Water Air Soil Pollut (2015) 226: 104
DOI 10.1007/s11270-015-2357-y

Microbial Additives in Controlling Odors from Stored Swine Slurry

Eunsun Choi · Jaehyuk Kim · Il Choi · Hyunmi Ahn · Jong In Dong · Hyunook Kim

Received: 9 June 2014 / Accepted: 17 February 2015 / Published online: 20 March 2015

Abstract At livestock farms, the most important thing is to control odors released from manure. In this study, four commercially available microbial additives designed to control odor and NH_3 emissions were applied to swine slurries stored in containers, and their effectiveness in odor reduction was statistically evaluated. Seventeen different odorous compounds in the headspace of each container were analyzed to calculate an overall odor index for slurries treated with different microbial additives over time. Of the four microbial additives tested in this study, only two were effective in reducing the odors from the swine slurry. After a 80-day storage period, the odor indexes of the slurries could be reduced by over 70 % with 50 % reduction in volatile fatty acids. In addition, a significant five orders of magnitude reduction in *Escherichia coli* could be achieved within 60 days. The other two microbial additives did not affect the odor characteristics of swine slurries under storage; their time profiles were statistically identical with that of the control. Results of this study imply that farmers considering applying microbial additives for controlling odors from swine manure should be careful in choosing an additive.

Keywords Swine manure odor · Odor reducing additives · Deodorants · Microbial additives

1 Introduction

The size of swine operations in many countries, especially those in Asia and in America, has increased over the past decades (Suresh and Choi 2011). As a result, more animal manure is generated, causing unpleasant odor issues to nearby residential area and deteriorating the residents' quality of life and property value (Blanes-Vidal et al. 2009). Therefore, the public, regulatory, and legal attention regarding odor problems from the swine operation has increased, forcing swine producers to remove odor emissions from their animal housings and manure handling facilities (Wing et al. 2008).

A variety of treatment technologies have been applied to control odors from animal manure treatment facilities. These treatments include scrubbing (Melse et al. 2009), adsorption (Shuler and Kargi 2002), absorption (Zhang et al. 2013), biofiltration (Sheridan et al. 2003), composting (Canovai et al. 2004), incineration (Melse and Timmerman 2009), and addition of a masking agent or chemical/microbial odor-reducing agents (Melse and Timmerman 2009). Scrubbers transfer odorous pollutants from the gas phase to the aqueous

Electronic supplementary material The online version of this article (doi:10.1007/s11270-015-2357-y) contains supplementary material, which is available to authorized users.

E. Choi · J. Kim · J. I. Dong · H. Kim (✉)
Department of Environmental Engineering, University of Seoul, Seoul 130-743, Republic of Korea
e-mail: h_kim@uos.ac.kr

I. Choi
Department of Civil and Environmental Engineering, University of Delaware, Newark, DE, USA

H. Ahn
Department of Nursing, Korea Bible University, Seoul, Korea

phase often in acidic or basic conditions for controlling odorants, such as H_2S, dimethyl sulfide (DMS), and NH_3 (Zhang et al. 2013). In some cases, oxidants such as hypochlorite (Bejan et al. 2013), chlorine dioxide (Zhang et al. 2013), potassium permanganate (Bejan et al. 2013; Moreno et al. 2010), or ferric sulfate (Canovai et al. 2004) are also added into the scrubbing solution to destroy odorants. Nonetheless, this technology is limited to odorants with a high solubility (Theodore 2008), and resultant spent solution causes secondary pollution.

Another commonly applied technique is adsorbing odorants onto a solid medium. The media include silica gel, activated carbon, activated alumina, and synthetic resins, among others (Canovai et al. 2004; Shuler and Kargi 2002). The biofiltration methods such as biofilter, bioscrubber, and biotrickling filter are known to efficiently reduce odor emission from swine slurry with low maintenance and operating costs (Sheridan et al. 2003). However, biofiltration often encounters clogging problem in the summer due to high microbial growth, and lower odor removal efficiency in the winter due to low microbial activity at low temperature. In addition, its installation is often more expensive than other physicochemical odor reduction technologies (Kim et al. 2008; Moreno et al. 2010; Mudliar et al. 2010).

Off-gases from animal facilities can be incinerated, especially when odorant concentrations are very high. Although the incineration is efficient, it is costly and impractical (Melse and Timmerman 2009). Masking agents have been used to cover odors emitted from various sources, especially animal housings and manures (McCrory and Hobbs 2001; Zhang et al. 2000). If a masking agent is used in the open air, however, it can be diluted and lose its masking ability. In addition, the smell of a masking agent applied for reducing odor sensation may yield more odorous compounds. From this point of view, masking agents are not effective for animal manure odor control.

Some of the technologies stated above require a ventilation system for capturing odorous gas. In many countries, especially those in Asia and the North Ameria, most swine producers cannot afford the odorous compounds capturing and treating facilities since their pig houses and manure storages are open to air, which hinders these technologies from being readily applied, rather, they prefer adding a so-called odor-reducing agent to feeds or to generated manure. In addition, the application of an additive does not require high operational expertise (Zhang et al. 2000). Therefore, famers find this technology as the easiest way to control odors from their various odor sources including swine housings, manure storage facilities, and wastewater treatment facilities (McCrory and Hobbs 2001).

There are a variety of additives on the market for controlling odors emitted from swine slurry pits or storages, including enzymatic additives and a mixture of selected functional microorganisms for degrading odorants (Zhu 2000), chemical additives (e.g., $KMnO_4$, H_2O_2, Cl_2, O_3) (Varel 2002) for destroying odorants and for disinfection, and essential oils and soybean oil (Kim et al. 2008) for preventing odorants from releasing from slurry. Some deodorizing agents like chemical additives have been shown effective in reducing odors from animal manures (Zhu 2000). However, most of the deodorizing additives on the market, especially microbial additives for swine slurry, have not been objectively and systematically evaluated for their effectiveness in odor reduction. Furthermore, most of previous studies on additives for swine slurry odor control were performed in small-scaled laboratory settings (Zhu 2000). Moreover, in these studies, only few gaseous compounds (most H_2S and NH_3) were monitored over a short period of time. Some odorants with extremely low threshold levels or gaseous volatile fatty acids (VFAs) were not monitored. Considering that swine manure odor is caused by a mixture of numerous compounds generated through slow and complex manure decomposition process (Varel 2002), any odor control measure should be evaluated through a more comprehensive and long-term study.

