I. Project Title: Gas and Odor Emission Variability by Production Phase, and Manure Storage and Treatment

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II. Abstract

Measurement of gas emissions from area sources (manure storages, lagoons, open feedlots, etc.) poses considerable challenges. Mass transfer of gas from a manure source is a function of several parameters, including manure temperature, pH, dissolved gas concentration, solids content, and nutrient characteristics; as well as atmospheric temperature and pressure, surface wind velocity, etc. Two sets of manure samples (fall and spring) were collected from distinct manure sources (nursery, finishing, wean-to-finishing, gestation, and farrowing sites). Various manure collection types (slotted flooring, high-volume flush, or pull-plug / gravity-drain); manure storage types (deep-pit, tank, or earthen basin); manure storage stage (single, first, or second); or treatment systems (none, additives, or anaerobic digestion) were used. Physical and chemical parameters of the manure (e.g., total solids, total volatile solids, pH, total Kjeldahl nitrogen, ammonia-N, total COD, soluble COD, and total sulfide) were measured. Manure samples were evaluated for ammonia, hydrogen sulfide, total reduced sulfur, and odor flux using the microtunnel method. Statistical comparisons will be made between air pollutant flux, manure sampling site characteristics, and manure properties. The largest correlation coefficient was between air ammonia flux and manure ammonia concentration at 0.65. The predictive model for gas fluxes was for ammonia flux based on the ammonia concentration and pH of the manure. Other predictive models were more complex and not as good.

III. Introduction

Gas emission measurements from area sources (manure storages, lagoons, open feedlots, etc.) poses considerable challenges. Gas mass transfer from a manure source is a function of several parameters, including manure temperature, pH, dissolved gas concentration, solids content, and nutrient content; as well as atmospheric temperature and pressure and surface wind velocity.

Several methods are available to measure gas and odor emissions, including micrometeorological techniques, wind tunnels, and flux chambers. There are tradeoffs between accuracy and costs associated with each measurement method. After reviewing methods for determining emissions, the National Research Council's National Academy of Science recommended use of process-based mathematical models (2003). Unfortunately, standard mass transfer models and coefficients currently used to predict emissions from dilute aqueous solutions (low concentrations of chemicals in water) are not accurate when used with high concentrations of mixed chemicals in manure (Arogo et al., 1999).

Researchers at the Department of Bioproducts and Biosystems Engineering, University of Minnesota, in cooperation with others at the Department of Agricultural and Biosystems Engineering, Iowa State University, and with funding by the USDA National Research Initiative (NRI), have developed a laboratory method to quantify and compare air pollutant flux from liquid manure using a small wind tunnel (Fig. 1; Schmidt et al., 2007). This method allows for flux measurements (mass of the pollutant per time per surface area) under a variety of microclimate conditions (air temperature, manure temperature, surface wind velocity, etc.). This methodology can be used to develop or validate process-based mathematical models for emission estimation. In addition, the technique can be used to compare and quantify air pollutant flux resulting from different manure handling systems, manure treatment systems (e.g., aeration, anaerobic digestion, and separation), and modifications to diet using manure samples taken from full-scale farms, rather than from laboratory testing of these mitigation technologies.

