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ODOR AND HYDROGEN SULFIDE EMISSION FROM A DAIRY MANURE STORAGE

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ABSTRACT

Ambient H_2S air concentrations were measured continuously for a period of approximately 30 days around a manure storage basin at a 700-dairy cow operation in Minnesota. Manure was agitated and pumped from the basin during the first week of monitoring. Odor samples were taken on two different occasions during the monitoring period using a wind tunnel placed just above the manure basin surface. Odor plume measurements were also made, but on a single day only.

Barn emissions did not seem to contribute much to hydrogen sulfide concentrations measured around the manure storage. This was verified by sorting the H_2S measurements obtained when wind was blowing from the barn toward the manure storage for the two monitors located at the south side of the basin. Mean H_2S concentrations downwind of the barn were between 0.02 and 5.7 ppb, while mean H_2S concentrations around the storage varied between 0.9 and 20 ppb.

A limited number of odor samples taken during the monitoring period suggested that the manure storage contributed significantly to odor emission as compared to the barn. Emission from the storage was between 7 and 10 OU/m^2-s, while emission from the barn was between 2 and 3 OU/m^2-s. Odor plume measurements taken at 60 and 120 m downwind from the barn indicated a decrease of 10 OU per 60 m.

KEYWORDS. Odor, hydrogen sulfide, manure, dairy, housing, storage.

INTRODUCTION

Liquid manure storage can be a significant odor source. The anaerobic nature of manure stabilization can produce offensive odors and release hydrogen sulfide and ammonia along with other gases during storage, agitation and subsequent land application. Prolonged storage of liquid manure results in the production of malodorous compounds such as ammonia (NH_3), sulfides (S^{-2}), volatile fatty acids (VFA), phenols, p-cresol, indoles, etc. that can potentially contribute to contamination of the atmosphere around livestock production facilities. Some of these compounds have been included in the U.S. EPA priority pollutants list and identified as respiratory tract, skin, or eye irritants.

Greater potential for odor emission from waste management or treatment systems occurs when retention times are too short, or organic loading rates increase due to expanding animal numbers, slug loading, concentrated waste streams, and/or inadequate water for dilution. Odor emission from storages and anaerobic lagoons is more likely when the liquid surface is disturbed during windy conditions, during agitation and pumping for land application, during spring turnover – defined as very vigorous bacterial activity during the spring due to incomplete metabolism of material during winter.

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Relatively few researchers have attempted to quantify odor and gas emissions rates from either animal housing or manure storage units. The emission rate values that have been reported vary widely due to the lack of standardized methods used to measure, calculate, and report odor and gas emissions rates. Calculation methods to quantify odor or gas emission rates from buildings and manure storages are dependent on accurate air sampling methods and proper determination of ventilation rates.

Zhu et al. (2000) measured odor at a 200-head dairy facility to determine daily variations. Air samples were collected every two hours over a 12-hour period during the day. Odor flux rates varied from 0.3 to 1.8 OU/m^2-s. Ventilation rates were estimated using mass exchange rates based on the carbon dioxide (CO_2) level between the inside and outside of the buildings.

Quantitative information about H_2S livestock building emissions is available in only a limited number of publications, primarily related to swine housing. There is very little information related to the emission of hydrogen sulfide (H_2S) from dairy farms. Clark and McQuitty (1987), for example, recorded a maximum H_2S level of 145 ppb in four of six commercial free-stall dairy barns in Alberta. Patni and Clarke (1991) measured H_2S concentrations before, during, and immediately following manure agitation and pumping from a 240-head free stall barn and also from a heifer barn. Average H_2S concentrations were between 1 and 14 ppm in the free stall barn and between 0 and 8 ppm in the heifer barn. Peak concentrations (during manure agitation) varied between 11 and 63 ppm in the free stall barn, and between 5 and 41 ppm in the heifer barn.

The objective of this paper was to characterize odor and H_2S emissions from a free-stall barn and its manure storage. Information on continuous H_2S concentrations in ambient air is also given.

