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Abstract. As dairy production evolves towards larger and more concentrated operations, air and water quality on and around dairy farms is becoming a significant concern. It is necessary to understand air emission temporal variations for development and implementation of effective abatement technologies and management practices. The objectives of this study were to understand temporal variations in H2S, NH3, and odor emissions from a dairy manure storage pond, the effects of manure characteristics and environmental conditions on gas emissions, and gas management need of dairy manure storage ponds. One representative Ohio dairy farm with a 675-cow free-stall barn and one outside earthen manure storage pond was selected as the experimental farm. Monthly measurements of H2S, ammonia, and odor emissions from the dairy manure storage pond were conducted using a convective flux chamber and gas analyzers. Surface manure was sampled for manure characteristics analysis. Manure temperature and weather conditions were measured. The data was analyzed using general statistical description, correlation, and regression analysis.

The results showed there were large temporal variations in NH3, H2S, and odor emissions among months of the year. The daily mean NH3, H2S, and odor emission rates ranged from 5.7 to 174.8 µg s⁻¹ m⁻², 0.1 to 4.6 µg s⁻¹ m⁻², and 0 to 10.34 OU s⁻¹ m⁻², respectively. The daily H2S emission was not a concern relative to the EPCRA and CERCLA’s 100 lb d⁻¹ reporting requirement for NH3 and H2S. However, NH3 emission from the 650-700 dairy operation exceeded 100 lb d⁻¹ in warmer months. Daytime NH3 emission variations were small and within about 10-20% of the mean. However, the daytime H2S emission variations were significant. Odor and NH3 emission was strongly correlated with the ambient air temperatures. Higher ambient temperature resulted in higher odor and NH3 emissions. However, H2S emissions were not clearly associated with the ambient temperatures and fluctuated month by month without a clear statistical trend. Higher surface air velocities resulted in higher gas and odor emissions. However, the exact correlation relationship was not easily determined from the limited field studies.

Keywords. Hydrogen sulfide, odor, ammonia, emission, variations, dairy facilities, manure storage.

Introduction

As dairy production evolves towards larger and more concentrated operations, air and water quality on and around dairy farms is becoming a significant concern. Odor and gas emission from manure storage at the farm remains a major challenge to producers and some have been subject to court actions based on nuisance complaints (Ronald, 1997). Previous scientific studies and published data on air quality at large dairy facilities are insufficient to identify specific sources and factors that influence the emission rates from manure storage facilities. The lack of studies has limited the development and evaluation of effective odor and gas abatement technologies.

A preliminary study (Zhao et al. 2007) indicated air quality inside dairy free-stall buildings is relatively good with H2S, NH3, and odor concentration ranging from 2 to 30 ppb, 1.4 to 3 ppm, 90 to 140 OU m⁻³, respectively. However, the manure storage ponds had the greatest effect on the dairy farm air quality as represented by warm and hot season odor levels as high as 1,256 OU m⁻³ and H2S concentrations reaching 1,400 ppb.

Odor has been the prominent complaint regarding dairy operations in Ohio. It is caused by gases and volatile organic compounds generated during anaerobic decomposition of organic matter and manure. Odor emission from swine lagoons have been extensively studied (Heber et al., 2002; Lim et al., 2003; Guo et al.,...
However, only a few studies quantified odor emission from dairy manure storage ponds for short durations (Gay et al., 2002; Bicudo et al., 2003). Each of these studies based their odor analysis on a convective emission chamber technique and a dynamic forced-choice olfactometry method, which is known as the most accurate method to assess livestock odor (Hobbs et al., 1998).

H_{2}S is regarded as the most dangerous gas emission from manure storage, especially during manure agitation, because of its adverse effects at high concentration on human and animal health. NH_{3} emission causes significant public concerns on environmental acidity, formation of small aerosol particles, and odor (Angeja et al., 2000). The state of Minnesota has established a concentration limit of 30 ppb H_{2}S at farm property lines. NH_{3} and H_{2}S emissions from swine lagoon and manure pits have been extensively studied (Zhu et al., 2000; Lim et al., 2003; Gay et al., 2003; Schmidt et al., 1999; Hobbs et al., 1998). Only limited studies have measured H_{2}S and NH_{3} emissions from dairy manure storage ponds for short durations during hot months at sample farms (Gay et al., 2003). Characteristics and variations of gas emissions from dairy manure storage ponds are not clearly known.

It will be very useful to know when and at what conditions the dairy manure storage ponds release significant amounts of gases and odor; how weather conditions affect the dispersion of gases and odor; and if there is any relationship between odor and gas emissions? This information will help dairy producers understand the performance of manure storage ponds and to adopt proper odor abatement practices during the most critical time periods.

Understanding odor and gas emission trends and variations is important for development, implementation and evaluation of effective odor and gas abatement technologies. Unfortunately, there is no universally accepted standard technique for the measurement of odor and gas emissions from lagoons (Guo et al., 2006; Smith & Watts, 1994a). The convective flux chamber (CFC) has been the most commonly used method for measurement of air emissions from area sources (Reinhart et al., 1992; Jiang et al., 1995; Misselbrook et al., 1998; Hobbs et al., 1998; Schmidt et al., 1999; Angeja et al., 2000; Heber et al., 2002; Lim et al., 2003). Even though the design and measurement protocol of a CFC is not standardized, researchers have been improving the CFC design. A CFC chamber designed and used by Heber et al. (2002) and Lim et al., (2003) was used in this study.

