microbial community and chemical characteristics of swine manure during maturation. *J. Environ. Qual., 45*(4), 1144-1152. https://doi.org/10.2134/jeq2015.09.0446

USDA. (2014). 2012 Census of Agriculture: United States summary and state data. Geographic Area Series Part 51. Washington, DC: USDA.

Van Kessel, T., & Van Kesteren, W. G. (2002). Gas production and transport in artificial sludge depots. *Waste Mgmt., 22*(1), 19-28. https://doi.org/10.1016/S0956-053X(01)00021-6

Ye, Z., Saha, C. K., Li, B., Tong, G., Wang, C., Zhu, S., & Zhang, G. (2009). Effect of environmental deflector and curtain on air exchange rate in slurry pit in a model pig house. *Biosyst. Eng., 104*(4), 522-533. https://doi.org/10.1016/j.biosystemseng.2009.09.015

Zahn, J. A., Tung, A. E., Roberts, B. A., & Hatfield, J. L. (2001). Abatement of ammonia and hydrogen sulfide emissions from a swine lagoon using a polymer biocover. *J. Air Waste Mgmt. Assoc., 51*(4), 562-573. https://doi.org/10.1080/10473289.2001.10464295

Zhao, L. Y., Manuzon, R., Brugger, M., Arnold, G., & Bender, R. (2005). Air quality of swine wean-finish facilities with deep-pit and pull-plug-lagoon manure storage systems. *Proc. 7th Intl. Livestock Environment Symp.* (pp. 207-215). St. Joseph, MI: ASABE. https://doi.org/10.13031/2013.18366

Zhu, J. (2000). A review of microbiology in swine manure odor control. *Agric. Ecosyst. Environ., 78*(2), 93-106. https://doi.org/10.1016/S0167-8809(99)00116-4

Zong, C., Zhang, G., Li, H., & Rong, L. (2014). Investigation on ventilation characteristics in a full-scale model pig house with partial pit ventilation system. *Proc. Intl. Conf. of Agricultural Engineering (AgEng 2014).* European Society of Agricultural Engineers (EurAgEng).