

# Odorous Chemical Emissions from Animal Buildings

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### Summary and Implications

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 gas concentrations and emissions of twenty odorous gases from four sites. All the gas concentrations were reported at dry standard conditions, i.e. 1atm, 20 °C. Based on the one-year measurement for four selected sites, the average volatile fatty acids (VFAs) concentrations ranged between 1.1 and 98  $\mu\text{g dm}^{-3}$ . The average phenolics and indolics concentrations varied from 0.8 to 31.3  $\mu\text{g dm}^{-3}$ . The average sulfur containing compounds concentrations were from 0.02 to 1.5  $\mu\text{g dm}^{-3}$ . The total volatile organic compound VOC emission rates for 20 compounds for four sites ranged between 33.9 and 743 mg/hr-AU. 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-methylbutanoic 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.

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

There have been many studies for monitoring of air quality in concentrated animal feeding buildings, but most focused on  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  and PM monitoring, very few studies have been performed to quantify the odorous chemicals emitted from animal feeding operations (AFOs).

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  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , PM,  $\text{N}_2\text{O}$ , 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.

The 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

### Sample Collection and Analyses

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). 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 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 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. 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  $\mu\text{g/s}$ )

$Q_o$ -Barn outlet moist airflow rate at  $T_o$  ( $\text{m}^3/\text{s}$ )

$P_o$ -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 ( $^{\circ}\text{C}$ )

$c_o$ -Exhaust air concentration (ppm or ppb)

$c_i$ -Ambient or ventilation air inlet concentration (ppm or ppb)

### Statistic 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

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

where:  $Y_{ijk}$  is the compound emission rates;  $u$  is the overall mean;  $\rho_i$  is the block effect;  $\alpha_j$  is the effect of main factor A (site);  $\varepsilon_{ij}$  is the random effect of the whole-plot units involving main factor A;  $\beta_k$  is the effect of the repeated measure (season);  $(\alpha\beta)_{jk}$  is the interaction effect for factors site and measurement season, and  $\varepsilon_{ijk}$  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

### V VOC concentrations

Odorous gases emitted from livestock operations are very complex mixtures made up by hundreds of odorous compounds. However, only a portion of these compounds are the likely contributors of the odor nuisance from the previous studies. In this study, 20 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) and five sulfides (dimethyl disulfide, diethyl disulfide, dimethyl trisulfide, dimethyl sulfoxide and dimethyl sulfone). The seasonal comparison of concentrations of total 20 target odorants for the four cycles of one swine site (IN3B) and one dairy site (WI5B) are shown in Figure 1 and 2.

The average VFA dry standard concentrations from the barn exhaust fan ranged between 2.7 and 210  $\mu\text{g dsm}^{-3}$  and the average VFA concentrations at the inlet air (ambient) ranged between 0.2 and 26.5  $\mu\text{g dsm}^{-3}$  at all four sites. The average phenolics and indolics concentrations in the barn exhaust air varied from 1.6 to 76.6  $\mu\text{g dsm}^{-3}$  and varied from 0.1 to 2.5  $\mu\text{g dsm}^{-3}$  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. Production of certain VFAs also result from anaerobic microbial fermentation of soluble carbohydrates. Previous research 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%.

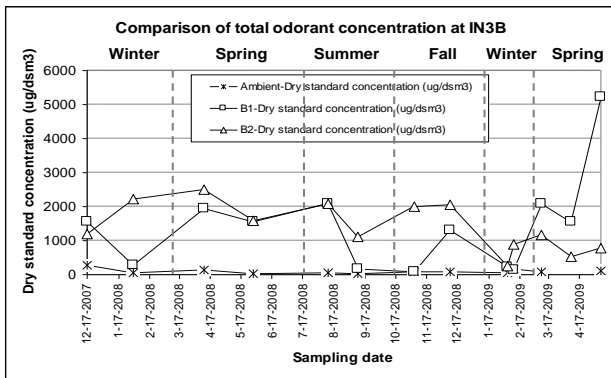


Figure 1. Seasonal pattern for total odorant concentration for IN3B swine finishing site.

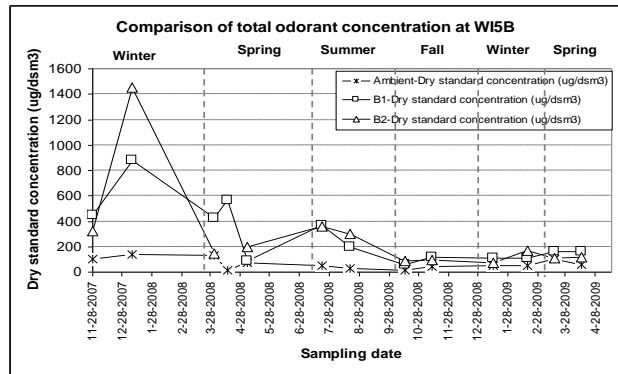


Figure 2. Seasonal pattern for total odorant concentration for W15B Dairy site.

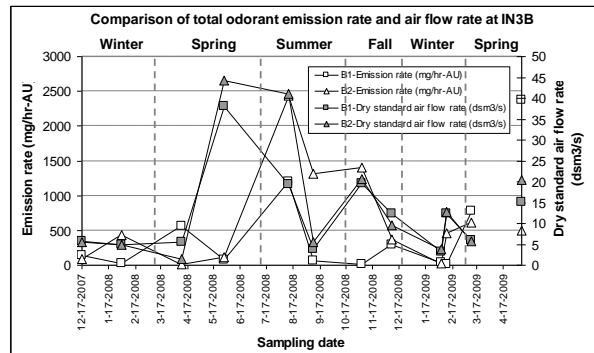


Figure 3. Seasonal pattern for total odorant emission rates for IN3B swine site.

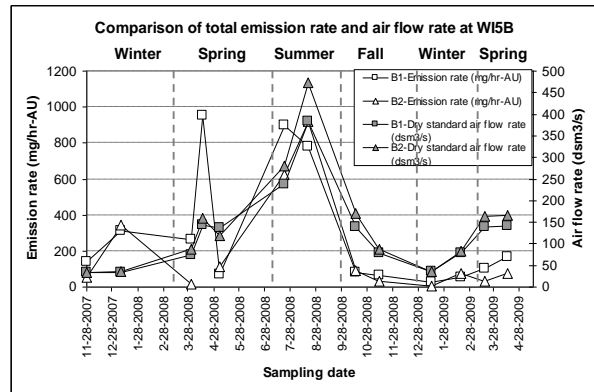


Figure 4. Seasonal pattern for total odorant emission rates for W15B dairy site.

### *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 20 odorants were calculated by summing up the mean emission rate for each odorant for the entire study, and were 290 mg/hr-AU (WI5B Dairy site), 36.0 mg/hr-AU (IN5B Dairy site), 743 mg/hr-AU (IN3B Swine finisher site), 33.9 mg/hr-AU (IA4B Swine gestation barn) and 91.7 mg/hr-m<sup>2</sup> (IA4B Swine farrowing room). The IN3B finishing site had the highest apparent odorant emission rate, it is probably due to collecting air samples from pit line at this site. The odorant emission rates varied seasonally, with relatively high emission rates for all sites during warm seasons (Spring and Summer).

### *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-methylbutanoic 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 wine 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 different between swine and dairy sites; acetic acid, heptanoic acid, phenol, 4-ethyl phenol, 1-(2-aminophenyl) ethanone were not significantly different.

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