Odor and gas emissions from a surface are governed by mass transfer processes through which gases from a surface transfer to the atmosphere. The process is highly dependent on micrometeorological variables such as wind speed, temperature, and humidity, and gas concentration differences between the surface source and ambient air. Basic mass transfer principles from surfaces suggest emissions are affected significantly by surface air velocity (Schmidt & Bicudo, 2002; and Ecklund, 1992). Smith and Watts (1994b) evaluated the odor emission from open cattle feedlots for wind speeds from 0.2 m/s to 2.1 m/s and concluded a power equation relating the odor emissions to wind speed as:

\[ \frac{E_v}{E_{1}} = 1.05 V^{1.000}, R^2 = 0.69 \]  

Where \( V \) =given wind speed (m/s), \( E_{1} \)=odor emission at 1m/s and \( E_{v} \)=odor emission at speed \( V \).

Heber et al. (2002) concluded the odor emission rate (E) from a swine lagoon is affected by wind speed in a relationship defined by equation 2:

\[ \log(E) = -0.56 + 0.67 V, R^2 = 0.77 \]  

However, a research void exists in the understanding of gas and odor emissions from dairy manure ponds. The goal of this study was to quantify the annual trend of odor and gas emissions from dairy manure storage ponds. This new knowledge will be used to help Ohio dairy producers proactively abate gas and odor emissions from manure storage ponds.

Specifically, the study objectives were to:
1. Determine variations of gas emissions (NH_{3}, H_{2}S and odor) from a manure storage pond of a typical commercial dairy facility,
2. Explore effects of weather conditions and manure characteristics on gas and odor emissions, and
3. Evaluate odor and gas management need of dairy manure storage ponds.

Materials and Methods

Since ammonia and hydrogen sulfide are two gases released by dairy manure ponds that cause major environmental and health concerns and odor causes significant complaints from neighbors, each was measured once a month from April to November when the ambient temperature was higher than 50°F, which is a critical condition for biological activity. Ten total sampling events were conducted and each was completed between the daytime hours of 10:00am to 5:00pm. The sampling events were intended to be on
the same day each month. However, due to the weather condition and time conflicts, the actual sampling dates were between the 14th and 29th of each month. No sampling was conducted during winter months because the manure storage pond was frozen and not likely to cause air emission concerns.

Gas emissions are affected by weather conditions, operations of animal facilities, and manure management practices. Therefore, manure characteristic, fullness of the pond (height), pumping activity, agitation or recycling of manure water, crust on the surface, and height of surface waves were measured or observed during each sampling event. Manure management practices, dairy cattle inventory, and milk production data were also acquired from the producers. Weather conditions were measured by an electronic weather station (Cole Parmer catalog number C-99756-17) and a TSI anemometer (model 8384, TSI Inc., Shoreview, MN). In addition, weather data, such as temperature, humidity, wind speed, and rainfall was downloaded from a local weather station.

The Dairy Facilities

A dairy farm with a naturally ventilated, 6-row freestall dairy barn, having cow numbers ranging from 650 to 700, and an adjacent manure storage pond was selected for this study. It is a modern dairy barn with a 6 m (19.7 ft) wide center drive-through feed alley, 122.5 m (402 ft) long, 33 m (108 ft) wide, and 7.6 m (25 ft) high at the ridge. Natural ventilation is provided by 3.5 m (12') high sidewall curtains, 0.609 m (24") wide open ridge, and overhead doors at the end of service and feed alleys. The building has circulating fans above the freestalls and water misters along the drive-through feed alley line. The free stalls are sand bedded. The feed consumption was about 50 kg as fed (AF) (110 lb AF) per cow per day and the feed included corn silage (54%), hay silage (7%), ground corn (9%), soy bean meal (4.5%), mineral mix (5.5%), wheat (2%), and wet brewer's grains (18%). The annual average drinking water consumed was about 91 kg (200 lb) per cow per day. The herd total daily milk production varied with seasons from 20,400~25,000 kg (45,000~50,000 lb) per day and the typical milk protein content was 2.93%.

A tractor scraper was used to push the manure to a center cross alley where recycled flush water carried the manure to a solids/sand settling basin. The liquids flowed from the settling basin to an earthen manure storage basin. The sand settling basin was emptied several times a year. The manure storage pond is 61 m (200 ft) wide, 128 m (420 ft) long, and 4.6 m (15 ft) deep (Fig.1) and receives 6,000 metric ton of solids, sand, straw and other manure waste annually. The capacity of the manure storage pond is approximately 34 million litters (9 million gallons) and the volume of the manure slurry varies with seasonal rainfall, surface water evaporation, manure and waste water accumulation, and the manure removal. The manure storage pond was emptied twice a year in April and September. Before emptying the storage, the manure was agitated with a tractor powered chopper/agitator pump. Once agitated, the manure was pumped through soft hoses to a drop-hose manure applicator which injects the manure into the soil.