METHODS

Measurements were taken at a 670-head dairy farm located in Minnesota. The layout of the farm is shown in Figure 1. The free-stall barn was 179 m long and 30 m wide. The manure storage was 150 m long and 57 m wide at the berm. Agitation and pumping of manure was carried out during a 10-day period (9/13/99 to 9/22/99), not necessarily on a consecutive basis. The basin was not completely empty after manure pump out. By the end of September manure depth was estimated at 0.50 m from the bottom of the basin, or about 1/3 of the basin capacity.

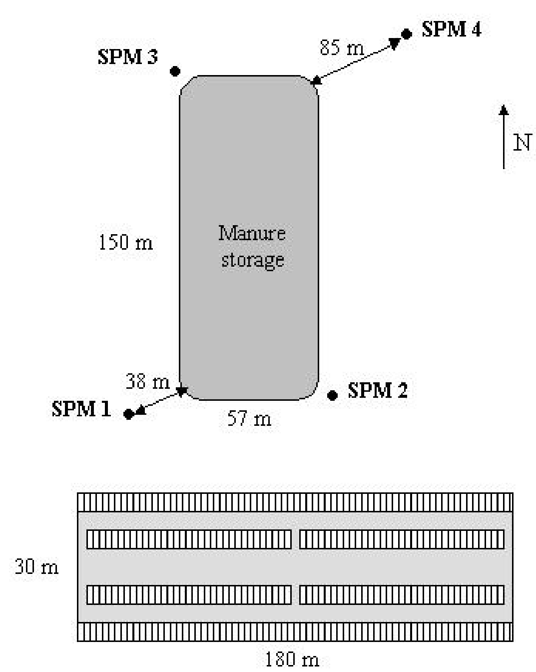

Figure 1. Layout of the dairy farm (not to scale)

H_2S measurements were not taken at property lines or in locations to which the general public had access. This was done in order to avoid compliance monitoring. The Minn. R. 7009.0200 prohibits violation of the state hydrogen sulfide ambient standards (30-minute average of 30 ppb found more than twice in five days, or a 30-minute average of 50 ppb found more than twice per year) beyond the property line or in locations to which the general public has access.

H_2S concentrations were measured continuously for a period of approximately 30 days during fall of 1999 (9/10/99 to 10/14/99) using MDA Single Point Monitors (SPM) (Zellweger Analytics, Inc., Lincolnshire, IL). The SPMs were located at the four corners of the manure storage basin as shown in Figure 1. SPMs 2 and 3 at the NW and SE corners of the basin, respectively, were located within 10 m of the berm. SPM 1 (SW corner) was located 38 m from the berm and SPM 4 (NE corner) was located 85 m from the berm. These monitors are equipped with a Chemcassette® Detection System and use a paper tape treated with a dry reagent medium - the Chemcassette® tape - to measure the gas concentration. Upon exposure to the target gas, the paper-tape changes color in direct proportion to the ambient gas concentration in the sample. A photo-optic system within the SPM measures the color intensity change and determines the sampled gas concentration based on 15-minute averages**.** The measuring range for H_2S is from 0 to 92 ppb. The accuracy of the instrument is ± 20% of the actual reading.

A limited number of odor samples were collected from the surface of the manure storage and also downwind from the barn on 9/30/99 and also on 10/12/99. A wind tunnel was used to collect samples on the surface of the manure storage (Schmidt and Bicudo, 2002). Equipment used to collect air samples from the odor sources included a vacuum box, an air pump, Teflon tubing and 10 L Tedlar bags (SKC Inc., Eighty Four, PA). The vacuum box (Vac-U-Chamber, SKC-West, Inc., Fullerton, CA) and air pump (Aircheck, Model 224-PCXR3 (or 4), SKC Inc., Eight Four, PA) were used to draw the odorous air into a sampling bag. Samples were taken at 3 L/min for about 3 minutes. The tubing used in the sampling apparatus was 1/4" Teflon FEP tubing (Cole-Parmer Instrument Company, Vernon Hills, IL). Concentrations in the exhaust air stream and airflow in the wind tunnel were used to estimate the odor flux rate from the surface of the manure storage. The volume flow rate is the product of the bulk wind speed of the air passing through the tunnel and the cross sectional area of the tunnel. Odor emission from the barn was estimated using odor concentration measurements taken at the curtain side and mass exchange rates based on the carbon dioxide (CO_2) level between the inside and outside of the barn (Albright, 1990, Phillips *et al*., 1998).

