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Odor and Odorous Chemical Emissions from Animal Buildings: Part 4—Correlations Between Sensory and Chemical Measurements

Larry D. Jacobson  
University of Minnesota–Twin Cities

Neslihan Akdeniz  
University of Minnesota–Twin Cities

Brian Hetchler  
University of Minnesota–Twin Cities

S. D. Bereznicki  
Purdue University

Albert J. Heber  
Purdue University

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Abstract
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Keywords
Olfactometry, odor emission, dairy, swine, gas chromatography-mass spectrometry

Disciplines
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Comments

Authors

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ODOR AND ODOROUS CHEMICAL EMISSIONS FROM ANIMAL BUILDINGS: PART 4- CORRELATIONS BETWEEN SENSORY AND CHEMICAL MEASUREMENTS

L.D. Jacobson¹, N. Akdeniz¹, B.P. Hetchler¹, S.D. Bereznicki², A.J. Heber², R.B. Jacko², K.Y. Heathcote², S.J. Hoff³, J.A. Koziel³, L. Cai³, S. Zhang⁵, D.B. Parker⁴,⁶, E.A. Caraway¹

ABSTRACT

This study supplemented the National Air Emissions Monitoring Study (NAEMS) by making comprehensive measurements, over a full calendar year, of odor emissions from five swine and four dairy rooms/buildings (subset of the total number of buildings monitored for the NAEMS project). The measurements made in this project included both standard human sensory measurements using dynamic forced-choice olfactometer and a novel chemical analysis technique for odorous compounds found in these emissions. Odor and hydrogen sulfide (H₂S) and ammonia (NH₃) concentrations for all dairy and swine buildings had a statistically significant correlation. A higher number of correlations between odor and volatile organic compounds (VOCs) were found for the five swine rooms/buildings (two rooms in a pig finishing barn, two sow gestation barns, and a farrowing room) compared to the four dairy buildings. Phenol and 4-methyl phenol (p-cresol) concentrations were well correlated (R² > 50%) with odor concentrations in the five swine rooms/buildings but not significantly correlated in the four dairy buildings.

KEYWORDS. Olfactometry, odor emission, dairy, swine, gas chromatography-mass spectrometry

INTRODUCTION

Odor emission from animal production buildings is a critical local issue according to the National Research Council report to the livestock and poultry industries (NRC, 2003). Even though federal and some state agencies do not regulate odors, emission of odorous compounds remains a high priority for animal producers and for neighbors living near livestock and poultry operations. There is an urgent need for odor emission factors from animal confinement buildings since very limited data is presently available.

This USDA, National Research Initiative (NRI) funded study was awarded in 2005 to supplement the National Air Emissions Monitoring Study (NAEMS) with comprehensive measurements of odor from four of the NAEMS sites, two swine and two dairy facilities (total of nine buildings). The NAEMS was initiated to comply with the Environmental Protection Agency (EPA) regulations concerning potential regulated pollutants by monitoring particulate matter continuously and certain gases (H₂S and NH₃) semi-continuously (consecutive 10 minute sampling during two hour cycles) for 24 months to fulfill the requirements of a consent agreement. Although odor is the air pollutant that plagues the animal industry, it was not included in the NAEMS because it is not regulated by the EPA and thus not written into the consent agreement.

¹ Department of Bioproducts and Biosystems Engineering, University of Minnesota, St Paul, MN
² Department of Agricultural and Biological Engineering, Purdue University, West Lafayette, IN
³ Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA
⁴ Department of Environmental Science and Engineering, West Texas A&M University, Canyon, TX
⁵ Present address Environmental Science and Engineering, Fudan University, Shanghai, PR China
⁶ Present address USDA Meat Animal Research Center, Clay Center, NE