Consequently, this study was undertaken to systematically evaluate effectiveness of four different commercial microbial additives for minimizing odor emissions from swine slurry. A total of 16 odorous compounds in addition to NH_3 were quantified using solid-phase microextraction (SPME) followed by gas chromatograph (GC) analysis. The target gas compounds analyzed in this study have been considered as major odorants released from animal manure collection, handling, storage, and application practices (Filipy et al. 2006; Kim et al. 2003; Otto et al. 2003). The measured concentrations of all the target analytes were converted to individual odor indexes (Knudsen et al. 1999), to evaluate the contribution of each odorant to the overall odor sensation. In addition, the odor indexes were summed up to qualitatively describe the extent of odor reduction by different additives.

In addition to the monitoring of odor emissions from slurries under storage, a variety of manure quality parameters were monitored to evaluate the extent of changes in slurry characteristics though long-term (more than 80 days) observation. Changes in these parameters indicate microbial activity responsible for odor generation as well reduction of odor-causing substances during long-term storage. The parameters evaluated included pH, oxidation-reduction potential (ORP), temperature, solids contents, chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), and *Escherichia coli* of bulk liquid manure. The paper will provide swine producers with a guidance to seect the best microbial additive for their usage.

2 Materials and Method

2.1 Manure Source

Swine slurry stored in this study was collected from a receiving pit of a finishing swine barn in Suwon, Korea. The pigs were fed with a typical diet including corn, soybean, and a mixture of tallow, mineral, vitamin, and ground fish. The characteristics of the swine slurry are summarized in Table 1.

2.2 Experimental Setup

For the experiment conducted in the field, there were ten storage containers (80 L each) with each container containing 60-L swine slurry under darkness. In order to simulate the actual practice, the containers were placed in a barn windows of which were open, so the inside temperature was almost the same with the outside, and condudcted from January to April; during the period, manure slurry from swine producers is strored in tanks in Korea. Four microbial additives were evaluated; two contained facultative microbes (A1 and A2), and the other two contained anaerobic microbes (A3 and A4). Each additive was added into two of the ten swine slurry containers for duplicated test with two other containers used as a control (without additive). Information about the microbial additives evaluated in this study is provided in Table 2 along with manufacturers' suggested application dose. Slurries under storage were slowly agitated using a mechanical mixer which was installed on each container once every 2 h for 4 h to homogenize the bulk liquid.

For about 80 days, samples of swine slurry were taken about once every 7–10 days from all the containers for analysis. Before samples were collected on each sampling event, pH, ORP, and temperature of the slurry were measured. Whenever a sampling event was conducted, the swine slurry was mixed using a mechanical mixer to allow the liquid to be homogenized. Once samples were collected, they were transported to a laboratory for analysis of total solid (TS), total volatile solid (TVS), TKN, COD, and *E. coli* according to the Standard Methods (Clesceri et al. 2008).

Table 1 Characteristics of raw liquid slurry used in this study

Parameters	Value (RSD[a], %)
pH	7.6–8.4
ORP (mV)	−290 (2)
Temperature (°C)	1.0 (5)
COD (mg L^{-1})	22,000 (5)
TKN (mg L^{-1})	2600 (6)
NH_4^+-N (mg L^{-1})	2200 (4)
TS (%)	1.2 (10)
TVS (%)	0.6 (15)
Total P (mg L^{-1})	270 (30)
VFA (mg L^{-1})	6000 (9)
E. coli (CFU mL^{-1})	7.2×10^4 (15)

RSD relative standard deviation, % (n=3)

2.3 Collection and Analysis of Odorous Compounds

2.3.1 Odorants Including VFAs

Gas extraction for all the odorants except NH_3 was performed using SPME in the headspace over the swine slurries. Before each gas sampling event was conducted, a specially designed cover in lieu of old cover was placed on each container to allow gas sampling using SPME. Each cover has two injection ports, sealed with a Teflon coated septa through which the needle of a SPME device was inserted, so that duplicate sampling could be made. Clean sweep gas (odor-free nitrogen gas) was flown through the headspace of each container at 2 L min^{-1} for 30 min before two SPME fibers were exposed in the headspace for another 30 min. After sampling, SPME fibers were placed in a cooler with dry ice and transferred to the laboratory for analysis.

Table 2 Characteristicsof microbial additives and recommended application rate

Additives	Manufacturer country	Characteristics[a]	Recommended amount per liter of slurry[b]
A1	Korea	Facultative microbial agent (*Bacillus licheniformis* ≥ 1×10^8 CFU g^{-1}) Reduces odor emissions Increases the fluidity of manure slurry	0.2 g (once a month)
A2	Australia	Facultative microbial agent (*Bacillus subtilis* ≥ 5×10^8 CFU g^{-1}) Reduces odor and NH_3 gas emission Reduces pathogenic bacteria	0.02 g (twice a month)
A3	Japan	Anaerobic microbial agent (*Rhodopseudomonas capsulata* ≥ 5×10^9 CFU mL^{-1}) Reduces odor Increases the fluidity of manure slurry Reduces pathogenic bacteria	0.2 mL (once a month)
A4	USA	Anaerobic microbial agent(*Lactobacillus casei* ≥ 1×10^8 CFU g^{-1}) Reduces odor emission and vector attractions	0.5 g (twice a month)

[a] From product brochures

[b] From the manufacturers application manual

The target analytes adsorbed on the SPME fibers were thermally extracted in the GC injection port and then quantified. The target analytes included indole, skatole, *p*-cresol, trimethylamine (TMA), VFAs [i.e., acetic acid (AA), propionic acid (PA), iso-butyric acid (iso-BA), butyric acid (BA), iso-valeric acid (iso-VA), valeric acid (VA), iso-caproic acid (iso-CA), and caproic acid (CA)], volatile sulfur compounds [VSCs: ethyl mercaptan (EM), propyl mercaptan (PM), butyl mercaptan (BM), DMS, dimethyl disulfide (DMDS), and carbon disulfide (CS_2)].

Analysis of VFAs was performed using a Hewlett-Packard 5890 GC coupled to flame ionization detection (Avondale, PA, USA). GC conditions were as follows: 30-m DB-Innowax column (J&W Scientific, Folsom, CA, USA) 0.25-mm id; 0.25-μm film thickness; injection port, 250 °C; detector, 280 °C; 30-min desorption time; initial temperature, 70 °C for 2 min; 4.5 °C min^{-1} to 170 °C; held for 2 min; 10 °C min^{-1} to 200 °C; held for 2 min; splitless injection mode.