A triangular forced-choice dynamic dilution olfactometer (AC'SCENT® BETA-1, St. Croix Sensory, Inc., Stillwater, MN) was used to measure odor threshold. Odor measurements were performed according to European Standards (CEN, 1999).

Odor plume measurements were made at one occasion after manure was pumped from the basin with seven individuals who were trained to determine odor intensity in the ambient air. The odor intensity is determined by matching the strength of the air being sampled to a series of concentrations of the reference odorant with different odor intensities, usually 1-butanol. Individuals are trained to assess the odor level instantaneously using a numerical scale, typically 0 to 5, with 0 being no odor and 5 being a very strong odor. A relationship between odor intensity and odor threshold was developed experimentally and was used to convert between these values (Guo et al., 2001). This method provides greater sensitivity to odors at the lower end of the threshold scale than is typically possible with olfactometry.

A Jerome Hydrogen Sulfide Analyzer (Model 631-X. Arizona Instrument, Phoenix, AZ) was used to measure H_2S concentration during odor sample collection. This instrument measures total reduced sulfur (TRS) compounds, including alkyl sulfides, disulfides, mercaptans, and cyclic sulfur compounds. Winegar and Schmidt, 1998 showed that the response of the Jerome meter was 100% to H_2S and between 0 and 45% for other reduced sulfur gases when exposed to calibrated mixtures. The data presented in this paper are described as TRS but reported as H_2S equivalent. The measuring range is 0.001 to 50 ppm. The accuracy is ± 0.003 ppm at 0.050 ppm.

An automated weather station (Campbell Scientific, Logan, UT) was used. The weather station continuously recorded wind speed, wind direction, temperature, relative humidity, rainfall, solar radiation, and barometric pressure.

RESULTS AND DISCUSSION

Atmospheric conditions

Mean atmospheric conditions during the monitoring period are shown in Table 1. There was a wide variation in all parameters measured. Wind direction was predominantly from the South and West.

Table 1. Mean atmospheric conditions

Parameter	Mean	Minimum	Maximum
Air temperature (^oC)	10.6	-4.3	30.0
Relative humidity (%)	60	0	99
Wind speed (m/s)	3.2	0	11

Ambient H_2S concentrations

Ambient H_2S data is summarized in Table 2. The percentage of values greater than 92 ppb, which is equivalent to the upper detection limit of the SPMs, was fairly small, between 0.12 and 3.5% for all SPMs. The highest percentage of values greater than 92 ppb was observed at the SE corner of the storage basin. These values were not removed from the data set for statistical analysis.

H_2S values were categorized in terms of wind direction in order to separate the effects of the free-stall barn and manure storage. The two SPMs located at the south side of the storage were used to verify the effect of the barn on ambient H_2S when the wind directions were between 135 and 225^o.

Table 2. Mean H_2S concentration (ppb) with one standard deviation around the manure storage

SPM	1	2	3	4
Location	SW	SE	NW	NE
During pumping	4.8 ± 18.2	19.6 ± 30.4	2.9 ± 12.1	5.0 ± 16.6
After pumping	0.4 ± 2.5	7.2 ± 13.9	0.0 ± 0.0	0.7 ± 2.5
Downwind from barn	0.0 ± 0.2	5.7 ± 13.9	-	-
Downwind from manure storage	4.0 ± 16.4	20.0 ± 29.2	0.9 ± 5.0	2.0 ± 9.1

H_2S concentrations were higher during pumping of manure, as it would be expected. T-test statistics indicated that all mean values obtained during pumping were significantly different from mean values obtained after pumping at the 5% level. Figure 2 shows the variation of H_2S concentration at the SW location along time.