The dairy feed consisted of a total mixed ration with corn and haylage stored in bunker silos adjacent to the barn. Dry grains were stored in grain bins near the bunker silos. The cows were fed twice a day with feed being pushed up several times during a day. A milking center and dry cow area was located adjacent to the freestall barn. About 85% of the cows were lactating at any time during this study. The cows were milked three times per day. The average daily milk production per cow was 36 kg cow−1 d−1 (80 lb cow−1 d−1).

The dairy facility was designed by a commercial developer, who has established more that 25 large dairy operations in Ohio. All have very similar layouts as well as management practices. Therefore, the facility selected is a representative of new large dairy operations in Ohio.
Gas and Odor Sampling

A CFC developed by the Purdue Agricultural Air Quality Laboratory (Heber et al., 2002) was used for gas and odor flux measurement on the surface of the manure storage pond. The CFC was placed at the upwind side of the manure storage pond. It covered 0.74 m² (7.96 ft²) of slurry surface over which air was blown at approximately 1 m s⁻¹ (197 fpm) and surrounded by rigid waterproof insulation to keep the top 0.17 m (0.56 ft) of the CFC floating above manure surface. Air followed a horizontal hairpin (0.31 m (1 ft) wide) by (2.4 m (7.9 ft) long) path across the exposed liquid surface (Heber et al. 2002). A variable speed blower forced air through a gas absorption unit, a long Teflon air supply duct, and then into the emission chamber (Heber et al. 2002). The CFC was held stationary in the manure pond by steel tension wire which connected the chamber to anchor points driven into the pond berm.

Ammonia, hydrogen sulfide, and odor were sampled at the inlet and outlet of the CFC unit. At noon during each sampling event, hydrogen sulfide was monitored upwind of the pond, at the downwind berm of the manure storage pond, and 152 m (500 ft) and 304 m (1000 ft) downwind of the manure storage pond (figure 1) to study the impact of the dairy facility on the hydrogen sulfide level of the neighboring area. Odor concentration was also measured at the downwind berm of the lagoon to examine the worst scenario of odor concentration on the farm. Figure 1 shows the dairy farm layout and gas sampling locations.

Figure 2 shows the gas and odor sampling system. Inlet and outlet air samples were separately drawn to two stainless steel sampling manifolds using Teflon tubing (1/4" OD x 1/8" ID) and two air pumps (Model #107CAB18TFEL, Thomas Industries). A manifold and valve system was used to supply gas analyzers with sampled air. All materials in contact with the sample gas were Teflon, Tedlar, or stainless steel. Each gas analyzer was connected to the inlet manifold and the outlet air manifold by way of a selection valve. Quasi-continuous H₂S and NH₃ concentrations from the inlet to the outlet locations were measured. This was accomplished by alternating the measurement of ammonia and hydrogen sulfide concentration. Each sampling period lasted for 20 minutes, thus the inlet ammonia was measured for 20 minutes followed by the outlet ammonia concentration being measured for the same duration. Only the last 5 minutes of data from each 20 minute sampling interval was used for analysis to ensure the gas analyzer had reached steady state. This sampling cycle was repeated throughout each sampling day from 10 AM until 4 PM. The six-hour sampling duration resulted in nine average gas generation rates for both ammonia and hydrogen sulfide. The data was logged by a portable microcomputer.

Hydrogen sulfide was measured using a Jerome H₂S analyzer (631-X, Arizona Instruments, Tempe, AZ). The measurement range of 0.003 ppm (3 ppb) to 50 ppm makes it appropriate for monitoring H₂S concentrations at typical livestock facilities. The resolution is 0.001 ppm. The accuracy is about 6% of measured values. The Jerome Meter was calibrated by the manufacturer before the study to ensure reliable data collection.
Ammonia concentration was measured using a Single Point Air Monitor (SPM) (MDA Scientific Single Point Monitor, 970889, Zellweger Analytics, Lincolnshire, IL) initially and then by an MSA Chingard RT® NH₃ analyzer (MSA Inc., Pittsburg, PA) during warm months when the sample air humidity was high and affected the performance of the SPM ammonia analyzer. The MSA NH₃ analyzer is a photoacoustic sensor calibrated for NH₃ with an accuracy of ± 2 ppm. It draws samples at a flow rate of 0.75 liter min⁻¹ and produces a 90% response within 70 seconds from a step change input concentration. It can also operate at temperature from 0 to 50°C (32°F to 122°F) and relative humidity from 0 to 95%, respectively. Data collection was enabled by a personal computer running a customized Visual Basic (Microsoft Inc., Redmond, WA) data logging program. A Matheson-Kitagawa (model 8014-400A) hand-held pump and NH₃ colorimetric tubes (Matheson-Kitagawa Precision Gas Detector Tubes, Matheson Tri-Gas Inc., Montgomeryville, PA) with range of 0.2 to 20ppm, ±15% error (Matheson Tri-Gas Inc., Montgomeryville, PA) were used to verify the NH₃ readings obtained from the NH₃ analyzers.