TMA, the sulfur-containing compounds, and indole, skatole, and *p*-cresol were analyzed using a Hewlett-Packard GC/mass spectrometry detector (MSD) System (G1800A GCD, Palo Alto, CA, USA). GC conditions were as follows: 60-m DB-1 column (J&W Scientific, Folsom, CA, USA) 0.25-mm id; 1.0-μm film thickness; injection port, 270 °C; 30-min desorption time; initial temperature, 35 °C for 5 min; 3.0 °C min^{-1} to 70 °C; held for 2 min; 4.0 °C min^{-1} to 200 °C; held for 4 min; 10 °C min^{-1} to 250 °C; held for 1 min; splitless injection mode.

Both GC systems were equipped with a Merlin microseal septum designed for SPME to insure reproducibility between injections and 0.75-mm id glass liner (Supelco, Bellefonte, PA, USA). The MSD was set as a selected ion monitoring mode. The method detection limit of each along with its corresponding odor threshold is provided in Table 3. The needle with the exposed fiber was left in the heated injector until the end of the GC run to eliminate any possible carryover of material. The fibers were cleaned prior to use by baking them in the injection port for 30 min.

Gas standards were generated using certified Teflon membrane permeation tubular devices (NIST traceable, VICI Metronics, Santa Clara, CA) for each compound as in Susaya et al. (2011). The permeation tubular devices were placed in a thermostatedglass chamber (Model 320 Dynacalibrator, VICI Metronics). The flow rate of high purity (>99.99 %) nitrogen gas through the permeation chamber was 72 mL min^{-1}, and the gas concentration could be varied using additional N_2 dilution gas.

The standard curve for each odorant was made with at least five points, except for VFAs (four points), and each point was repeated a minimum of three times (each point repeated with different fibers). The resultant calibration curves were linear (R^2=0.997–0.999).

2.3.2 NH_3

Clean sweep gas (odor-free nitrogen gas) was flown through the headspace of each container for 30 min, and then, the additional sweep gas was collected for NH_3 measurement (2 L min^{-1} directly to impingers for 30 min). NH_3 concentration was measured using the

Table 3 Odor thresholds and MDLs for target compounds([a] Schiffman et al. 2001)

Compound analyzed	Odor threshold[a] (ppb)	MDL (ppb)	Compound analyzed	Odor threshold[a] (ppb)	MDL (ppb)
TMA	2.4	2.4	iso-BA	19.5	17.6
DMS	2.3	0.07	BA	3.9	1.32
DMDS	12	0.06	iso-VA	2.5	3.6
CS_2	95	0.2	VA	4.8	1.6
EM	1.1	15	iso-CA	0.6	3.5
PM	1.3	10	CA	0.4	2.5
BM	1.4	12	*p*-Cresol	1.9	0.5
AA	150	4	Indole	0.032	0.8
PA	35.5	1.8	Skatole	0.56	0.94

indophenol method (Verdouw et al. 1978). With the measured NH_3 mass in a given volume (60 L) and surface area, the NH_3 emission flux can be determined.

2.3.3 Odor Index

The measured concentration of individual odorous gas was converted to an odor index using Eq. 1 (Knudsen et al. 1999), so the contribution of each gas to odor sensation could be assessed. Then, all the individual odor indexes were summed to produce an overall odor index (Eq. 2). Using RStudio for Mac (RStudio, Boston, MA, USA), the analysis of variance (ANOVA) was performed to statistically evaluate differences between treatments, and Tukey test was performed as a post-ANOVA analysis.

$$\text{Individual odor index} = \frac{C_i}{OT_i} \quad (1)$$

$$\text{Overall odor index} = \sum_{i=1}^{n} \textit{individual odor index}_i \quad (2)$$

where C_i and OT_i is the measured concentration and odor threshold of an individual odorant, respectively.

3 Results and Discussion

3.1 Time Profiles of pH, ORP, Temperature, and Ammonia Emission Rate of Swine Slurries Under Storage

Figure 1a, b shows the time profiles of temperature and ORP of the swine slurries under storage over 80-day period (from January 19 to April 10). The temperature of all the slurries increased from 0.8–1 to 9–12 °C (Fig. 1b) due to seasonal change while ORP values decreased from −280–297 to −328–392 mV, indicating the stored swine slurries became more septic. In fact, the ORP of the slurries did not change in the initial 20 days due to the low atmospheric temperature; in Korea, the atmospheric temperature is normally often <0 °C from December to February. The low temperature certainly hindered microbial reactions from occurring in the slurries under storage.

In the case of pH, however, slurries treated with different microbial additives exhibited different profiles (Fig. 1c); it was confirmed with ANOVA test ($p<0.01$). The pH of slurries treated with additives A1 and A2 increased from 8 to >9, while the pH of the slurries amended with A3 and A4 stayed relatively constant or decreased slightly. In fact, the pH of the slurries tereated with A3 and A4 was similar to that of control ($p=0.29$). Apparently, the materials present in A1 and A2 may facilitate some reactions causing pH increases. As shown in Fig. 1c, NH_3 emission rates slightly decreased at the beginning; the exact reason is unclear. However, after February 22, NH_3 emission rate started to increase as the slurry temperature increased (Fig. 1b); the rates are much higher for A1 and A2 addition partially due to higher pHs in these two additives (pK_a for NH_3 is about 9.5). The fact that increased pHs positively correlated with NH_3 emission ($r=0.61$ and 0.63 for A1 and A2, respectively) has also been reported by others (Heber et al. 2000). It should be noted that the ammonia emission rates of the slurries amended with A3 and A4 were almost the same with that of the control ($p=0.76$). It is noted that comparison of NH_3 emission flux with literature data should be made with care since conditions