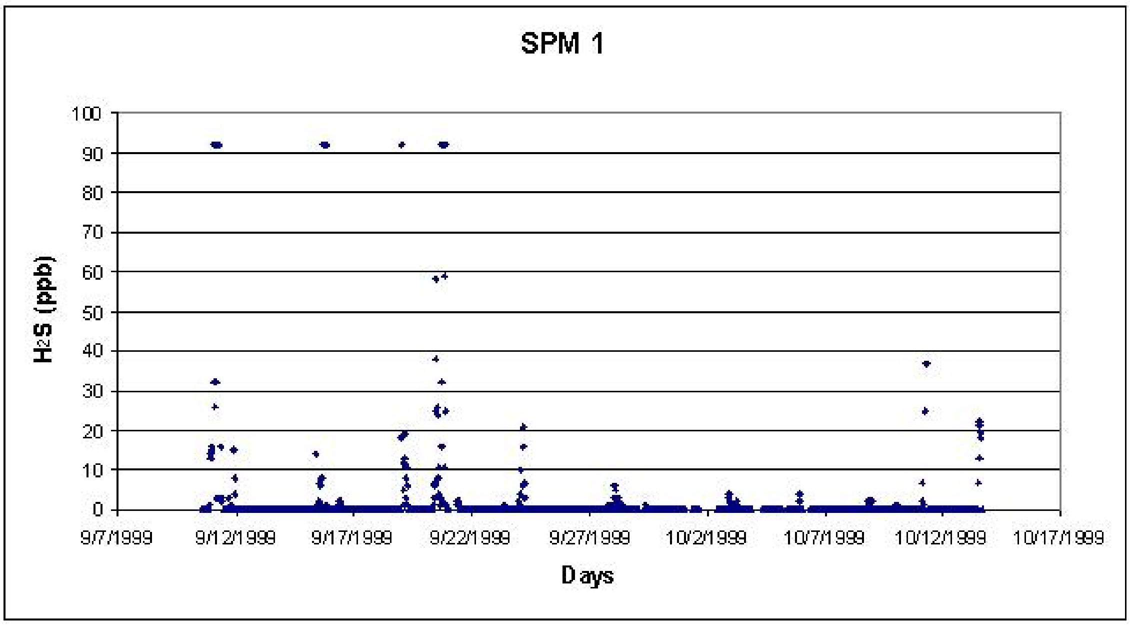

Figure 2. Variation of H_2S concentration at the SW corner of the basin

Values equal or greater than 92 ppb were only recorded during the pumping period (9/13 to 9/22). Results obtained from other SPMs were similar to results showed for SPM 1. The H_2S values obtained during manure pumping were significantly smaller than values obtained by Patni and Clarke (1991), but conditions in which values were measured in both studies were different. Patni and Clarke (1991) measured H_2S concentrations at the floor level just above the manure pits.

The two SPMs located at the south side of the basin indicated a reasonably small effect of the barn on ambient H_2S as compared to the effect of the manure storage. Bicudo et al. (2002) observed a similar effect when monitoring ambient H_2S near swine housing and manure storages.

H_2S data was subjected to reasonably large variations as shown by the value of standard deviation in Table 2. These variations are basically due to the diurnal pattern of ambient H_2S around livestock housing and manure storages. This pattern is graphically shown in Figure 3 for the SE corner of the basin (SPM 2). Values equal or greater than 92 ppb (upper limit of the SPM) were removed for clarity purposes. The H_2S concentrations increase during early morning hours (from midnight to 5:00 am), decrease during the day (from 5:00 am to 4:00 pm), and started increasing again in late afternoon till midnight. Bicudo et al. (2000) observed similar patterns around swine manure storages.