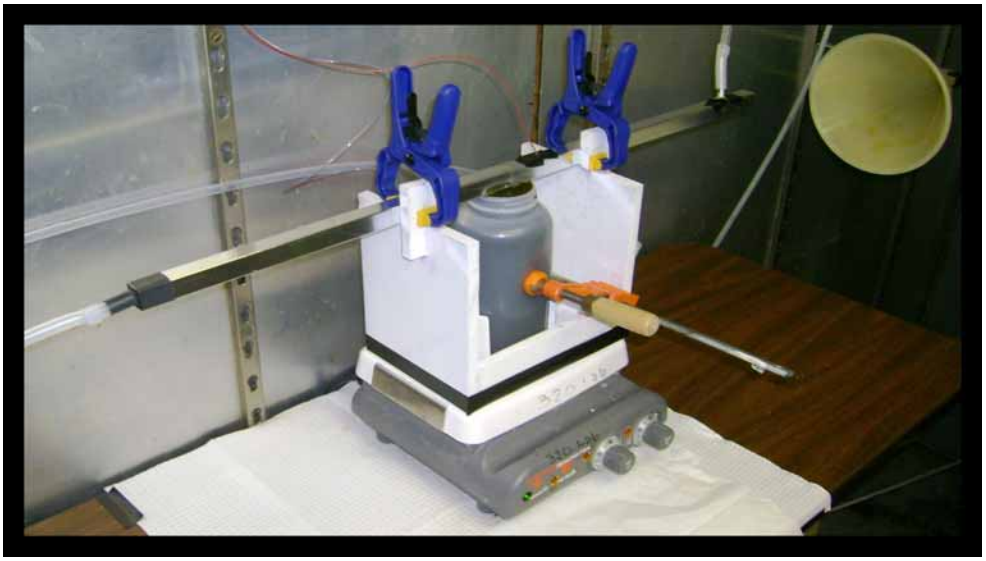

Figure 1. Laboratory equipment for flux determination using the microtunnel techniquie.

Mitigation technology testing has included assorted laboratory and field experiments using a variety of air sampling methods, air constituent measurements, statistical methods, and data analysis techniques. Current standard operating procedures (SOP) used in the long-term emission studies sited above are expensive, labor-intensive, and require several months or even years to obtain results. The estimated cost of a long-term emissions measurement at a single facility is approximately $500,000. Complex SOP are useful in determining absolute emissions from facilities, but these absolute values are not necessary for evaluation of mitigation technologies where the requirement is to document emission reductions. Requiring developers of a mitigation technology to invest the time and money necessary for such an evaluation would limit development of new technologies.

Although using the flux determination method proposed in this study does not provide absolute flux rates, the method offers a fast, inexpensive, accurate way to compare source emissions, evaluate emission reduction from treatment technologies, and determine key parameters for process-based emission models.

IV. Objectives

This project used a new gas and odor flux measurement technique to quantify air emission variability based on production phase, geographic location, and manure storage type, along with reductions from various manure treatment technologies and diet/management changes.

Flux data and relationships to physical and chemical parameters can also be used to modify existing process-based emission models for predicting emission rates of odorous compounds and greenhouse gases for other production units.

V. Procedures

It is recognized that there is variation within a single emitting source (same site has different emissions over time) and variation between similar sites (for instance, variation between two finishing barn sites). This same variability is typical with manure nutrient evaluation and cannot be avoided. However, this project was structured to take data in such a way to capture both of these sources of variability and stay within the budgetary constraints of the grant.

Two sets of manure samples (fall and spring) were collected from distinct manure sources (nursery, finishing, wean-to-finishing, gestation, and farrowing sites). Various manure collection types (slotted flooring, high-volume flush, or pull-plug / gravity-drain); manure storage types (deep-pit, tank, or earthen basin); manure storage stage (single, first, or second); or treatment systems (none, additives, or anaerobic digestion) were used. One set of samples were collected in the fall prior to manure pumpout and a second set collected in late spring but prior to manure pumpout. Manure samples were collected from manure storage systems in Minnesota by producers, extension educators, and/or researchers trained in proper sampling technique.

Manure samples were evaluated for ammonia, hydrogen sulfide, total reduced sulfur, and odor flux using the microtunnel method recently developed by the principle investigators on this project and discussed in the proposal literature review. In this process, a known quantity of clean air is blown across a known surface area (microtunnel system shown in fig. 1). As air passes over the manure the air sample increases in concentrations of gasses that are being emitted from the manure. Knowing the concentration of these gases, area of emitting manure surface, and the flow rate of the air, flux is determined and reported in mass/time/area (micrograms/second/square meter). Note that flux is a measure on a per unit area basis. To estimate total emissions (units of mass per time), the flux rate must be multiplied by the area of the source. Current regulations are typically based on total site emissions.

In addition, the physical and chemical parameters of the manure (e.g., total solids (TS), total volatile solids (TVS), pH, total Kjeldahl nitrogen (TKN), ammonia-N (NH_3-N), total chemical oxygen demand (TCOD), soluble chemical oxygen demand (SCOD) and total sulfide (TS_d)) were measured. Manure analysis to define the physical and chemical manure characteristics were done according to the methods outlined in Table 1.