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There are two general approaches used to measure odor. One is to measure the concentrations of individual odorant gases and the other is to use the human nose to evaluate the entire gas mixture. Both approaches have strengths and weaknesses. The key advantage of olfactometry is the direct correlation with odor and its use of the human's highly sensitive sense of smell. Olfactometry also has the advantage that it analyses the complete gas mixture so that contribution of each compound in the sample is included in the analysis. On the other hand, olfactometry suffers from a lack of precision compared to some of the sophisticated chemical sensors available. The lack of precision in olfactometry is due in part to the variability in each person's sense of smell and their reaction to an odor. Also, olfactometry does not identify the individual compounds that make up the odor. Individual compounds can be identified using chemical analysis techniques. But, most odors are a mixture of many different gases at extremely low concentrations. The composition and concentrations of the gas mixtures affects the perceived odor. To completely measure an odor, each gas would need to be measured. The fact that most odors are made up of many different gases at extremely low concentrations makes it very difficult and expensive to determine the exact composition of an odor. The odor measurements done in this study includes both human sensory measurements using the dynamic forced-choice olfactometer and chemical analysis technique for odorous compounds using gas chromatograph-mass spectrometry (GC-MS).

Several studies attempted to correlate human sensory measurements and chemical concentrations but no universally applicable relationships were found. Blanes-Vidal et al. (2009) analyzed the relationship between concentrations of odorous gases above agitated swine slurry and overall odor concentrations. Odor concentrations were found to be most strongly related to H2S concentrations. Gostelow and Parsons (2000) investigated the correlation between odor and H2S concentrations. They reported good correlations for sludge storage/handling units but poor correlations for aeration tanks. Noble et al. (2001) measured odor and gas concentrations from mushroom composting sites. High correlations were reported between odor and H2S and dimethyl disulfide concentrations while NH3 concentrations were not found to be correlated to odor concentrations. In some studies, hydrogen sulfide and ammonia were not found to be well correlated to livestock odor concentrations (Jacobson et al., 1997; Zahn et al., 1997). Lo et al. 2008 reported nearly 300 compounds emitted from swine manure. The challenge relative to the odor issue is to extract from this large field of 'potential' odorants, the compounds that constitute the primary odor impact relative to these environments. Given sufficiently comprehensive and accurate reference and analytical data regarding the volatile compounds present in these environments, it would seem possible to accurately predict and rank the primary odor impact compounds. However, from a practical standpoint, this does not produce satisfactory results in most cases. The factors working against such success are incomplete or imprecise odor threshold data in concert with the extremely low odor thresholds of many if not most of the key odorants present.

This paper is part four of a five-paper series presenting results from this NRI funded project. In part 1, the overall project description and overview with comparisons between olfactometry labs are presented. Part 2 focuses on odor emissions as measured using olfactometry. Part 3 deals with the VOC emissions from the GC/MS-Olfactometry (GC/MS-O). In part 4 (this paper), the correlations between the sensory (olfactometry) and chemical measurements are reported, and part 5 deals with correlations between GC/MS-O sensory data and chemical measurements.

**MATERIALS AND METHODS**

For this study, data collection began in November of 2007 while the National Air Emissions Monitoring Study (NAEMS) started taking measurements in the spring/summer of 2007. Data was collected at four different NAEMS sampling sites, which consisted of two freestall dairy sites (2 barns/site), one “sow” swine site (2 sow barns and one farrowing room), and one swine finishing site (2 rooms in one barn) for a total of nine buildings/rooms. Full descriptions of the four NAEMS sampling sites are given in part 1 (Bereznicki, et al. 2010) of this series. A brief summary of these NAEMS sites used in this study are listed below:
W15B – located in Wisconsin, 2 barns housing total of 650 cows that were cross ventilated.
IN5B - located in Indiana, 2 barns housing total of 3200 cows that were tunnel ventilated.
IN3B –located in Indiana, 2 rooms housing total of 2000 finishing pigs that were tunnel ventilated.
IA4B – located in Iowa, 2 barns housing total of 1100 gestation sows that were tunnel ventilated
and 1 room housing total of 24 lactating sows and litters that were mechanically ventilated

Data collection was done in four- 13 week rounds or cycles to cover the seasonal effects from
these four different sites. The odor and chemical samples were collected weekly 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. On the last (13th) week of each cycle, one of the sites was
sampled exclusively with both odor and chemical samples.

