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ODOR AND ODOROUS CHEMICAL EMISSIONS FROM ANIMAL BUILDINGS: PART 3- CHEMICAL EMISSIONS

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ABSTRACT

This study was an add-on study to the National Air Emission Monitoring Study (NAEMS). The objective of this study was to measure odor emissions and corresponding concentrations and emissions of target odorous gases. Odor and odorous gas measurements at four NAEMS sites (dairy barns in Wisconsin-WI5B and Indiana-IN5B, swine finisher barn in Indiana-IN3B and swine gestation/farrowing barns in Iowa-IA4B) were conducted during four-13 weeks periods over ~1 year. Odorous gas samples were collected every two weeks using sorbent tubes and analyzed by the automated one-step thermal desorption-GC-MS-Olfactometry. In this paper, we summarize measured concentrations and emissions of 15 odorous gases from four sites. The average volatile fatty acids (VFAs) concentrations ranged between1.1 and 121 μg m^{-3}. The average phenolics and indolics concentrations varied from 0.03 to 42 μg m^{-3}. The total volatile organic compound VOC emission rates for 15 compounds for four sites ranged between 8.89 and 546 mg/hr-m^2. Only acetic acid ($p<0.05$) and propanoic acid ($p<0.1$) had a seasonal significant difference for IA4B. For IN3B, 4-ethyl phenol and indole and most of VFAs (except hexanoic and heptanoic acid) have the seasonal significant differences. At the WI5B dairy site, there were five VFAs (acetic, propanoic, 2-methyl propanoic, butyric and 3-methylbuanoic acid) and one phenolics (4-methyl phenol) showing a seasonal significant difference. Only three compounds (2-methoxyphenol, 1-(2-aminophenyl)-ethanone and indole) had a seasonal significant difference for IN5B. Between dairy sites (WI5B vs. IN5B), acetic, propanoic, 2-methyl propanoic, butyric, and 3-methyl butanoic acids were significantly different. Most of odorants were significantly different except heptanoic acid, 1-(2-aminophenyl)-ethanone and 3-methyl indole, between the two swine sites (IA4B vs. IN3B). Between the two different species (Dairy vs. Swine), five odorants including acetic and heptanoic acid, phenol, 4-ethylphenol, 1-(2-aminophenyl) ethanone were not significantly different, whereas the other 10 compounds measured were.

KEYWORDS. Odor, volatile organic compounds (VOCs), VOC emissions, volatile fatty acids (VFAs), phenolics, indolics, dairy, swine, sorbent tube, thermal desorption, gas chromatography-mass spectrometry

INTRODUCTION

Over the past decade, an increasing number of large confined animal feeding operations (CAFOs) have been built in the U.S. and other parts of the world. The large number of animals raised in CAFOs can affect air quality by emissions of odor, volatile organic compounds (VOCs) and other

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gases, and particulate matter (PM) (NRC, 2003). The NRC report identified odors as the most significant animal emission at the local level (NRC, 2003). Nuisance odors related to intensive commercial animal operations have been implicated as a cause of decreased quality of life (Thu et al., 1997) and declined property values for surrounding communities (Palmquist et al., 1997).

There have been many studies for monitoring of air quality in concentrated animal feeding buildings, but most focused on NH_3, H_2S and PM monitoring (Ni et al., 2002; Heber et al., 2006.), very few studies have been performed to quantify the odorous chemicals emitted from animal feeding operations (AFOs) (Trabue et al., 2008; Trabue et al., 2009).

To date, there is no published data on the emission factors of characteristic odorants from AFOs. This project funded by USDA-NRI supplemented the recently completed National Air Emission Monitoring Study (NAEMS) with comprehensive measurements of odor emissions and chemical analysis of odorous compounds from four NAEMS sites including two swine sites and two dairy sites. The NAEMS was initiated to comply with the Environmental Protection Agency (EPA) regulations concerning regulated gases and particulate matter (PM) emitted from livestock facilities, including poultry, dairy, and swine operations. The 2.5 year long study measured levels of NH_3, H_2S, PM, N_2O, VOCs, and non-methane hydrocarbons released from livestock facilities. NAEMS does not include odor and odorant emissions measurements because EPA did not regulate odor.

The objectives of this study were to (1) determine odor emission factors from four selected NAEMS sites using common protocol and standardized olfactometry, (2) develop a comprehensive chemical library that delineates the most significant odorants and correlate this library with olfactometry results for the selected sites, and (3) disseminate information to stakeholders.