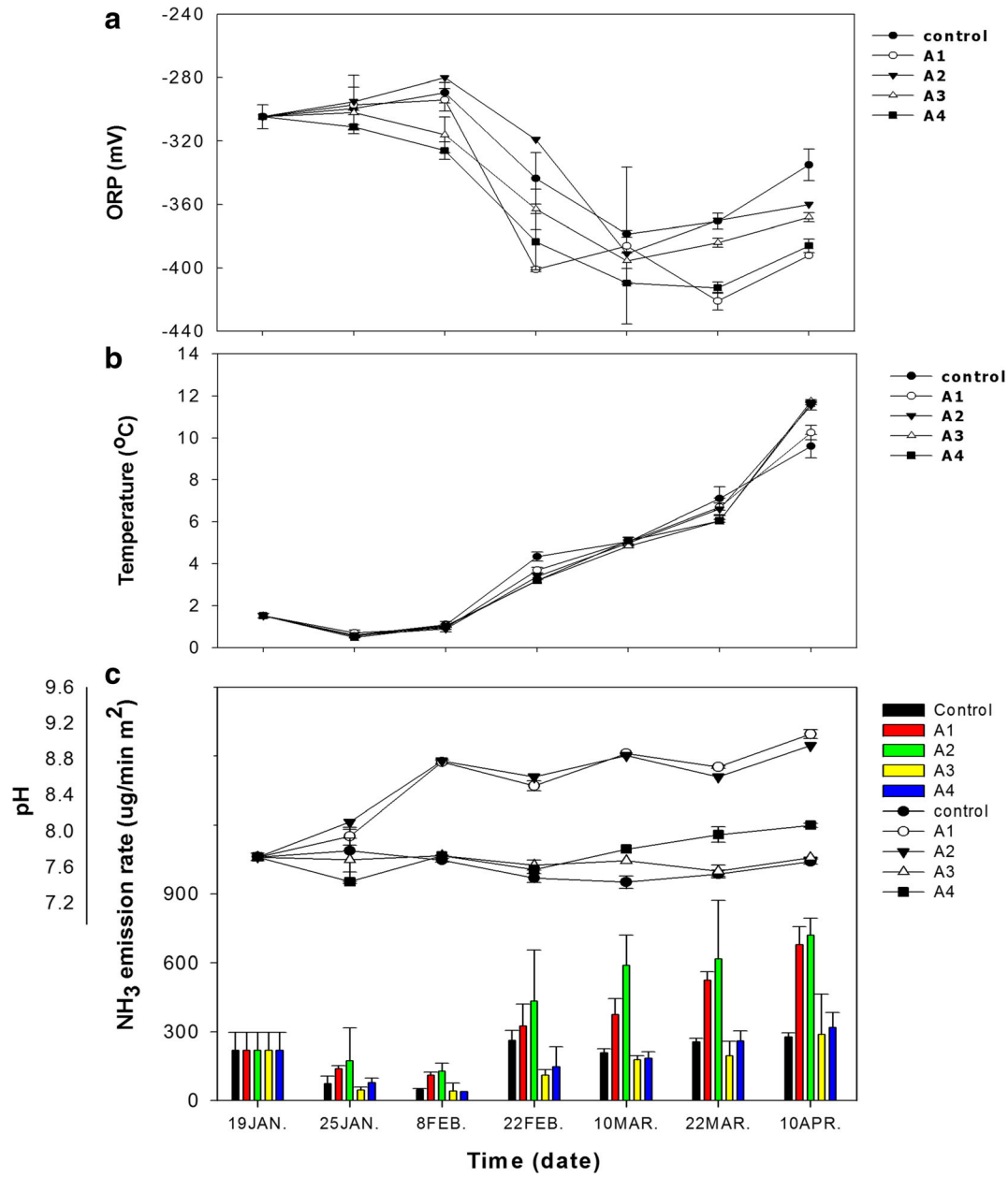

Fig. 1 Time profiles of swine slurries under storage (mean value of duplicate storages). **a** ORP, **b** temperature, **c** pH and NH3 emission rate

(e.g., temperature) and slurry characteristics (e.g., age of and solids contents) are different, e.g., in thousands of μg min^{-1} m^{-2} (Hobbs et al. (1999) from stirred aging pig slurry; Wheeler et al. (2010) from dairy manure slurry; Lim et al. (2003) from swine manure lagoon). Probably due to the low temperature, the NH_3 emission observed in our study was one magnitude lower than the ones reported in literature.

3.2 Odor Indexes for Each Storage

Typically, odor generation potential is related to solids concentration, organic carbon contents, and environmental conditions. Primary odor-causing compounds originate from degraded proteins and other nitrogenous compounds in animal manures (Nahm 2003). In particular, amines are produced through the removal of the

carboxyl (COOH) group from amino acids (Filipy et al. 2006) with *p*-cresol generated through microbial degradation of tyrosine. Degradation of tryptophan can bring about the production of indole and skatole (Mackie et al. 1998). VSCs are produced from the reduction of sulfate and from the metabolism of sulfur-containing amino acids (Zhu 2000).

Since many chemicals have different human detection thresholds, concentration values must be normalized to provide the reference as to the contribution of each compound to the overall odor characteristics for each treatment. Therefore, an odor index of each individual compound was calculated by dividing the average concentration of an odorant from swine slurries by its published odor threshold as shown in Eq. 1.

Figure 2a shows the overall odor index of each treatment over time. Several points need to be noted. Firstly, there is a trend of increasing odor index with time and then decreasing until the end of experiments. Secondly, the overall index profiles over time were different between treatments; the differences were verified statistically significant through the ANOVA test ($p<0.01$). In fact, only the overall odor indexes for A1 and A2 were found statisitcally different from that for control through Tukey test; the p values for the difference between the control and A1 and for that between the control and A2 were 0.007 and 0.006, respectively (see Table SM-1). Therefore, after 80-day period of storage, the overall odor indexes for the swine slurries treated with A1 and A2 were 73 and 76 % lower than that of the control. On the other hand, the overall odor indexes in slurries treated with additives A3 and A4 remained almost the same for the entire study period; the odor index profiles for A3 and A4 did not show