Odor samples were collected from each barn inlet (duplicate) and exhaust locations (triplicate) via
a gas sampling systems using Tedlar bags. On the 13th week of each sampling cycle, a round robin
test was done where an additional two sets of odor samples (8 samples per set) were collected and
a set of samples were sent to all three university olfactometry laboratories (U of MN, Iowa State
Univ., and Purdue Univ.) for comparative analysis between labs. This process was rotated so every
building site was evaluated by the extra sets of odor samples over the course of the one-year study.
All air samples were evaluated for dilution-to-threshold (DT), hedonic tone, and intensity by all
the three laboratories within 30 hours of collection using the same type of olfactometer
(AC'SCENT™ International Olfactometer, St. Croix Sensory, Inc., Lake Elmo, MN). The details of
the sites and sample collection were described in part #1 (Bereznicki et al., 2010), Jacobson et al.
(2008), and Jacobson et al. (2010).

Chemical measurements were made by sampling the barn sites with sorbent tubes at the same time
that odor bag collections were made. One set of Tenax sorbent tubes were used to measure
concentrations of 15 different volatile organic compounds (VOCs) (Zhang et al. 2010) with the
GC-MS-O. Because of the length of time to analyze samples with the GC-MS-O, only one set of
samples were analyzed each week by the Iowa State laboratory. Therefore, each site was only
sampled half the number of times with sorbent tubes as for odor samples. Compound identity
(chromatograms/spectral matches) was evaluated based on the existing library of 350,000+ compounds. Multidimensional GC separation was used to identify co-eluting compounds of
significant malodor.

Hydrogen sulfide (H2S) and ammonia (NH3) concentrations were measured continuously (every
one minute during 60 min sampling) by gas analyzers (H2S: 450i, Thermo Electron Corporation,
Franklin, MA and NH3: INNOVA Model 1412 Photoacoustic IR multi-gas monitor and/or 17C,
Thermo Electron Corporation, Franklin, MA). For the W15B and IA4B sites, averages of the 60
readings were calculated. For the IN5B and IN3B sites, only one data point was used (the data
point recorded manually during 60 min sampling).

The correlations between odor concentrations (OU/m³) and gas concentrations (µg/m³) were
investigated by fitting a linear regression line (JPM v.8.0.1, SAS Institute Inc, Cary, NC).
Significance of the correlation coefficients (R²) was determined at the 5% significance level. All
the data was natural log transformed. Emission rates of odors and gases were calculated by
multiplying standardized data (ambient data was subtracted from barn data) by air flow rates.
Ventilation air flow rate measurements were determined by recording exhaust fan run times for
each barn/room and fan performance were measured in situ with a special fan measurement
device, the Fan Assessment Numeration System (FANS) (Jacobson et al., 2008). The correlations
between odor and gas emissions were also investigated by fitting a linear regression line.
RESULTS AND DISCUSSION

No significant difference was found between the three olfactometry laboratories (Bereznicki, et al. 2010) so all the DT data was treated as they were analyzed in the same laboratory. The odor DT, intensity, and hedonic tone concentrations and barn emission values collected during this study are presented in paper #2 (Akdeniz et al., 2010) of this series of papers. In this paper, correlations were prepared between the odor DT and GC-MS-O laboratory VOC datasets.

Correlations between the sensory DT and the H₂S and NH₃ concentrations/emissions are listed in Table 1. Table 1 shows odor (DT) and H₂S and NH₃ concentrations (left side of table) for dairy or swine buildings have a significant correlation at the 5% significance level. The correlation equations of H₂S and NH₃ are shown in Figure 1.

Also in Table 1, correlations of odor DT and H₂S and NH₃ emissions rates are shown (right side of table). These differ from the concentration correlations since emission uses the net (building-ambient) concentrations for odor and gases. For emissions, relatively strong correlations (R² > 80) are seen between odor and H₂S and NH₃ for IA4B (swine) site.