Odor samples were collected into 10L Tedlar bags (SKC Inc., Eighty Four, PA) using an SKC Vacuum Chamber (SKC Inc., Eighty Four, PA), and a Buck I.H. Pump (SKC Inc., Eighty Four, PA). Two air samples at the inlet of the CFC chamber, two at the outlet of the CFC chamber, and one near the downwind berm of the manure pond were collected at noon during each sampling event. Odor samples were sent to the Iowa State University Olfactometry Lab to be analyzed for odor concentration, i.e., odor detection threshold, by a dynamic olfactometer (AC'SCENT international Olfactometer, ST. Croix Sensory, Inc., MN) within 24 hours of collection.

![Figure 2. The gas and odor sampling system.](image)

**Emission Rate Determination**

The sample concentrations, Cₘᵢᵣ and Cₗᵢᵣ, were converted to emission rates, E, by application of the continuity equation 3 (Smith, 1994).

\[
E = \frac{(C_{\text{out}} - C_{\text{in}}) V A_t}{A_s}
\]  

(3)

Where \( C_{\text{out}} \) is the NH₃ concentration at the chamber air outlet; \( C_{\text{in}} \) is the NH₃ concentration at the chamber air inlet; \( V \) is the air velocity through the air supply duct; \( A_t \) is the duct cross-sectional area; and \( A_s \) is the surface area covered by the chamber. Application of this equation assumes complete mixing between the gases and the airflow in the chamber upstream of the sampling point.

**Manure Sampling and Analysis**

Ten 250 mL manure samples were obtained from ten equally distributed locations around the pond’s edge and less than 0.3 m (1 ft) from the pond water surface using a 3 m (10 ft) polyethylene grab manure
sampler for manure characteristics analysis. All samples were evenly mixed in a 19 L (5 gallon) plastic bucket, from which a 500 mL aliquot of sample was obtained and transferred into a wide-mouth polyethylene bottle. The entire manure sampling procedure was repeated three times to obtain three replicate samples. All samples were collected starting at noon of each monitoring day. Manure samples were refrigerated and transported to the Star Lab (OARDC, Wooster, OH) to be analyzed. Analysis included manure pH, percentage of solids, ash, total nitrogen, ammonia nitrogen, and nitrate-nitrogen.

In addition, manure temperature was measured. General observation on the manure ponds, such as fullness of the pond (height), pumping situations, agitation or recycling of manure water, crust on the surface, and height of surface waves were recorded.

**Data Analysis**

Data was analyzed by general descriptive statistical analysis. The association between odor and gas emissions, weather conditions, and manure characteristics were evaluated using statistical regression and correlation analyses. Two-way analysis of variance (ANOVA) using SAS software was performed on the data to indicate the possibility of cause and relationships among the affecting variables and NH₃, H₂S and odor emissions at a 0.05 significant level.

**Results and Discussions**

**Weather Conditions**

Table 1 summarizes weather conditions near the dairy farm on the test days. Average ambient temperature started at 10.6°C (51°F) (in April) and increased during warmer months (July and August). This was followed by a decline in temperature near the end of the study period (September). In late October and mid November, the average ambient temperature had dropped below the freezing point. The temperature varied from -2 to 31°C (29°F to 87°F) during the study period. Relative humidity started low at 54% and then increased to 91% in May with a whole test variation from 30%-94%.

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<tbody>
<tr>
<td>Daily Average Temperature (°C) (low-high)</td>
<td>11 (6-16)</td>
<td>21 (17-29)</td>
<td>20 (14-27)</td>
<td>26 (22-31)</td>
<td>26 (17-29)</td>
<td>15 (11-18)</td>
<td>4 (-2-11)</td>
<td>0 (-1-7)</td>
</tr>
<tr>
<td>Daily Average Relative Humidity (%) (low-high)</td>
<td>54 (30-93)</td>
<td>73 (43-91)</td>
<td>65 (37-90)</td>
<td>74 (58-88)</td>
<td>49 (36-77)</td>
<td>69 (51-95)</td>
<td>68 (36-91)</td>
<td>85 (73-94)</td>
</tr>
<tr>
<td>Daily Average Wind Speed (mph) (low-high)</td>
<td>2.4 (0-6)</td>
<td>3.4 (0-7)</td>
<td>1.4 (0-4)</td>
<td>0.9 (0-4)</td>
<td>1.1 (0-4)</td>
<td>2.5 (0-6)</td>
<td>0.2 (0-3)</td>
<td>0.2 (0-3)</td>
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**Manure Pond Conditions and Manure Characteristics**

Table 2 summarizes manure pond conditions during the study period. The first gas measurement started in April. Manure depth was about 3 m (10 ft) with manure temperature of 9.4°C (49°F), which is close to the critical condition for biological activities. Manure application occurred two times during the study in May and September. Surface water was continuously pumped to the dairy barn for manure cleaning throughout the study. In the warmer months from June to September, about 40% of the manure surface formed a thin crust. During most of the test events, the weather condition was mild and manure surface waves were visually observed as less than 7.6 cm (3 in.) high.