This paper is Part 3 in the five-paper series presenting results from this NRI funded project. Part 1 focuses on project overview and collection methods; Part 2 reports odor emission factors from four NAEMS sites; Part 3 (this paper) focuses on measured gas concentrations and chemical emission factors; Part 4 addresses correlations between sensory and chemical emissions; Part 5 deals with correlations between odor intensities measured with GC-MS-O and chemical concentrations. The specific objectives of this paper are: 1) to identify the characteristic odorous chemicals related to livestock operations and 2) to estimate odorous chemical emission factors from four NAEMS sites.

MATERIALS AND METHODS

<u>Sample Collection and Analyses</u>

In this study, data collection began in November of 2007 for four selected NAEMS sites. Data collection was done in four-13 week round or cycles to cover the seasonal effects from these four different sites (WI5B-dairy, IN5B-dairy, IN3B-finishing, and IA4B-sow).

Seasons were defined as the following: winter (12/4/07 to 1/31/08-2 sample times and 1/20/09 to 2/24/09-2 sample times), summer (7/28/08 to 9/9/08-2 sample times), spring (3/26/08 to 5/29/08-2 sample times and 3/10/09 to 5/7/09-3 sample times) and fall (10/22/08 to 12/9/08-2 sample times). Detailed farm descriptions and sample collection and analyses techniques are presented in Part 1 of this paper series.

The ISU sorbent tube samples were collected biweekly from two of the four building sites one week and collected from the other two building sites the next week and alternated in that order for 12 weeks.

Field air samples were collected by sampling air through sorbent tubes packed with 65 mg Tenax TA (Zhang et al., 2010) from a manifold using a portable SKC 210-1002 sampling pump (SKC Inc.) with a flow rate at 70 mL/min for 1 hour; the gas was delivered to a manifold from a multipoint air sampling system that drew air sequentially from representative locations in the barns or rooms. For each sampling event, one sample per location, a trip blank sample was also included. The ambient air entering into to the barn was also sampled. The sampling flow rates were checked with a NIST-traceable digital flow meter (Bios International, Butler, NJ, USA). After sampling, the sorbent tubes were wrapped in aluminum foil and stored in a cooler to be sent back to Atmospheric Air Quality Laboratory at Iowa State University for thermal desorption-gas chromatography-mass spectrometry (TD-MDGC-MS) analysis.

Validation of the TD-MDGC-MS method showed good selectivity, sensitivity and precision. Method detection limits ranged from 7.1 pg for 3-methylindole to 49.6 pg for guaiacol. In addition, odor character, odor intensity and hedonic tone associated with each of the target odorants were also analyzed simultaneously using the sniffing port on the GC-MS-O (Paper 5). The emission rates were calculated values based on measurements of odorant concentration and barn ventilation rates.

Emission rates are expressed as mass per hour per animal unit, mass per hour per barn floor area and mass per hour per head. The calculation of emission with a single ventilation exhaust sampling location was as follows:

$$E = Q_O \cdot \frac{P_O \cdot M}{R \cdot (273 + T_O)} \cdot (c_O - c_i)$$

Where:

E	Barn emission rate (mg/s or µg/s)
Q_O	Barn outlet moist airflow rate at T_o (m^3/s)
P_O	Pressure at the sampling location (atm)
M	Gas molecular weight (g/mol)
R	Universal Gas Constant (0.08206 L-atm/mol-K)
T_O	Temperature at the sampling location (°C)
c_o	Exhaust air concentration (ppm or ppb)
c_i	Ambient or ventilation air inlet concentration (ppm or ppb)

Statistical analysis

For the statistical analysis of the compounds from the four sites with the same animal species (dairy and swine) or different species (dairy vs. swine), each season was treated as a repeated factor. The site variable was a main factor having two levels: WI5B vs. IN5B or IA4B vs. IN3B for the same species comparison and WI5B+IN5B (Dairy) vs. IA4B+IN3B (Swine) for different species comparison. The two barns for each site were considered in each block.