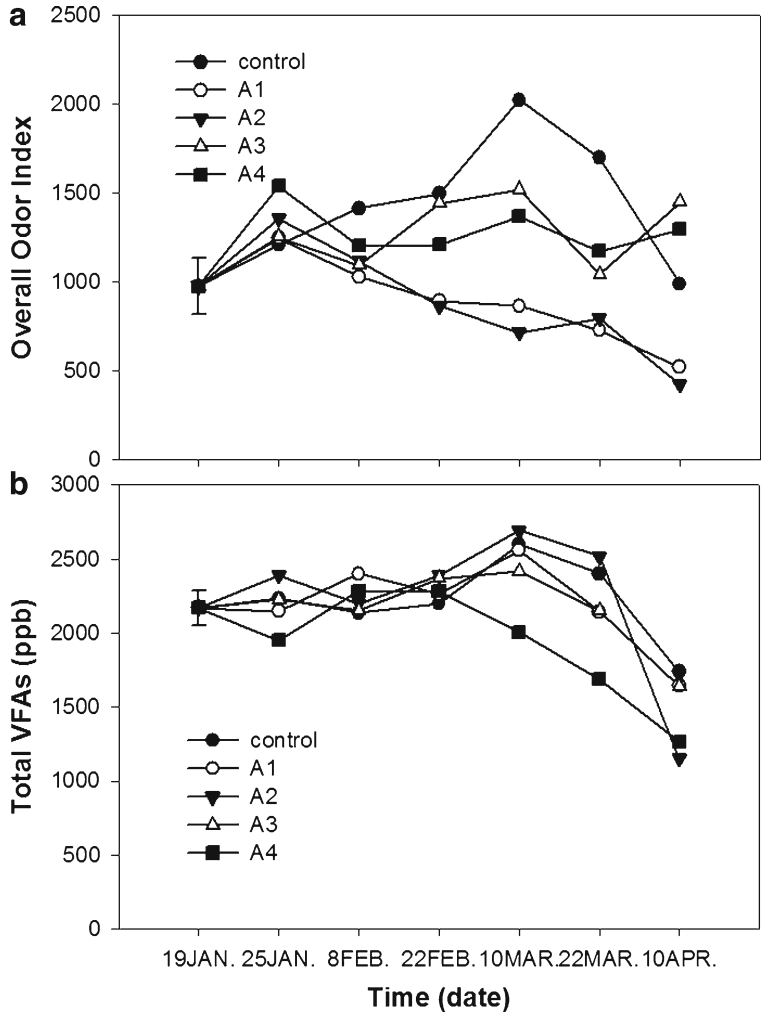

Fig. 2 Overall odor index and TVFAs of swine slurries with different treatments (mean value of duplicate storages)

statistically siginificant difference from that for the control (see Table SM-1). Thirdly, there are still relatively high index values even after a prolonged period (up to 80 days). Although the overall odor index used here is to qualitatively describe the extent of odor reduction during the slurry storage, it can provide indirect quantitative information as shown in Kim and Park (2008). Considering the high odor index values, it could be concluded that still odors from the slurries were quite strong even after the 80-day storage; in fact, the all the treatments were still odorous.

Major odorous compounds contributing to the overall odor index of each treatment were DMS, DMDS, *p*-cresol, skatole, and indole. Although the concentration of NH_3 in the headspace is relatively high (2 to 95 ppm), its contribution to the overall odor index was not significant due to its high odor detection threshold (47 ppm; Leonardos et al. 1969). On the other hand, although the concentrations of skatole and indole ranged from 4.5 to 163 ppb and from 1.9 to 36.0 ppb, respectively, their contribution to the overall odor index was significant due to their extremely low odor detection thresholds (i.e., 0.03 ppb for indole and 0.56 ppb for skatole (Table 3)).

3.3 VFAs from Swine Slurries Under Storage

VFAs, produced from the deamination of amino acids and from the degradation ofcarbohydrates and lipids (Zhu 2000), have been measured to evaluate the effectiveness of techniques to reduce swine manure odor (Zhang et al. 2000; Zhu et al. 2001). Therefore, the concentrations of VFAs produced from the swine slurries were measured (Table 4); individual VFA concentrations were summed and presented as a total VFA (TVFA) in Fig. 2b. In general, the TVFA concentration of each treatment gradually increased until March 10 and then decreased afterward. The TVFA reduction could be attributed to the anaerobic methane production and consumption of easily biodegradable components present in swine slurry (Mackie et al. 1998). Compared to the initial level, the TVFA level of each treatment was reduced by 30–50 % at the end of 80 days. It noted that even after 70-day period, the TVFA concentrations were still relatively high (from 1150 to 2500 ppb) depending on the type of additive used. This may partially explain high odor index observed during later stage of storage (Fig. 3a). Nonetheless, at the end of 70 days, the TVFA concentrations in all four treatments were all below that of the control, albeit treatment A2 only slightly below.

Nonetheless, AA accounted for major fraction of the TVFAs. At the end of 80-day storage period, the AA portion of the TVFAs in the swine slurries treated with A1 and A2 slightly increased;it accounted for 65 and 55 % of the total VFAs in the swine slurry amended with A2 and A1, respectively (data not shown). For comparison, in control and other additive systems (A3 and A4), AA was <50 % of the TVFAs. Lower contents of short-chain VFAs imply lower biological reactions in the slurry.

The odor threshold of AA is much higher than that of PA, VA, or BA (Table 3). Therefore, the slurries with higher AA content would be less odorous than slurries containing longer-chain VFAs under the condition where the TVFA level is similar as also reported by Zhu et al. (1996). In fact, VA, iso-CA, and CA were not detected from the headspace of the storage tanks for swine slurries treated with A1 and A2 after the 80-day storage period, but they could be detected from other slurries (Table 4).

The statistical analysis indicates that little correlation between odor index and TVFAs (e.g., r=0.04 for A3, etc.). This is due to the simple fact that major contributors to the overall odor index are from those compounds with lower odor threshold levels which are not belonging to VFAs, such as *p*-cresol and indole; the correlation coefficients between the overall odor index and *p*-cresol and indole for A2, for example, were 0.66 and 0.94, respectively (Fig. 3). From the result, it was conjectured that these indoles and cresol are more susceptable to facultative microbes than strict anaerobes, since the ring on each of them are more difficult to be degraded by anaerobes (Díaz et al. 2013). In fact, Zhu et al. (1996) have also reported that the malodor intensities are not proportionally related to the overall amount of volatile fatty acids existing in the swine manure. Rather indole was considered the major contributor to odor intensity of swine slurries (Trabue et al. 2011).

3.4 Effect of Microbial Additives on *E. coli* Population

On each sampling date, three aliquots of each treatment were collected and analyzed for *E. coli* population (Fig. 4a). The number of *E. coli* in slurries treated with A1 and A2 additives significantly decreased over the initial 60-day period of storage, particularly after January 25. The profiles for the *E. coli* numbers of the slurries treated A1 and A2 were siginificantly different

Table 4 Concentrations of VFAs (ppb) in swine slurries under storage (mean value of duplicate storages)