The average measured manure surface temperature and ambient air temperature were 17.2±6.3°C (63±11.3°F), and 21.7±6.8°C (71.0±12.3°F) respectively. The manure surface temperatures ranged from 8.1°C to 28.7°C (46.6°F to 83.7°F) and ambient air temperatures ranged from 9.2°C to 30.3°C (48.5°F to 86.5°F) over the study period. There is a strong linear relationship between water and air temperature with a correlation coefficient of 0.93 and an R² value of 0.63.
Table 2. The manure storage pond conditions

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<tr>
<td>Manure depth, m (ft)</td>
<td>3</td>
<td>2.1</td>
<td>1.5</td>
<td>1.8</td>
<td>2.1</td>
<td>2.7</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Manure temperature (°C)</td>
<td>±0.6</td>
<td>±2.7</td>
<td>±0.9</td>
<td>±5.0</td>
<td>±0.5</td>
<td>±1.8</td>
<td>±1.6</td>
<td>±0.2</td>
</tr>
<tr>
<td>Air temperature (°C)</td>
<td>28±1</td>
<td>25±1</td>
<td>29±6</td>
<td>28±6</td>
<td>19±1</td>
<td>19±5</td>
<td>11±1</td>
<td>11±1</td>
</tr>
<tr>
<td>Manure application</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
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<tr>
<td>Surface water recycling</td>
<td>On</td>
<td>On</td>
<td>On</td>
<td>On</td>
<td>On</td>
<td>On</td>
<td>On</td>
<td>On</td>
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<tr>
<td>Surface crust (% of area)</td>
<td>&lt; 10%</td>
<td>&lt; 25%</td>
<td>&lt; 40%</td>
<td>&lt; 40%</td>
<td>&lt; 40%</td>
<td>&lt; 10%</td>
<td>&lt; 10%</td>
<td>&lt; 10%</td>
</tr>
<tr>
<td>Wind Speed (mph)</td>
<td>3.3</td>
<td>6.3</td>
<td>2.9</td>
<td>2.3</td>
<td>2.0</td>
<td>4.6</td>
<td>2.2</td>
<td>2.9</td>
</tr>
<tr>
<td>Waves height</td>
<td>&lt; 3&quot;</td>
<td>&lt; 2&quot;</td>
<td>&lt; 3&quot;</td>
<td>&lt; 3&quot;</td>
<td>&lt; 3&quot;</td>
<td>&lt; 3&quot;</td>
<td>&lt; 0.5&quot;</td>
<td>&lt; 2&quot;</td>
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</table>

Table 3 shows manure characteristics. The manure storage pond received about 6,000 metric ton of solids, sand, and other manure waste annually as well as waste water from the milking center and the dairy barns. The volume of the manure in storage clearly varied with manure and waste water deliver to storage and the manure removal.

Total nitrogen varied from 5.47% to 8.07% with an average of 7.2%. Ammonia nitrogen varied from 32.1 to 75.4 mg g⁻¹ with an average value of 56 mg g⁻¹. Percentage of solids varied from 1.52% to 3.66% with an average value of 2.2%. Percentage of volatile solids was relatively stable with an average of 61% of total solids with a very small variation. The pH value of the manure was also very stable with an average value of 7.7 with a very small variation of 0.1.

Table 3. Manure characteristics

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<tr>
<td>Total Nitrogen (% of Total Solids)</td>
<td>7.38±0.3</td>
<td>6.76±0.4</td>
<td>6.66±0.5</td>
<td>9.04±0.7</td>
<td>5.47±2.2</td>
<td>8.07±2.5</td>
<td>7.2±1.2</td>
</tr>
<tr>
<td>NH₃-N (mg/g manure)</td>
<td>68.2±3.2</td>
<td>51.4±3.7</td>
<td>53.5±8.5</td>
<td>75.4±9.2</td>
<td>32.1±18.2</td>
<td>55.2±20.7</td>
<td>56.0±15</td>
</tr>
<tr>
<td>Solids Content (%)</td>
<td>1.66±0.1</td>
<td>2.18±0.2</td>
<td>2.21±0.3</td>
<td>1.52±0.0</td>
<td>3.66±1.4</td>
<td>1.84±0.5</td>
<td>2.2±0.8</td>
</tr>
<tr>
<td>Volatile Solids (% of Total Solids)</td>
<td>63.4±0.9</td>
<td>63.4±0.6</td>
<td>61.2±0.5</td>
<td>57.4±0.6</td>
<td>58.1±2.5</td>
<td>64.5±1.6</td>
<td>61.3±3</td>
</tr>
<tr>
<td>pH</td>
<td>7.76±0.0</td>
<td>7.50±0.0</td>
<td>7.70±0.0</td>
<td>7.83±0.0</td>
<td>7.53±0.0</td>
<td>7.58±0.0</td>
<td>7.7±0.1</td>
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Seasonal Variations of Gas and Odor Emissions