In the SAS (SAS Windows Version 8.02) program, the model of a split-block in time analysis was used. It was composed of two parts, a treatment part and a time part. The model (Sun et al., 2010) can be expressed

$$Y_{ijk} = u + (\rho_i + \alpha_j + \varepsilon_{ij}) + \beta_k + (\alpha\beta)_{jk} + \varepsilon_{ijk} \qquad (1)$$

where: Y_{ijk} is the compound emission rates; u is the overall mean; ρ_i is the block effect; α_j is the effect of main factor A (site); ε_{ij} is the random effect of the whole-plot units involving main factor A; β_k is the effect of the repeated measure (season); $(\alpha\beta)_{jk}$ is the interaction effect for factors site and measurement season, and ε_{ijk} is the random effect of the time portion. To apply the split-block model, it was assumed that there was equal variance for random effects among both subjects and across time intervals. ‘Proc MIX’ and ‘Proc GLM’ (SAS Windows Version 8.02) were used to evaluate if there was a significant difference (at the 5% level) between the sites for each compound emission rates.

RESULTS AND DISCUSSION

VOC concentrations

Odorous gases emitted from livestock operations are very complex mixtures made up by hundreds of odorous compounds (Lo et al., 2007). However, only a portion of these compounds are the likely contributors of the odor nuisance from the previous studies (O’Neill and Phillips, 1992, Bulliner et al, 2005; Koziel et al., 2006). In this study, 15 characteristic odorous compounds were quantified including eight VFAs (acetic, propanoic, 2-methylpropanoic, butyric, 3-methylbutanoic, pentanoic acid, hexanoic and heptanoic acid), seven non-VFAs or phenolics and indolics (guaiacol, 4-methylphenol, 1-(2-aminophenyl)-ethanone, indole and 3-methylindole). The average concentrations of 15 target odorants for the four cycles of four sites collected by sorbent tubes and analyzed using the GC-MS-O are listed in Table 1.

The average VFA concentrations from the barn exhaust fan ranged between 2.8 and 121 $\mu g\ m^{-3}$ and the average VFA concentrations at the inlet air (ambient) ranged between 1.1 and 32 $\mu g\ m^{-3}$ at all four sites. The average phenolics and indolics concentrations in the barn exhaust air varied from 1.0 to 42 $\mu g\ m^{-3}$ and varied from 0.03 to 1.5 $\mu g\ m^{-3}$ in the inlet air for all four sites.

Volatile fatty acids originate in part from amino acid (AA) deamination by anaerobic bacteria in the gastrointestinal tract and feces (Mackie et al., 1998). Production of certain VFAs also result from anaerobic microbial fermentation of soluble carbohydrates (Mackie et al., 1998). Previous research (Imoto and Namioka, 1978) found the proportion of VFA in feces to be about 50:40:10 for acetate, propionate, and butyrate, respectively, for pigs fed either a low- or high-carbohydrate diet. In this study, the percentage proportion of VFA for swine sites in the exhaust air for IA4B site and in the pit fan air for IN3B is 21:29:30 for acetic, propanoic and butyric acid. The difference between this study and the previous study could be the different diet, age of manure, different sample sources, i.e., from fresh manure in the previous study whereas from the air in the exhaust fan (IA4B) and pit fan (IN3B) in this study.

Patni et al. (1985) reported changes in the volatile fatty acids (VFA) content of dairy-cattle liquid manure slurry during its storage in covered concrete tanks. On the average, acetic acid constituted 65-70% of the total VFAs in manure slurry, while isobutyric, valeric and isovaleric acids together accounted for only 6 - 8%. In this study, the average acetic acid concentration for two dairy sites is about 67% of the total VFA, the propanoic acid is about 29% of the total VFA and butyric acid is about 6%.

VOC emission rates for target pollutants

The average emission rates for fifteen target odorants for four seasons of the four sites over four seasons are listed in Tables 2 through 6. The total odorant emission rates for 15 odorants were calculated by summing up the mean emission rate for each odorant for the entire study, and were 41.2 mg/hr-m^2 (WI5B Dairy site), 8.98 mg/hr-m^2 (IN5B Dairy site), 107 mg/hr-m^2 (IN3B Swine finisher site), 8.89 mg/hr-m^2 (IA4B Swine gestation barn) and 546 mg/hr-m^2 (IA4B Swine farrowing room). The IA4B farrowing room had the highest apparent odorant emission rate. Overall, the target odorant emissions from swine sites were higher than emissions from dairy sites.

The odorant emission rates varied seasonally, with relatively high emission rates for during the summer for IA4B gestation barns, IN3B, IN5B and WI5B. The IA4B farrowing room had the highest emission rates during the spring season.