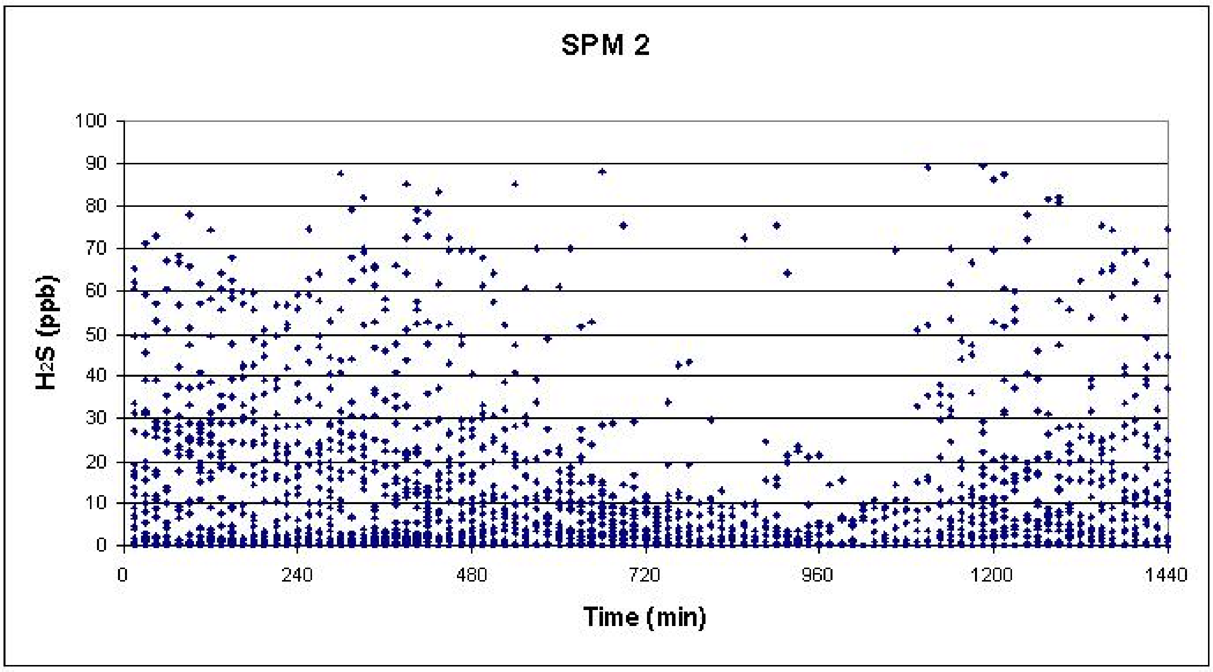

Figure 3. Diurnal variation of H_2S concentration at the SE corner of the storage basin

H_2S diurnal variation downwind from the source may be related to weather conditions, but no significant correlation was found between ambient H_2S concentrations and air temperature, relative humidity, or wind speed. Variation due to day and time was significant at the 5% level for SPMs 2 and 4 located at SE and NE corners, respectively. Variation due to time was not significant at the 5% level for SPMs 1 and 3 located at the SW and NW corners, respectively. Therefore, diurnal variation at the west side of the basin was not as pronounced as it was in the east side. This was probably due to wind direction effects. The highest potential for exceeding the Minnesota H_2S ambient standard would be during early morning hours (between midnight and 4 or 5 am) when atmospheric conditions are mostly stable.

Odor

A series of odor samples were collected on 9/30/99 and 10/12/99 from the manure surface and also downwind from the barn. At that time there was about 0.50 m of manure left in the basin. The results are summarized in Table 3.

As with the ambient H_2S data, emission of odor from the barn was much smaller than emission from the manure storage. Although this is a limited data set, it shows that odor emission from dairy operations can be significantly lower than emissions from swine operations. Bicudo et al. (2000) reported odor emissions from several swine operations (housing and manure storages) between 8 and 82 OU/m^2-s.

Table 3. Odor flux rates

Date	Location	Odor flux (OU/m^2-s)
9/30/99	Manure storage	10
10/12/99	Manure storage	7
9/30/99	Curtain side	2
10/12/99	Curtain side	3

Odor plume measurements were taken on 9/30/99 (Figure 4) in order to verify odor dispersion due within the farm.