Figure 3 shows daily mean ammonia concentrations at the inlet and outlet of the CFC and the calculated ammonia emission rates during the whole eight-month study period. The overall mean inlet NH₃ concentration was 2.6±1.2 ppm and the daily mean NH₃ inlet concentrations ranged from a minimum of 0.79 ppm in April to a maximum of 3.76 ppm in August. The overall mean outlet NH₃ concentration was 4.1±2.0 ppm and the daily mean NH₃ outlet concentrations ranged from a minimum of 1.2 ppm in November to a maximum of 7.39 ppm in July. It is clear inlet and outlet NH₃ concentrations were low in cold months such as April and November and high in hot months such as July and August. Ammonia emission rates were calculated according to concentration difference between the inlet and outlet and airflow rate through the CFC. The overall mean NH₃ emission rate was 71.6±57.8 µg s⁻¹ m⁻² and the daily mean NH₃ emission rates ranged from the lowest emission rate of 5.7 µg s⁻¹ m⁻² in November to the peak emission rate of 174.8 µg s⁻¹ m⁻² in July. Ammonia emissions peaked during the hot July and August sampling periods. These NH₃ emission rates are within the emission range (46.1-198 µg s⁻¹ m⁻²) measured by Gay et al. (2003) at 3 dairy facilities during short-term survey sampling studies.
Figure 3. Mean NH₃ inlet and outlet concentrations and emission rates during the sampling days

Under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and the Environmental Planning and Community Right-to-Know Act (EPCRA) federal air quality laws, a business is required to report any NH₃ emissions exceeding 100 lb (45.45 kg) in any 24-hour period. To evaluate the likelihood of dairy farm’s compliance with the air quality laws, NH₃ emission rate was converted to daily emission in pounds (Figure 4). Assuming uniform manure storage surface emission, daily NH₃ emissions from the manure storage pond was estimated as from 8.2 lb d⁻¹ in November to 251.2 lb d⁻¹ in July. Starting in May, the emission rate reached the 100 lb d⁻¹ limit. Note, this study only measured daytime ammonia emission rates and diurnal variations in ammonia emission were ignored in the daily emission rate calculations. Therefore, the daily ammonia emission rate in May and early June might be just under or close to the 100 lb d⁻¹ limit. Clearly for this dairy operation, NH₃ emission rates were higher than the reporting criteria in late June to August.

Figure 4. Estimation of daily NH₃ emission from the manure pond (lb d⁻¹) and comparison with the EPCRA and CERCLA reporting requirement, 100 lb d⁻¹.

Figure 5 shows daily mean and variations of H₂S concentrations at the inlet and outlet of the CFC and the calculated H₂S emission rates during the whole eight month study period. The overall mean inlet H₂S concentration was 16.1±10.1 ppb and ranged from 5.3 ppb in June to 31.6 ppb in Oct. The overall mean outlet H₂S concentration was 33.3±25.8 ppb and the daily mean outlet H₂S concentrations range from 2.2 ppb in May to 71.5 ppb in October. The daily mean H₂S emission rates varied from 0.1 µg s⁻¹ m⁻² in May to 4.6 µg s⁻¹ m⁻² in October. Peak H₂S emission occurred in October and August. These emission rates are lower than the total reduced sulfur emission rate (7.56-37.8 µg s⁻¹ m⁻²) measured by Gay et al. (2003) at two
dairy farms and close to the mean H$_2$S emission rates (5.7 µg s$^{-1}$ m$^{-2}$) measured by Lim et al. (2003) from anaerobic treatment swine lagoons. The facts that this study period included cold and hot months and Gay et al. (2003) collected data mostly in summer months likely accounts for some differences in the emission results.

The H$_2$S emission rate trend was different from that of NH$_3$ emission rate. High temperatures usually resulted in high H$_2$S emission rates. However, there were two low H$_2$S emission points, one in May and one in September. This was likely associated with manure agitation and application, since the gas sampling in May and September were both after a manure removal and application event. It is known manure agitation results in significant H$_2$S emission. H$_2$S emission rates from the manure surface were significantly decreased after manure agitation events.

The CERCLA and EPCRA’s 100 lb d$^{-1}$ reporting requirement also applies to H$_2$S. To evaluate the likelihood of dairy farm’s compliance with the air quality regulations, H$_2$S emission rate is converted to daily emission in pounds (Figure 6). Uniform emission from manure storage surface was assumed. Daily mean H$_2$S emission rate ranged from 0.1 lb d$^{-1}$ in May to 6.6 lb d$^{-1}$ in October. It is clear the daily H$_2$S emission from this dairy manure storage pond was much lower than the reporting criteria and was not a concern regarding compliance with the CERCLA and EPCRA air laws.

**Figure 5.** Mean inlet and outlet H$_2$S concentrations and emission rates during the sampling days in the months.

**Figure 6.** Estimation of daily H$_2$S emission from the manure pond (lb d$^{-1}$) and comparison with the EPCRA and CERCLA reporting requirement, 100 lb d$^{-1}$. 