Seasonal patterns for each compound emission rates for each site

The statistical analysis results show where there were significant differences between the four seasons for each compound at each site. For IA4B swine gestation barns, only acetic acid ($p<0.05$) and propanoic acid ($p<0.1$) had a seasonal significant difference. For IN3B swine finisher site, 4-ethyl phenol and indole, and most of the VFAs (except hexanoic and heptanoic acids) had the seasonal significant differences. For WI5B dairy site, there were five VFAs (acetic, propanoic, 2-methyl propanoic, butyric and 3-methylbuanoic acid) and one phenolics (4-methyl phenol) having the seasonal significant difference. Only three compounds (2-methoxyphenol, 1-(2-aminophenyl)-ethanone and indole) had a seasonal significant difference for the IN5B dairy site.

The statistical analysis was also conducted for the difference between two sites within the same species and between the different species. Between the dairy sites (WI5B vs. IN5B), four acids including acetic, propanoic, 2-methyl propanoic, butyric, and 3-methyl butanoic acid were significantly different. For swine sites (IA4B Swine gestation vs. IN3B Swine finisher), most of these odorants were significantly different between sites with the exception of heptanoic acid, 1-

(2-aminophenyl)-ethanone and 3-methyl indole. For different species (Dairy vs. Swine), ten odorants were significantly differenct between swine and dairy sites; acetic acid, heptanoic acid, phenol, 4-ethyl phenol, 1-(2-aminophenyl) ethanone were not significantly different.

Table 1. Average concentrations (μg/m^3) and standard deviations (in parenthesis) of fifteen VOCs measured at the four sites. Amb-Ambient; B1-Barn 1; B2-Barn 2.

	WI5B Dairy Site			IN5B Dairy site			IN3B Swine finisher site			IA4B Swine gestation (B1 and B2) and farrowing (B3) site			
Compound	**Amb**	**B 1**	**B 2**	**Amb**	**B 1**	**B 2**	**Amb**	**B 1**	**B 2**	**Amb**	**B 1**	**B 2**	**B 3**
Acetic acid	47.2 (±29.4)	166 (±168)	185 (±272)	26.4 (±19.3)	46.4 (±28.4)	45.1 (±23.9)	33.5 (±32.6)	246 (±326)	192 (±112.8)	19.3 (±13.6)	60.8 (±38.9)	72.5 (±53.7)	69.8 (±62.0)
Propanoic acid	3.86 (±2.70)	40.0 (±29.4)	49.6 (±58.4)	3.02 (±3.21)	18.0 (±16.9)	30.8 (±30.8)	15.7 (±11.3)	367 (±408)	378 (±283.2)	4.58 (±5.39)	46.8 (±31.6)	71.4 (±46.9)	91.0 (±93.1)
2-Methyl propanoic acid	1.20 (±1.66)	6.82 (±7.47)	3.63 (±3.97)	0.863 (±1.57)	1.18 (±1.48)	0.990 (±1.51)	2.94 (±3.43)	52.8 (±50.0)	51.5 (±32.6)	1.31 (±1.77)	9.92 (±4.38)	14.5 (±17.5)	20.7 (±17.7)
Butyric acid	2.85 (±2.93)	16.4 (±12.9)	12.7 (±9.32)	1.92 (±2.53)	4.26 (±4.12)	7.25 (±7.51)	17.5 (±16.3)	369 (±396)	379 (±233.3)	2.83 (±3.11)	30.1 (±16.6)	47.4 (±41.6)	161 (±161)
3-Methyl butanoic acid	1.16 (±1.89)	5.13 (±5.19)	2.73 (±3.22)	1.07 (±2.01)	1.30 (±1.89)	1.79 (±2.71)	3.99 (±5.11)	52.5 (±51.8)	53.3 (±31.8)	1.33 (±1.97)	12.7 (±8.80)	19.9 (±28.8)	22.8 (±18.1)
Pentanoic acid	1.58 (±2.41)	6.48 (±9.48)	2.110 (±2.67)	1.47 (±2.93)	1.50 (±2.62)	1.77 (±3.04)	4.76 (±5.70)	79.0 (±93.0)	80.2 (±62.7)	1.51 (±2.32)	5.95 (±4.57)	8.52 (±8.36)	38.2 (±39.6)
Hexanoic acid	1.77 (±2.37)	6.07 (±8.35)	2.28 (±2.83)	1.77 (±4.71)	1.59 (±3.13)	2.05 (±3.70)	3.28 (±6.12)	16.5 (±17.6)	18.0 (±14.2)	1.16 (±1.78)	2.84 (±3.52)	3.61 (±4.23)	85.7 (±105)
2-Methoxy phenol	0.122 (±0.299)	0.191 (±0.237)	0.152 (±0.203)	0.033 (±0.028)	0.107 (±0.149)	0.121 (±0.115)	0.491 (±0.277)	8.12 (±8.10)	8.60 (±6.55)	0.099 (±0.166)	0.774 (±0.420)	0.568 (±0.313)	0.496 (±0.298)
Heptanoic acid	0.801 (±2.57)	5.58 (±10.9)	0.802 (±2.60)	1.36 (±3.14)	0.756 (±2.56)	0.750 (±2.56)	0.828 (±2.55)	6.10 (±10.8)	4.40 (±8.62)	1.43 (±3.36)	1.67 (±3.82)	1.45 (±3.38)	3.70 (±9.06)
Phenol	0.992 (±0.648)	4.56 (±4.94)	2.14 (±1.62)	1.19 (±0.792)	2.06 (±2.15)	2.90 (±2.38)	2.09 (±1.35)	13.2 (±12.1)	16.0 (±14.3)	1.17 (±0.832)	7.02 (±4.51)	5.73 (±5.16)	7.84 (±4.40)
4-Methylphenol	0.408 (±0.385)	4.56 (±3.04)	3.09 (±2.70)	0.568 (±0.399)	3.62 (±3.39)	6.31 (±6.57)	4.72 (±4.80)	81.2 (±84.5)	129 (±117)	0.437 (±0.306)	69.0 (±55.8)	56.0 (±75.0)	27.0 (±12.6)
4-Ethyl phenol	0.027 (±0.025)	1.24 (±2.30)	0.304 (±0.505)	0.372 (±0.638)	0.853 (±0.801)	1.35 (±1.10)	0.521 (±0.771)	6.13 (±7.45)	7.00 (±8.38)	0.287 (±0.613)	4.60 (±3.65)	3.93 (±4.80)	3.38 (±1.85)
1-(2-Aminophenyl)-ethanone	0.004 (±0.007)	1.0 (±2.32)	0.008 (±0.011)	0.580 (±1.91)	0.004 (±0.007)	0.010 (±0.010)	1.15 (±2.51)	2.14 (±3.03)	1.80 (±2.98)	0.541 (±1.78)	1.30 (±2.60)	1.18 (±2.43)	1.31 (±2.22)
Indole	0.006 (±0.006)	0.708 (±1.55)	0.007 (±0.009)	0.002 (±0.003)	0.012 (±0.013)	0.025 (±0.032)	0.076 (±0.159)	2.77 (±3.17)	3.00 (±3.77)	0.048 (±0.152)	0.868 (±0.676)	0.711 (±0.963)	1.18 (±1.14)
3-Methylindole	0.004 (±0.010)	0.581 (±1.29)	0.003 (±0.003)	0.002 (±0.005)	0.002 (±0.004)	0.007 (±0.013)	0.158 (±0.526)	3.30 (±4.89)	5.27 (±8.69)	0.148 (±0.508)	3.07 (±2.74)	2.87 (±5.35)	1.19 (±1.28)