Content Date	AA					PA					iso-BA					BA				
	Control	A1	A2	A3	A4	Control	A1	A2	A3	A4	Control	A1	A2	A3	A4	Control	A1	A2	A3	A4
Jan. 19	1270	1270	1270	1270	1270	470	470	470	470	470	32	32	32	32	32	290	290	290	290	290
Jan. 25	1310	1260	1500	1340	1140	480	470	470	470	420	34	32	34	33	29	310	290	290	280	260
Feb. 8	1260	1450	1390	1260	1350	450	480	420	460	490	35	41	37	35	36	290	310	250	290	300
Feb. 22	1270	1370	1540	1380	1330	470	440	440	510	490	38	42	42	41	37	310	290	260	320	310
Mar.10	1530	1600	1710	1390	1140	540	460	510	510	370	47	56	54	48	53	360	320	290	340	310
Mar. 22	1360	1400	1540	1240	970	500	350	500	460	310	50	56	57	46	41	340	250	290	310	250
Apr. 10	1010	1040	820	960	730	330	290	180	310	190	42	51	41	39	40	250	190	60	230	200
Content Date	iso-VA					VA					iso-CA					CA				
	Control	A1	A2	A3	A4	Control	A1	A2	A3	A4	Control	A1	A2	A3	A4	Control	A1	A2	A3	A4
Jan. 19	43	43	43	43	43	34	34	34	34	34	7.9	7.9	7.9	7.9	7.9	18	18	18	18	18
Jan. 25	45	42	43	42	39	21	32	34	32	31	7.5	6.7	10	8.9	13	18	19	17	19	16
Feb. 8	46	54	49	45	46	32	38	33	33	33	7.0	8.1	8.5	7.1	7.1	17	17	14	17	18
Feb. 22	52	56	55	54	50	35	36	34	36	34	8.1	8.3	8.5	8.1	7.9	19	15	12	19	18
Mar.10	62	68	68	66	71	37	35	36	36	37	8.3	8.5	9.1	8.5	8.7	20	3.1	11	20	20
Mar. 22	70	62	74	60	52	37	19	37	35	31	8.7	7.5	8.5	8.5	8.1	21	BDL	11	18	17
Apr. 10	56	59	37	50	54	33	11	BDL	29	28	8.1	4.1	BDL	7.1	7.5	17	BDL	BDL	15	16

BDL below detection limit

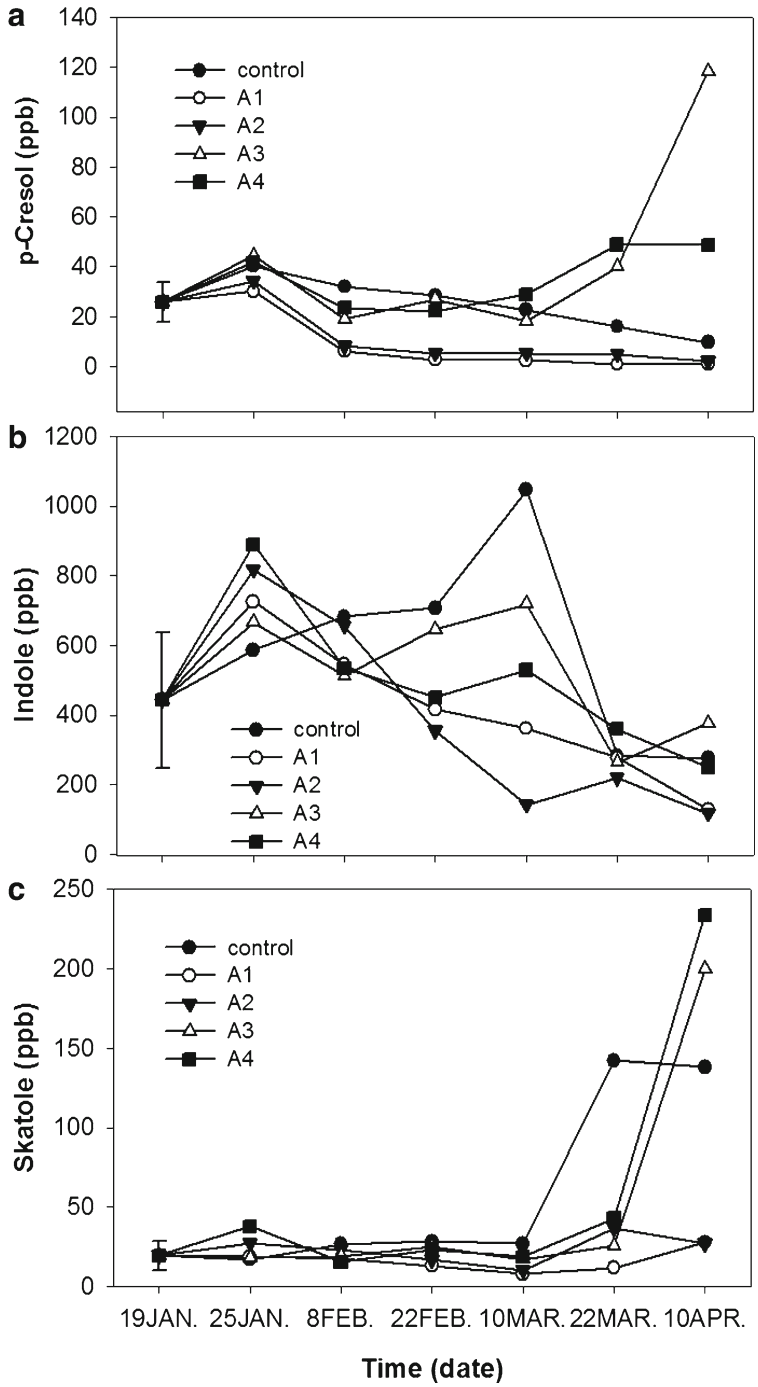

Fig. 3 Time profiles of swine slurries under storage (mean value of duplicate storages). **a** *p*-Cresol, **b** indole, **c** skatole concentrations

from that of the control; from the Tukey test, p values for the difference between the control and A1 and that between the control and A2 were found to be 0.09 and 0.04, respectively. The low *E. coli* countings of A1 and A2 were attributed to NH_3 gas formationin the treatments (r=−0.89 and −0.94 for A1 and A2, respectively) caused by the higher pHs (Fig. 1c). On the other hand, the number of *E. coli* in the control and in the slurries amended with A3 and A4 additives only decreased to a lesser extent; their *E. coli* countings were not statistically different (p>0.99). In practice, the number of *E. coli* in slurry can be used as an indicator for bacterial quality