![Figure 5](image1.png)  
![Figure 6](image2.png)
Figure 7 shows daily mean and seasonal variations of odor concentrations at the inlet and outlet of the CFC and the calculated odor emission rates during the study period. The overall mean inlet odor concentration was 135.8±53.1 OU m$^{-3}$, ranging from 97 OU m$^{-3}$ in November to 231 OU m$^{-3}$ in August. The overall mean outlet odor concentration was 218.8±99.3 OU m$^{-3}$ ranging from 96 OU m$^{-3}$ in November to 381 OU m$^{-3}$ in August. It is clear that inlet and outlet odor concentrations were low in cold months such as April and November and high in hot months such as July and August. Odor emission rates were calculated according to odor concentration difference between the inlet and outlet and airflow rate passing through the CFC. The overall mean odor emission rate was 4.7±4.3 OU s$^{-1}$ m$^{-2}$ and the daily mean odor emission rates ranged from 0 OU s$^{-1}$ m$^{-2}$ in November to 10.34 OU s$^{-1}$ m$^{-2}$ in August. These odor emission results agree well with odor emission rates (2-10 OU s$^{-1}$ m$^{-2}$) measured by Bicudo et al. (2003) and are less than the odor emission rates (13-51 OU s$^{-1}$ m$^{-2}$) measured by Gay et al. (2003). Again, the sampling time difference might contribute to the differences in the results.

Clearly, odor emission rate and concentrations reached peak values in hot months of the year. If odor is a concern to neighbors and limited mitigation can be afforded, then warmer months are definitely the time to apply odor abatement practices.

Figure 7. Mean inlet and outlet odor concentrations and emission rates during the sampling days in the months.

Daytime Variations of NH$_3$ and H$_2$S Emission Rates

Information of daily variations of gas emission help to determine sampling procedures when only short-term sampling is feasible. Figure 8 shows NH$_3$ emission and ambient temperature variations on days in April, July, and November, which represent cold to hot months. From month to month, NH$_3$ emission varied significantly. However, on any particular day, ammonia emission during the daytime did not vary significantly and was about 10-20% of the daytime mean values. Mean daytime NH$_3$ emission rates were 49.5±9.5, 174.8±17.9, and 5.7±4.4 µg s$^{-1}$ m$^{-2}$ in April, July, and November, respectively. Small standard deviations were found in comparison to the mean values in warmer months (July and April). When ammonia emission rates were very low in November, the absolute variations were small even though the variations were large relative to the mean value. If the sampling time is limited, this suggests sampling at any time during daytime in warmer months will result in a representative NH$_3$ emission rate value of the sampling day.
Figure 8. Variations of daily ammonia emission rates and ambient air temperatures.

Figure 9 shows H$_2$S emission rate and temperature variations on days in April, July, and October. Mean daytime H$_2$S emission rates were 1.78 ± 0.69, 2.94 ± 0.55, and 4.57 ± 1.85 µg s$^{-1}$ m$^{-2}$ in April, July, and October, respectively. In comparison with NH$_3$ emission, relatively large variations were observed, especially in October. Previous research also documented large variations of H$_2$S emission from swine manure storage pits (Ni et al., 2000) and variation of H$_2$S concentrations at a dairy manure storage pond (Bicudo et al., 2003). This denotes that sampling of H$_2$S emission and concentration needs a relatively long sampling period to account for the large variations.

Figure 9. Variations of daily H$_2$S emission rate and ambient air temperature

**Effect of Temperature on Odor and Gas Emissions**

Since the gas and odor emission rate sampling was conducted from April to November, the measurement covered ambient temperature conditions from about 10°C (50°F) to 28.8°C (84°F). Gas emission rates varied monthly and high gas and odor emission rates were observed in hot months (July and August). It is clear temperature condition affects gas and odor emission rates. Figures 10-12 demonstrated trends of temperature change and ammonia, odor and H$_2$S emission rate variations, respectively. It is clear high ammonia and odor emission rates correspond to high temperatures (Figure 10 and 11). It is not obvious high H$_2$S emission rates always corresponded with high temperatures. Manure agitation in May and September resulted in low subsequent H$_2$S emission rates. In October, even though the ambient temperature dropped significantly, the highest H$_2$S emission rate was measured.
Figure 10. Seasonal variations of ammonia emission rates and ambient temperatures.

Figure 11. Seasonal variations of odor emission rates and ambient temperatures.
Figure 12. Seasonal variations of H$_2$S emission rates and ambient temperatures.

Correlation analysis was conducted to examine the correlation relationships between ambient temperature and NH$_3$, H$_2$S, and odor emission rates. Table 3 lists the correlation coefficients for ambient temperature, NH$_3$, H$_2$S, and odor emission rates. Odor and NH$_3$ were strongly correlated with ambient temperature with high correlation coefficients of 0.88 and 0.87, respectively. H$_2$S emission rate was weakly correlated with ambient temperature condition, with a low r value of 0.41. In addition, both NH$_3$ and H$_2$S were strongly correlated with odor emission rate with r values of 0.78 and 0.7, respectively. However, the correlation coefficient for NH$_3$ and H$_2$S emission rates was relatively smaller (0.63).

Table 3. Correlation coefficients (r) for NH$_3$, H$_2$S, and odor emissions, and air temperature.