Table 2 Average emission rates for fifteen target odorants in WI5B Dairy site.

WI5B Dairy Site	**Winter***			**Summer***			**Spring***			**Fall***		
Compound	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU
Acetic acid	12.3	129	92.0	60.2	628.9	447	10.5	121	74.4	4.73	50.3260	35.8
Propanoic acid	2.63	27.1	19.3	37.7	390.3	278	4.19	48.8	29.6	1.93	20.2209	14.4
2-Methylpropanoic acid	0.256	2.81	2.00	1.90	20.7	14.7	0.686	8.32	4.98	0.182	1.9238	1.37
Butyric acid	0.456	4.88	3.47	13.6	149	106	1.69	19.0	11.9	0.914	9.7131	6.91
3-Methylbutanoic acid	0.171	1.88	1.33	1.431	15.7	11.2	0.512	6.13	3.69	0.188	2.0136	1.43
Pentanoic acid	0.070	0.779	0.554	0.843	9.29	6.61	0.908	11.1	6.62	0.087	0.9212	0.655
Hexanoic acid	0.066	0.729	0.518	0.478	5.14	3.66	0.797	9.79	5.82	0.070	0.7250	0.516
2-Methoxyphenol	0.013	0.134	0.095	0.010	0.116	0.083	0.001	0.012	0.008	nd	nd	nd
Heptanoic acid	0.001	0.013	0.009	0.011	0.130	0.092	0.918	11.3	6.72	0.0001	0.0007	0.0005
Phenol	0.119	1.24	0.883	0.547	5.88	4.18	0.672	8.24	4.90	0.056	0.589	0.419
4-Methylphenol	0.180	1.83	1.30	1.117	12.4	8.79	0.836	9.64	5.93	0.1865	1.9959	1.42
4-Ethyl phenol	0.018	0.176	0.125	0.062	0.682	0.485	0.215	2.62	1.56	0.0125	20.00	0.098
1-(2-Aminophenyl)-ethanone	nd	nd	nd	0.007	0.073	0.052	0.186	2.29	1.36	0.0000	0.0005	0.0003
Indole	0.0008	0.009	0.006	0.002	0.017	0.012	0.124	1.53	0.905	0.0005	0.006	0.004
3-Methylindole	0.00002	0.0003	0.0002	0.002	0.022	0.016	0.103	1.27	0.752	0.0002	0.002	0.001