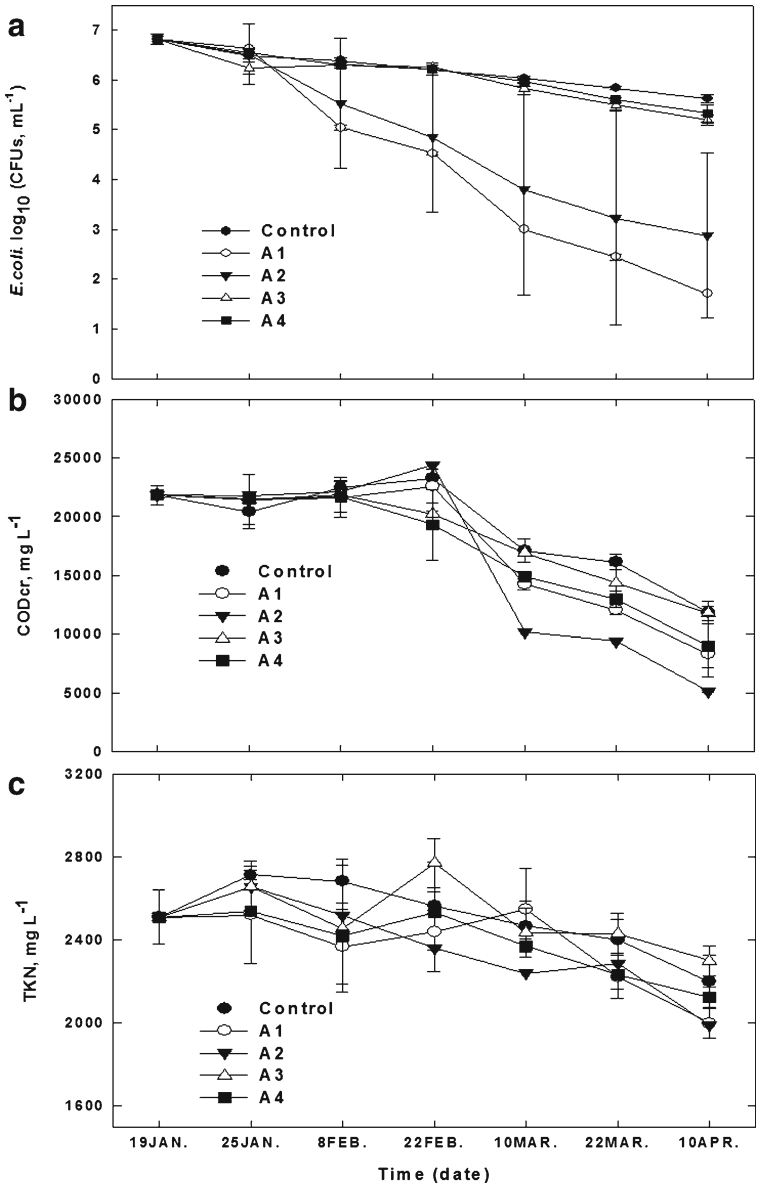

Fig. 4 Slurry quality parameters in swine slurries under storage. **a** *E. coli*, **b** COD, and **c** TKN

of slurry. In that sense, the slurries treated with A1 and A2 with negligible *E. coli* presence could be safely disposed off despite the fact they still emit VFAs and exhibit odor.

3.5 Effect of Microbial Additives on Organic and Nitrogen Contents of Slurries Under Storage

Over the entire period, COD and TKN of collected sample were analyzed and the results (Fig. 4b, c) indicated that COD reduction in the slurries treated with A1, A2, and A4 ranged from 66 to 77 % and those of control and the slurry treated with A3 only 43–48 %. In the case of TKN, all the treatments showed similar levels of TKN reduction (15–25 %). The reduction of COD and TKN after February 22 (beginning the warm season) clearly reflects higher microbial activity which is responsible for generating odors as well as reduction of odor-causing substances.

In short, along with previous parameters evaluated (e.g., odor index, TVFAs, and the *E. coli*), COD and TKN data all reveal the relative effectiveness of additive A1 and A2 among 4 agents used.

4 Conclusions

In this study, four commercially available microbial additives, i.e., A1, A2, A3, and A4, each of which is supposedly designed to control odor and NH_3 emissions from swine slurry, were evaluated. Of the four microbial additives tested in this study, only additives A1 and A2 could effectively reduce the odors from swine slurry.

More NH_3 gas was released from the slurries amended with the A1 and A2 than those treated with A3 and A4. In fact, the higher NH_3 emissions from the slurries treated with A1 and A2 were also related to the gradual increases of slurry pH over storage time. Also, the concentrations of other volatile odorants such as sulfurs, skatole, and indole in the slurries treated with A1 and A2 were lower than those in the slurries treated with A3 and A4 and the control. These odorants have much lower odor thresholds than NH_3. Therefore, overall odor indexes of the slurries with A1 and A2 were much lower than those of the control and the slurries treated with A3 and A4.

Another benefit of applying additives A1 and A2 to swine slurry was that the time required for *E. coli* reduction could be significantly reduced. Almost all the *E. coli* in the slurries amended with A1 and A2 could be removed from the slurry within the 3-month storage period. Furthermore, additives A1 and A2 were more effective in reduction of organic and nitrogen contents of slurry than A3 and A4.

The use of microbial additives may be site-specific and depend on many factors, including dosage, temperature, and type and characteristics of slurry used, among others. Therefore, producers who are planning to apply a microbial additive to control odors from their manure storage facility should realize the fact that all treatment additives are not effective and hence, need to setup a field trail evaluation to identify the type of additive to be used and the optimized amount of dosage applied.

Acknowledgments This work was supported by the R&D program of MOTIE/KEIT (R&D program number 10037331, Development of Core Water Treatment Technologies based on Intelligent BT-NT-IT Fusion Platform).

References

Bejan, D., Graham, T., & Bunce, N. J. (2013). Chemical methods for the remediation of ammonia in poultry rearing facilities: a review. *Biosystems Engineering, 115*, 230–243.

Blanes-Vidal, V., Hansen, M. N., Adamsen, A. P. S., Feilberg, A., Petersen, S. O., & Jensen, B. B. (2009). Characterization of odor released during handling of swine slurry: Part II. Effect of production type, storage and physicochemical characteristics of the slurry. *Atmospheric Environment, 43*, 3006–3014.

Canovai, A., Valentini, F., Manetti, E., & Zagaroli, M. (2004). Odor control in composting plants: results from full-scale experiences. *Journal of Environmental Science and Health Part A-Toxic/Hazardous Substances & Environmental Engineering, 39*, 927–937.

Clesceri, L. S., Greenberg, A. E., Eaton, A. D. & Eds. (2008). Standard methods for the examination of water and wastewater, 20th ed, *American Public Health Association*.

Díaz, E., Jiménez, J. I., & Nogales, J. (2013). Aerobic degradation of aromatic compounds. *Current Opinion in Biotechnology, 24*, 431–442.

Filipy, J., Rumburg, B., Mount, G., Westberg, H., & Lamb, B. (2006). Identification and quantification of volatile organic compounds from a dairy. *Atmospheric Environment, 40*, 1480–1494.

Heber, A. J., Ni, J. Q., Lim, T. T., Diehl, C. A., Sutton, A. L., Duggirala, R. K., Haymore, B. L., Kelly, D. T., & Adamchuk, V. I. (2000). Effect of a manure additive on ammonia emission from swine finishing buildings. *Transactions of the American Society of Agricultural Engineers, 43*, 1895–1902.