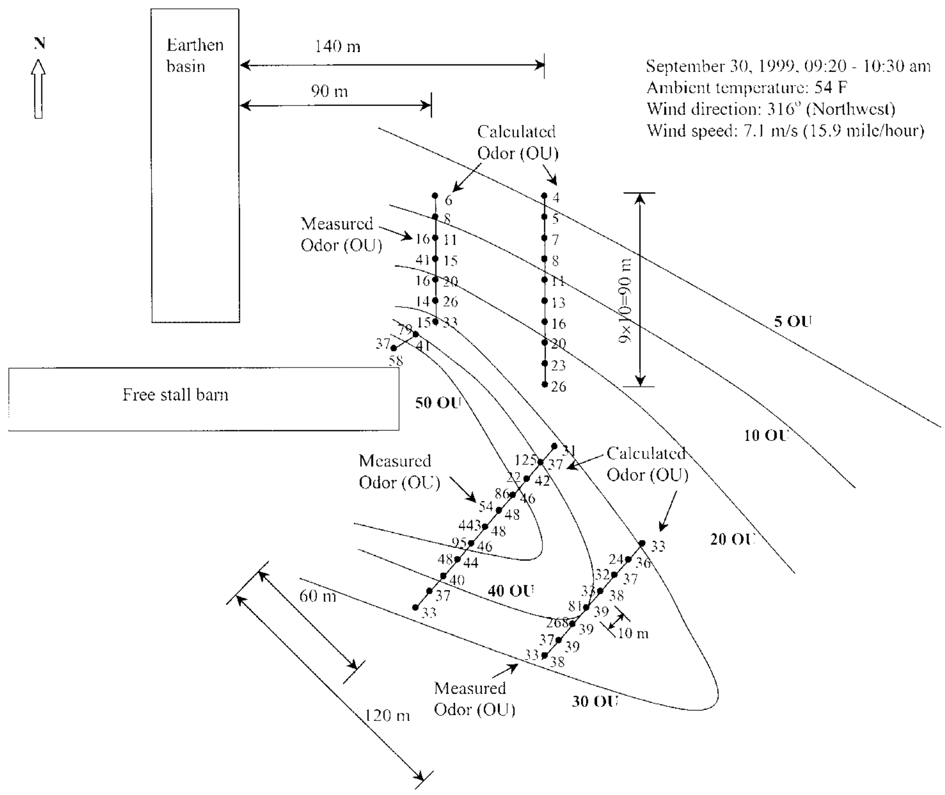

Figure 4. Odor plume measurements (9/30/99)

Measurements were first taken parallel to the manure storage basin and also on a 45^o angle from the edge of the barn. Odor profiles were calculated using INPUFF-2 model. The wind direction was such (316^o, NW) that it was difficult to isolate the two main odor sources (manure storage and free-stall barn). The results presented in Figure 4 show that odor decreased from 50 OU at 60 m downwind from the barn to 40 OU at 120 m from the barn, or about 10 OU per 60 m. A greater effect of dispersion on odor emission was expected based on the atmospheric conditions at the day measurements were taken. Wind was blowing from the northwest with a speed of approximately 7 m/s, air temperature of about 12 ^oC and relative humidity of 60%.

CONCLUSION

Continuous monitoring of ambient H_2S around a dairy manure storage indicated relatively low levels of H_2S except during agitation and pumping of manure. Mean H_2S concentrations were between 0 and 7 ppb after two thirds of manure was pumped out of the basin. The monitors used in this study could not detect concentrations higher than 92 ppb, but the number of times the monitors reached this level (92 ppb) were significantly higher during agitation and pumping than during the period after manure had been pumped out. Little contribution of the free stall barn to ambient H_2S was observed during the monitoring period.

H_2S data was subjected to reasonably large variations probably due to the diurnal pattern of ambient H_2S around livestock housing and manure storages. No significant correlations were found between H_2S concentrations and air temperature, relative humidity, and wind speed. However, the diurnal pattern of H_2S concentrations seem to indicate higher potential for exceeding the Minnesota standard on H_2S between during the night and early morning hours when atmospheric conditions are more stable.

Limited data on odor emission seem to confirm previous observations that manure storages are major odor sources in livestock farming. Odor emission from the manure storage was between 7 and 10 OU/m^2-s, while emission from the barn was between 2 and 3 OU/m^2-s. Plume measurement results indicated a relatively small effect of dispersion on odor emission, despite the high wind speed.

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