*Average emission rates for two Dairy barns; 4 samples from each barn collected in Winter; 2 samples from each barn collected in Summer; 5 samples from Barn 1 and 4 samples from Barn 2 collected in Spring; 2 samples from each barn collected in Fall. nd: not detected.

Table 3 Average emission rates for fifteen target odorants in IN5B Dairy site.

IN5B Dairy Site	Winter*			Summer*			Spring*			Fall*		
Compound	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU
Acetic acid	1.92	15.8	12.5	5.29	42.2	33.2	2.71	21.6	17.0	3.19	26.5	20.9
Propanoic acid	1.64	13.2	10.4	6.53	51.4	40.5	3.47	27.4	21.6	3.45	28.2	22.2
2-Methylpropanoic acid	0.012	0.093	0.073	0.074	0.589	0.463	0.102	0.805	0.634	0.105	0.863	0.679
Butyric acid	0.452	3.62	2.85	0.394	3.11	2.45	0.568	4.45	3.51	0.752	6.20	4.88
3-Methylbutanoic acid	0.055	0.433	0.341	0.050	0.394	0.311	0.045	0.350	0.276	0.132	1.08	0.852
Pentanoic acid	0.024	0.187	0.147	0.00005	0.0004	0.0003	0.036	0.279	0.220	0.100	0.820	0.645
Hexanoic acid	0.158	1.28	1.01	nd	nd	nd	0.014	0.110	0.086	0.017	0.140	0.110
2-Methoxyphenol	0.002	0.015	0.012	0.029	0.235	0.185	0.002	0.018	0.014	0.016	0.126	0.099
Heptanoic acid	0.0009	0.007	0.006	nd	nd	nd	0.001	0.010	0.008	nd	nd	nd
Phenol	0.037	0.291	0.229	0.495	3.93	3.10	0.315	2.49	1.96	0.305	2.46	1.94
4-Methylphenol	0.351	2.82	2.22	0.362	2.93	2.31	0.913	7.22	5.69	1.25	10.0	7.89
4-Ethyl phenol	0.042	0.340	0.268	0.151	1.19	0.933	0.131	1.04	0.819	0.223	1.79	1.41
1-(2-Aminophenyl)-ethanone	0.0001	0.0006	0.0005	0.002	0.016	0.012	0.0007	0.006	0.004	0.0006	0.004	0.004
Indole	0.0003	0.003	0.002	0.003	0.024	0.019	0.004	0.031	0.025	0.005	0.037	0.029
3-Methylindole	0.00004	0.0003	0.0003	0.002	0.012	0.01	0.001	0.009	0.007	0.0005	0.004	0.003

* Average emission rates for two Dairy barns; 4 samples from each barn collected in Winter; 2 samples from each barn collected in Summer; 4 samples from each barn 2 collected in Spring; 2 samples from each barn collected in Fall. nd: not detected.

Table 4 Average emission rates for fifteen target odorants in IN3B Swine finisher site.