### Table 1. Correlations between the sensory DT and the H₂S and NH₃ concentrations/emissions

<table>
<thead>
<tr>
<th>Odor conc. (OU/m³) and gas conc. (µg/m³)</th>
<th>Odor emission (OU/s) and gas emission (µg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W15B dairy site</td>
<td>IN5B dairy site</td>
</tr>
<tr>
<td>IN3B swine site</td>
<td>IA4B swine site</td>
</tr>
<tr>
<td>W15B dairy site</td>
<td>IN5B dairy site</td>
</tr>
<tr>
<td>IN3B swine site</td>
<td>IA4B swine site</td>
</tr>
<tr>
<td>H₂S</td>
<td></td>
</tr>
<tr>
<td>R²=50.80</td>
<td>R²=42.46</td>
</tr>
<tr>
<td>P&lt;0.001</td>
<td>P=0.015</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td></td>
</tr>
<tr>
<td>R²=52.93</td>
<td>R²=44.11</td>
</tr>
<tr>
<td>P&lt;0.001</td>
<td>P=0.0025</td>
</tr>
</tbody>
</table>

H₂S and NH₃ concentrations are the averages of 60 min continuous measurements for W15B and IA4B sites. For IN5B and IN3B sites, there was only one data point which was taken during 60 minute sampling. R² is the correlation coefficient (%). P is the P value at the 5% significance level. Bolded R² values are significant. Bolded and underlined R² values are significant and above 50%. All data was natural log transferred.

Correlations between the sensory DT and the VOC concentrations/emissions as measured by the ISU's GC-MS-O are listed below in Table 2. A higher number of significant concentration correlations (left side of table) were found for swine sites (IN3B and IA4B) compared to dairy sites (W15B and IN5B). When looking for individual VOC compounds with high correlation (R² > 50%) values with odor concentrations, phenol and 4-methyl phenol (p-cresol) appeared on the two swine sites but not on the dairy sites. There were statistically significant correlations of odor to total VFAs (8 VOCs) and total non-VFAs (7 VOCs) for the two swine sites. Potential explanations of the larger number of significant odor concentration correlations for the swine compared to the dairy sites, includes the more energy dense diet feed to swine compared to dairy, the digestive systems differences (non-ruminant vs. ruminant), and the manure handling differences (mostly long term manure storage in swine buildings vs. outside storage of manure for the dairy barns).

Emission correlations (right side of Table 2) of odor to total VFAs and total non-VFAs at the Iowa sow site (IA4B) had R² values of 59 and 75% respectively, while the statistically valid correlations for the two dairy sites where R² = 24% for W15B with VFAs and R² = 46% for IN5B with non-VFAs. Looking at individual VOC compound correlations for emissions yielded R² values > 50% for 4-methyl phenol, 4-ethyl phenol, and indole for both the Indiana dairy (IN5B) and Iowa swine (IA4B) sites. Nearly all (except hexanoic and heptanoic acids) of the VFAs and non-VFAs correlated with odor emissions significantly for the Iowa swine (IA4B) site while all but 2-methyl propanoic acid, 2-methoxy phenol, phenol, and indole were significantly correlated to odor emissions for the Wisconsin dairy (W15B) site. As for the concentration correlations, explanations for the emission correlation differences both between and within species sites are difficult to assess. Potential reasons include diet differences, the existence of an outside manure storage on the farm site (outside manure storages only at dairy sites), and frequent (daily or less) removal of manure from barns at dairy sites vs. long term storage on manure (deep pits) underneath.
barns/rooms at swine sites.

Figure 1. Correlations between sensory odor DT (OU/m³) and H₂S and NH₃ concentrations (µg/m³) of each site.
Table 2. Correlations between the sensory DT and the VOC concentrations/emissions