<table>
<thead>
<tr>
<th></th>
<th>NH$_3$</th>
<th>H$_2$S</th>
<th>Odor</th>
</tr>
</thead>
<tbody>
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<td>NH$_3$</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$S</td>
<td>0.63</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Odor</td>
<td>0.78</td>
<td>0.70</td>
<td>1</td>
</tr>
<tr>
<td>Ambient T</td>
<td>0.87</td>
<td>0.41</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Knowing the possible strong effects of ambient temperature conditions on NH$_3$ and odor emission rate, regression analyses were conducted to define any statistical relationships. Figures 13 (a) and (b) show possible regression relationships between ambient temperature and NH$_3$ emission rate and odor emission rate respectively. A two degree non-linear relationship described temperature effects on ammonia emission rate well with a $R^2$ value of 0.6 (equation 4). A similar relationship described temperature effects on odor emission (equation 5) with a relatively smaller $R^2$ value of 0.53. This may due to the small number of odor measurements in comparison with the ammonia measurements. More data points may improve the regression relationship.

\[
E_{NH3} = 0.151T^2 - 17T + 496 \quad (R^2=0.6) \quad (4)
\]

\[
E_{odor} = 0.0178T^2 - 2.2T + 68.7 \quad (R^2=0.53) \quad (5)
\]

Where, $E_{NH3}$ is the ammonia emission rate (µg s$^{-1}$ m$^{-2}$); $E_{odor}$ is the odor emission rate (OU s$^{-1}$ m$^{-2}$), and T is the air temperature (°F).
Effect of Wind Speed or Surface Air Velocity on Gas and Odor Emissions

Knowledge on effects of surface air velocities on gas and odor emissions from manure ponds will be useful to calibrate the CFC or wind tunnel measurements of gas and odor emissions for estimation of gas and odor emission under field weather conditions. Effects of air velocity at the manure surface on gas emission rate was tested by measuring gas emission rates under three different levels of air velocities, 0.6, 1 and 1.5 m/s, during two consecutive days in August. Weather conditions were identical with an average ambient temperature of 20.6°C (69°F), a temperature range of 13°C to 34°C (55°F-94°F), and a relative humidity of 69%. Figure 14 shows the effects of different surface air velocities on NH₃ and H₂S emission rates. Theoretically, higher air velocities result in higher average NH₃ and H₂S emissions rates. Based on 18 group data sets, power function relationships between gas emission rates and manure surface air velocities were summarized as equations 6 and 7. Due to field test limitations and a small number of data points, the R² values of the two equations are very small. Further studies are needed to delineate effects of surface air velocity on gas and odor emissions.

\[ E_{\text{NH}_3} = 113V^{0.3} \quad (R^2=0.1) \]  
\[ E_{\text{H}_2\text{S}} = 3.6V^{0.3} \quad (R^2=0.2) \]
**H₂S Distribution the Dairy Farm**

In addition to gas and odor emission rate measurements at the manure storage pond, H₂S concentrations at the upwind of the farm, at the downwind berm of the manure storage pond, and 152 m (500 ft) and 304 m (1000 ft) downwind of the manure storage pond were measured at noon during each sampling event to reveal the impact of the dairy facility on ambient H₂S levels. Figure 15 shows H₂S distribution on the dairy farm. Results showed overall H₂S concentrations at the dairy farm were very low. H₂S dispersed well at noon. At the upwind location, H₂S concentrations were less than 1 ppb at most times. At the downwind berm of the manure storage pond, H₂S concentrations were the highest. This indicated the dairy farm was the only source of H₂S at the neighboring areas. At the 152 m (500 ft) and 304 m (1000 ft) downwind locations, H₂S concentrations were less than 2 ppb at most times. The measurement data showed this dairy facility did not impact ambient H₂S levels at the neighboring areas during the study period.

**Conclusions**

There are large seasonal variations in NH₃, H₂S, and odor emission rates from the dairy manure storage pond. During an eight-month study period, the overall mean NH₃ emission rate was 71.6 ± 57.8 µg s⁻¹ m⁻² and the daily mean NH₃ emission rates ranged from 5.7 µg s⁻¹ m⁻² in November to 174.8 µg s⁻¹ m⁻² in July. The daily mean H₂S emission rates varied from 0.1 µg s⁻¹ m⁻² in May to 4.6 µg s⁻¹ m⁻² in October. The
overall mean odor emission rate was 4.7 ± 4.3 OU s⁻¹ m⁻² and the daily mean odor emission rates ranged from 0 OU s⁻¹ m⁻² in November to 10.34 OU s⁻¹ m⁻² in August.

NH₃ emissions from the 650-700 cow operations were likely more than 45.45 kg (100 lb) per day in warmer months. However, H₂S was not a concern at all in reference to the EPCRA and CERCLA reporting requirements. If odor is a concern to neighbors and limited mitigation can be afforded, then warmer months are the critical time for odor abatement practices.

Variations in daytime NH₃ emission rates from the dairy manure storage pond were very small. However, H₂S emission rates had large daily variations.

Odor and NH₃ emission rates were strongly correlated with ambient air temperature. High temperature in warmer months resulted in higher odor and NH₃ emission rates. However, H₂S emission rate was not clearly associated with ambient temperature and fluctuated month by month without a clear trend. Both NH₃ and H₂S emission rates were strongly correlated with odor emission. High surface air velocities or wind speeds resulted in high gas and odor emission rates. However, the exact correlation relationship was not easily acquired though the limited field studies. Future studies are needed.

H₂S concentrations on the dairy farm studied were generally low. H₂S dispersed well during noon sampling periods. The dairy facility did not significantly affect the ambient H₂S level at the 304 m (1000 ft) downwind neighboring areas during the study period.

References


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