IN3B Swine finisher site	Winter*			Summer*			Spring*			Fall*		
Compound	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU
Acetic acid	2.54	4.65	24.7	13.7	18.2	131	26.0	16.2	184	12.6	8.83	67.6
Propanoic acid	4.58	7.10	37.2	90.6	124	655	37.7	24.3	240	22.0	15.3	130
2-Methylpropanoic acid	0.700	1.16	6.05	4.49	6.05	36.8	7.09	4.60	43.1	4.22	2.95	23.1
Butyric acid	4.49	6.63	34.8	32.0	42.8	280	62.7	40.9	370	29.7	20.7	179
3-Methylbutanoic acid	0.868	1.36	7.15	4.54	6.09	38.5	6.24	3.99	40.2	3.91	2.74	21.1
Pentanoic acid	0.808	1.20	6.36	4.67	6.14	46.0	12.0	7.81	73.6	5.45	3.80	31.9
Hexanoic acid	0.192	0.338	1.83	1.10	1.48	9.29	2.35	1.56	13.5	1.33	0.921	8.34
2-Methoxyphenol	0.054	0.118	0.62	0.42	0.566	3.39	0.395	0.216	3.60	0.919	0.644	4.99
Heptanoic acid	0.068	0.096	0.476	0.016	0.018	0.287	1.01	0.704	4.66	0.026	0.018	0.164
Phenol	0.213	0.260	1.42	0.762	1.04	5.47	1.01	0.644	6.45	1.10	0.775	4.94
4-Methylphenol	3.29	3.93	21.6	4.74	6.45	34.9	6.63	4.13	45.4	7.62	5.34	39.9
4-Ethyl phenol	0.118	0.139	0.767	0.077	0.102	0.733	0.525	0.333	3.53	0.348	0.244	1.88
1-(2-Aminophenyl)-ethanone	0.007	0.008	0.044	0.020	0.026	0.151	0.218	0.152	1.02	0.020	0.014	0.126
Indole	0.078	0.079	0.426	0.027	0.037	0.219	0.228	0.141	1.63	0.159	0.112	0.731
3-Methylindole	0.200	0.209	1.14	0.022	0.030	0.182	0.167	0.107	1.10	0.233	0.165	0.937

*Average emission rates for two swine finisher barns; 4 samples from each barn collected in Winter; 2 samples from each barn collected in Summer; 3 samples from Barn 1 and 4 samples from Barn 2 collected in Spring; 2 samples from each barn collected in Fall.

CONCLUSIONS

The following conclusions can be drawn from this study:

1. The average exhaust VFA concentrations from barn exhaust air ranged between 2.8 and 121 µg m^{-3} and the average inlet VFA concentrations from the inlet air ranged between 1.1 and 32 µg m^{-3} for the four sites. The average phenolics and indolics concentrations from barn exhaust air varied from 1.0 to 42 µg m^{-3} and varied from 0.03 to 1.5 µg m^{-3} from inlet air for all four sites.

Table 5 Average emission rates for fifteen target odorants in IA4B Swine Gestation barns (B1 and B2).

IA4B Swine Gestation Barn	Winter*			Summer*			Spring*			Fall*		
Compound	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU
Acetic acid	0.898	1.85	3.72	3.85	6.22	12.5	2.43	5.03	9.76	0.631	1.307	1.904
Propanoic acid	1.02	2.06	4.12	4.03	5.67	11.4	2.90	6.07	11.3	1.22	2.531	3.518
2-Methylpropanoic acid	0.248	0.509	1.02	0.596	1.01	2.02	0.414	0.869	1.57	0.295	0.614	0.812
Butyric acid	0.660	1.35	2.71	1.96	2.97	5.96	1.95	4.07	7.36	0.920	1.913	2.549
3-Methylbutanoic acid	0.395	0.814	1.63	0.732	1.15	2.30	0.513	1.07	2.01	0.274	0.568	0.766
Pentanoic acid	0.125	0.259	0.519	0.450	0.622	1.25	0.272	0.567	1.06	0.104	0.215	0.311
Hexanoic acid	0.071	0.148	0.297	0.092	0.111	0.222	0.058	0.120	0.223	0.032	0.065	0.109
2-Methoxyphenol	0.007	0.014	0.029	0.021	0.050	0.100	0.016	0.032	0.064	0.020	0.043	0.043
Heptanoic acid	0.006	0.014	0.028	0.001	0.001	0.003	0.004	0.008	0.015	nd	nd	nd
Phenol	0.118	0.248	0.497	0.128	0.206	0.412	0.257	0.538	1.04	0.133	0.280	0.306
4-Methylphenol	1.73	3.62	7.26	1.59	2.63	5.28	2.40	5.06	9.72	1.118	2.356	2.37
4-Ethyl phenol	0.084	0.175	0.350	0.078	0.133	0.267	0.216	0.453	0.893	0.056	0.118	0.123
1-(2-Aminophenyl)-ethanone	0.026	0.056	0.112	0.040	0.069	0.138	0.009	0.019	0.036	0.003	0.007	0.006
Indole	0.019	0.041	0.081	0.024	0.058	0.116	0.028	0.058	0.116	0.017	0.036	0.030
3-Methylindole	0.055	0.114	0.229	0.036	0.155	0.310	0.135	0.284	0.569	0.069	0.146	0.094

*Average emission rates for two swine gestation barns; 4 samples from each barn collected in Winter; 2 samples from each barn collected in Summer; 3 samples from Barn 1 and 4 samples from Barn 2 collected in Spring; 2 samples from each barn collected in Fall. nd: not detected.