<table>
<thead>
<tr>
<th>Odor conc. (OU/m³) and VOC conc. (µg/m³)</th>
<th>Odor emission (OU/s) and VOC emission (µg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WISB dairy site</td>
<td>INSB dairy site</td>
</tr>
<tr>
<td>Total VFAs</td>
<td>R²=22.76</td>
</tr>
<tr>
<td>P = 0.0077</td>
<td>P = 0.53</td>
</tr>
<tr>
<td>Total non-VFAs</td>
<td>R²=13.99</td>
</tr>
<tr>
<td>P = 0.024</td>
<td>P = 0.70</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>R²=15.41</td>
</tr>
<tr>
<td>P = 0.03</td>
<td>P = 0.64</td>
</tr>
<tr>
<td>Propanoic acid</td>
<td>R²=23.93</td>
</tr>
<tr>
<td>P = 0.008</td>
<td>P = 0.19</td>
</tr>
<tr>
<td>2-methyl propanoic acid</td>
<td>R²=17.89</td>
</tr>
<tr>
<td>P = 0.024</td>
<td>P = 0.08</td>
</tr>
<tr>
<td>Butanoic acid</td>
<td>R²=23.57</td>
</tr>
<tr>
<td>P = 0.0065</td>
<td>P = 0.31</td>
</tr>
<tr>
<td>3-methyl butanoic acid</td>
<td>R²=52.4</td>
</tr>
<tr>
<td>P = 0.011</td>
<td>P = 0.07</td>
</tr>
<tr>
<td>Pentanoic acid</td>
<td>R²=52.43</td>
</tr>
<tr>
<td>P = 0.0117</td>
<td>P = 0.02</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>R²=14.83</td>
</tr>
<tr>
<td>P = 0.03</td>
<td>P = 0.4</td>
</tr>
<tr>
<td>Heptanoic acid</td>
<td>R²=2.72</td>
</tr>
<tr>
<td>P = 0.51</td>
<td>P = 0.04</td>
</tr>
<tr>
<td>2-methoxy phenol</td>
<td>R²=19.2</td>
</tr>
<tr>
<td>P = 0.07</td>
<td>P = 0.85</td>
</tr>
<tr>
<td>Phenol</td>
<td>R²=18.9</td>
</tr>
<tr>
<td>P = 0.06</td>
<td>P = 0.9</td>
</tr>
<tr>
<td>4-methyl phenol</td>
<td>R²=17.89</td>
</tr>
<tr>
<td>P = 0.06</td>
<td>P = 0.43</td>
</tr>
<tr>
<td>4-ethyl phenol</td>
<td>---</td>
</tr>
<tr>
<td>---</td>
<td>P = 0.8</td>
</tr>
<tr>
<td>1-(2-aminophenyl) phenone</td>
<td>R²=0.25</td>
</tr>
<tr>
<td>P = 0.9</td>
<td>P = 0.72</td>
</tr>
<tr>
<td>Indole</td>
<td>R²=21.52</td>
</tr>
<tr>
<td>P = 0.056</td>
<td>P = 0.08</td>
</tr>
<tr>
<td>3-methyl-1H-indole</td>
<td>R²=14.29</td>
</tr>
<tr>
<td>P = 0.18</td>
<td>P = 0.02</td>
</tr>
</tbody>
</table>

Total VFAs refers to the sum of acetic, propanoic, 2-methyl propanoic (isobutyric), butanoic, 3-methyl butanoic (isovaleric), pentanoic, hexanoic, and heptanoic acids. Total non-VFAs refers to the sum of 2-methoxy phenol (guaiacol), phenol, 4-methyl phenol (p-cresol), 4-ethyl phenol, 1-(2-aminophenyl) ethanone (2-aminoacetophenone), indole, and 3-methyl-1H-indole (scatole). R² is the correlation coefficient (%). P is the P value at the 5% significance level. Bolded R² values are significant. Bolded and underlined R² values are significant and above 50%. All data was natural log transferred.
CONCLUSION

The following conclusions were drawn from this research:

1. Odor (DT) and H₂S and NH₃ concentrations for either dairy or swine buildings have a statistically significant correlation. A very good correlation (>80%) was found between odor emissions (OU/s) and H₂S and NH₃ emission rates (µg/s) for the IA4B swine site.

2. A higher number of significant concentration correlations were found for the swine sites (IN3B and IA4B) compared to the two dairy sites for individual VOCs. Phenol and 4-methyl phenol concentrations were well correlated (R² > 50%) with odor concentrations at the two swine sites but not significantly correlated at the dairy sites.

3. The highest correlations between odor and VOCs were found for the IA4B swine site. At this site, odor emissions (OU/s) were highly correlated to 2-methoxy phenol emission rates (µg/s) (R² = 81%), while odor concentrations (OU/m³) were highly correlated to 4-methyl phenol concentrations (µg/m³) (R² = 73%).

Acknowledgement

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compounds from animal buildings. Air and Waste Management Association Annual Meeting, Charlotte, NC.