Hobbs, P. J., Misselbrook, T. H., & Cumby, T. R. (1999). Production and emission of odours and gases from ageing pig waste. *Journal of Agricultural Engineering Research, 72*, 291–298.

Kim, K.-H., & Park, S.-Y. (2008). A comparative analysis of malodor samples between direct (olfactometry) and indirect (instrumental) methods. *Atmospheric Environment, 42*, 5061–5070.

Kim, H., Murthy, S., Peot, C., Ramirez, M., Strawn, M., Park, C. H., & McConnell, L. L. (2003). Examination of mechanisms for odor compound generation during lime stabilization. *Water Environment Research, 75*, 121–125.

Kim, K.-Y., Ko, H.-J., Kim, H.-T., Kim, Y.-S., Roh, Y.-M., Lee, C.-M., & Kim, C.-N. (2008). Odor reduction rate in the confinement pig building by spraying various additives. *Bioresource Technology, 99*, 8464–8469.

Knudsen, H. N., Kjaer, U. D., Nielsen, P. A., & Wolkoff, P. (1999). Sensory and chemical characterization of VOC emissions from building products: impact of concentration and air velocity. *Atmospheric Environment, 33*, 1217–1230.

Leonardos, G., Kendall, D., & Barnard, N. (1969). Odor threshold determinations of 53 odorant chemicals. *Journal Air Pollution Control Assessment, 19*, 91–95.

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. *Journal of Environmental Quality, 32*, 406–416.

Mackie, R. I., Stroot, P. G., & Varel, V. H. (1998). Biochemical identification and biological origin of key odor components in livestock waste. *Journal of Animal Science, 76*, 1331–1342.

McCrory, D. F., & Hobbs, P. J. (2001). Additives to reduce ammonia and odor emissions from livestock wastes. *Journal of Environmental Quality, 30*, 345–355.

Melse, R. W., & Timmerman, M. (2009). Sustainable intensive livestock production demands manure and exhaust air

treatment technologies. *Bioresource Technology, 100*, 5506–5511.

Melse, R. W., Ogink, N. W. M., & Rulkens, W. H. (2009). Overview of European and Netherlands' regulations on airborne emissions from intensive livestock production with a focus on the application of air scrubbers. *Biosystems Engineering, 104*, 289–298.

Moreno, L., Predicala, B., & Nemati, M. (2010). Laboratory, semi-pilot and room scale study of nitrite and molybdate mediated control of H2S emission from swine manure. *Bioresource Technology, 101*, 2141–2151.

Mudliar, S., Giri, B., Padoley, K., Satpute, D., Dixit, R., Bhatt, P., Pandey, R., Juwarkar, A., & Vaidya, A. (2010). Bioreactors for treatment of VOCs and odours—a review. *Journal of Environmental Management, 91*, 1039–1054.

Nahm, K. H. (2003). Influences of fermentable carbohydrates on shifting nitrogen excretion and reducing ammonia emission of pigs. *Critical Reviews in Environmental Science and Technology, 33*, 165–186.

Otto, E. R., Yokoyama, M., Hengemuehle, S., von Bermuth, R. D., van Kempen, T., & Trottier, N. L. (2003). Ammonia, volatile fatty acids, phenolics, and odor offensiveness in manure from growing pigs fed diets reduced in protein concentration. *Journal of Animal Science, 81*, 1754–1763.

Schiffman, S. S., Bennetta, J. L., & Raymer, J. H. (2001). Quantification of odors and odorants from swine operations in North Carolina. *Agricultural and Forest Meteorology, 108*, 18.

Sheridan, B. A., Curran, T. P., & Dodd, V. A. (2003). Biofiltration of n-butyric acid for the control of odour. *Bioresource Technology, 89*, 199–205.

Shuler, M. L., & Kargi, F. (2002). *Bioprocess engineering basic concept, 2nd eds*. New Jersey: Prentice Hall.

Suresh, A., & Choi, H. L. (2011). Estimation of nutrients and organic matter in Korean swine slurry using multiple regression analysis of physical and chemical properties. *Bioresource Technology, 102*, 8848–8859.

Susaya, J., Kim, K. H., Cho, J. W., & Parker, D. (2011). The use of permeation tube device and the development of empirical formula for accurate permeation rate. *Journal of Chromatography A, 1218*, 9328–9335.

Theodore, L. (2008). *Air pollution control equipment calculations*. Hoboken: Wiley.

Trabue, S., Kerr, B., Bearson, B., & Ziemer, C. (2011). Swine odor analyzed by odor panels and chemical techniques. *Journal of Environmental Quality, 40*, 1510–1520.

Varel, V. H. (2002). Carvacrol and thymol reduce swine waste odor and pathogens: stability of oils. *Current Microbiology, 44*, 38–43.

Verdouw, H., van Echteld, C. J. A., & Dekkers, E. M. J. (1978). Ammonia determination based on indophenol formation with sodium salicylate. *Water Research, 12*, 399–402.

Wheeler, E., Adviento-Borbe, M., Brandt, R., Topper, P., Topper, D., Elliott, H., Graves, R., Hristov, A., Ishler, V. & Bruns, M. (2010). Amendments for mitigation of dairy manure ammonia and greenhouse gas emissions: preliminary screening, *ASABE Paper*.

Wing, S., Horton, R. A., Marshall, S. W., Thu, K., Tajik, M., Schinasi, L., & Schiffman, S. S. (2008). Air pollution and odor in communities near industrial swine operations. *Environmental Health Perspectives, 116*, 1362–1368.

Zhang, R. H., Tao, J., & Dugba, P. N. (2000). Evaluation of two-stage anaerobic sequencing batch reactor systems for animal wastewater treatment. *Transactions of the American Society of Agricultural Engineers, 43*, 1795–1801.

Zhang, X. L., Yan, S., Tyagi, R. D., & Surampalli, R. Y. (2013). Odor control in lagoons. *Journal of Environmental Management, 124*, 62–71.

Zhu, J. (2000). A review of microbiology in swine manure odor control. *Agriculture, Ecosystems & Environment, 78*, 93–106.

Zhu, J., Bundy, D. S., Li, X. W., & Rashid, N. (1996). Reduction of odor and volatile substances in pig slurries by using pit additives. *Journal of Environmental Science and Health Part a-Environmental Science and Engineering and Toxicology, 31*, 2487–2501.

Zhu, J., Ndegwa, P. M., & Luo, A. (2001). Effect of solid-liquid separation on bod and VFA in swine manure. *Environmental Technology, 22*, 1237–1243.