Table 6 Average emission rates for fifteen target odorants in IA4B Swine farrowing room (B3).

IA4B Swine Farrowing Room	Winter*			Summer*			Spring*			Fall*		
Compound	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU	mg/hr-m^2	mg/hr-hd	mg/hr-AU
Acetic acid	22.5	3.38	1.78	70.1	10.6	18.9	238	35.7	9.68	15.5	2.32	4.21
Propanoic acid	36.2	5.42	5.54	96.0	14.4	26.0	187	28.0	23.7	43.7	6.55	11.8
2-Methylpropanoic acid	12.5	1.88	2.69	21.2	3.18	5.74	29.1	4.36	4.11	12.4	1.86	3.39
Butyric acid	102	15.2	22.4	189	28.3	51.1	261	39.1	41.6	76.6	11.5	21.0
3-Methylbutanoic acid	24.8	3.72	5.64	24.5	3.68	6.64	35.0	5.26	2.80	10.9	1.63	2.97
Pentanoic acid	18.8	2.80	4.43	33.2	4.98	9.02	69.5	10.4	9.47	19.2	2.88	5.27
Hexanoic acid	23.4	3.51	5.48	73.2	11.0	20.0	179	26.9	23.6	50.8	7.63	14.1
2-Methoxyphenol	0.175	0.026	0.006	0.026	0.004	0.007	0.819	0.123	0.009	0.248	0.037	0.066
Heptanoic acid	0.091	0.024	0.041	0.507	0.076	0.137	6.72	1.01	1.77	0.097	0.015	0.027
Phenol	4.50	0.68	0.641	11.0	1.64	2.95	14.8	2.22	1.33	4.13	0.619	1.12
4-Methylphenol	22.8	3.42	2.93	29.2	4.39	7.91	67.4	10.1	3.29	14.1	2.11	3.83
4-Ethyl phenol	2.61	0.391	0.316	3.29	0.49	0.890	8.74	1.31	0.545	1.29	0.193	0.350
1-(2-Aminophenyl)-ethanone	2.32	0.348	0.561	1.13	0.170	0.306	1.98	0.296	0.332	0.066	0.010	0.018
Indole	0.708	0.106	0.141	0.481	0.072	0.130	3.26	0.488	0.242	0.589	0.088	0.160
3-Methylindole	0.851	0.128	0.203	0.133	0.020	0.036	3.91	0.586	0.206	0.579	0.087	0.158

*Average emission rates for one farrowing room; 3 samples collected in Winter; 2 samples collected in Summer; 4 samples collected in Spring; 2 samples collected in Fall.

2. The total odorant emission rates for four sites were 41.2 mg/hr-m^2 (WI5B), 8.98 mg/hr-m^2 (IN5B), 107 mg/hr-m^2 (IN3B), 8.89 mg/hr-m^2 (IA4B gestation) and 546 mg/hr-m^2 (IA4B farrowing). The IA4B farrowing room had the highest odorant emission rate.

3. Only acetic acid ($p<0.05$) and propanoic acid ($p<0.1$) showed a seasonal significant difference for IA4B. For IN3B, 4-ethyl phenol and indole and most of VFAs except hexanoic and heptanoic acid had seasonal significant differences. At the WI5B dairy site, there were five VFAs (acetic, propanoic, 2-methyl propanoic, butyric and 3-methylbuanoic acid) and one phenolics (4-methyl phenol) with a seasonal significant difference. Only three compounds (2-methoxphenol, 1-(2-amionphenyl)-ethanone and indole) had seasonal significant differences for IN5B.

4. Between dairy sites (WI5B vs. IN5B), acetic, propanoic, 2-methyl propanoic, butyric, and 3-methyl butanoic acid, were significantly different. Most odorants were significantly different (except heptanoic acid, 1-(2-amionphenyl)-ethanone and 3-methyl indole) between the two swine sites (IA4B vs. IN3B). Ten odorants (except acetic and heptanoic acid, phenol, 4-ethylphenol, 1-(2-amionphenyl) ethanone) were significantly different between dairy and swine sites (Dairy vs. Swine).

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