Statistical comparisons will be made between air pollutant flux, manure sampling site characteristics, and manure properties. Standard statistical procedures to evaluate data used SAS. Correlations between flux and manure characteristics were made. Multiple linear regressions to predict air pollutant flux was attempted.

Table 1. Procedures or methods used in laboratory evaluations.

Test	Equipment or Standard Method
Flux determinations	
Hydrogen sulfide (H_2S)	TEI 45C
Ammonia (NH_3)	TEI 17C
Odor	CEN 13725
Airflow rate	Calibration daily using mini-Buck calibrator meter (Model M-30)
Manure testing	
Total solids (TS) Total volatile solids (TVS) Total Kjeldahl nitrogen (TKN) Ammonia (NH_3) pH Total sulfide Chemical oxygen demand (COD)	Standard Methods for the Examination of Water and Wastewater. 1998. 20th edition. American Public Health Association. Washington, D.C.

VI. Results

Results of the study are summarized in the following set of tables listing the type of facility, mean flux rates of the various pollutants, variation of flux rates, and correlation between flux rates and manure characteristics.

Summary of collected manure samples

The following is a listing of characterizing the swine operation where the manure samples were collected that were used in the data analysis accounting for samples that could not be used or tested for various reasons and/or data that was eliminated using an outlier test procedure. (Each manure sample was classified in each of the six major categories as outlined in Table 2.

Table 2. Category classification of collected manure samples.

Sample number	Category classification of manure sample
	Season
36	Fall, 2008
35	Spring, 2009
	Manure source
12	Gestation
11	Nursery
36	Finish
7	Wean-to-finish
5	Farrowing
	Manure collection type
10	Flushing (high volume)
57	Slats / slotted flooring
4	Pull plug / gravity drain
	Manure storage type
55	Deep pit
1	Aboveground steel tank
15	Earthen basin
	Manure storage stage
60	Single stage
7	First stage
4	Second stage
	Treatment system
50	None
15	Additives
6	Anaerobic digestion

Manure characteristics

For the manure characteristics analysis, the overall means of all samples tested are located in Table 3. A simple analysis-of-variance (ANOVA) was performed using only the main categories of identify the manure sample. No interactions were included because of limited sample number and unbalanced experimental design. Table 4 contains the results of this statistical analysis. Table 5 contains the means of the various manure characteristics sorted by manure categorization for those categories that are significant.

Table 3. Overall means for whole data set of manure characteristics.

	Observations	Mean	Minimum	Maximum
Total solids (percent wet basis)	67	2.73	0.30	7.59
Total volatile solids (percent dry basis)	68	57.7	23.5	77.9
pH	68	7.89	6.72	9.03
Total Kjeldahl nitrogen (mg/L)	68	3680	420	7370
Ammonia-nitrogen (mg/L)	68	2590	87	5670
Total chemical oxygen demand (mg/L)	68	41,100	0	193,000
Soluble chemical oxygen demand (mg/L)	68	14,900	0	39,600
Total sulfide (mg/L)	68	21.7	0	225

Zero concentrations indicate reading below detectable levels.

Table 4. Statistical analysis (*p*-value) of manure characteristics. Those manure classifications that are significant at the *p*-value $\leq$ to 0.05 are bolded.

	Total solids	Total volatile solids	pH	Total Kjeldahl Nitrogen	Ammonia -N	Total COD	Soluble COD	Total sulfide
Season	0.0661	**0.0103**	**<0.0001**	0.355	**0.0144**	**0.0146**	0.189	**<0.0001**
Manure source	**<0.0001**	**<0.0001**	**0.0018**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	0.410
Collection type	**<0.0001**	**<0.0001**	**0.0015**	**<0.0001**	**<0.0001**	**0.0028**	**<0.0001**	0.385
Storage type	**0.0161**	0.287	0.849	**0.0416**	**0.0050**	0.335	0.0927	0.519
Storage stage	0.0728	**0.0005**	**0.0165**	0.1015	**0.0159**	0.0663	0.0714	0.592
Treatment	0.813	0.429	0.635	0.4641	0.954	0.168	0.534	0.954

Table 5. Means of manure characteristics that are significant at *p*-value $\leq$ to 0.05. Blank cells indicate non-significance.

	Total solids percent	Total volatile solids percent	pH	Total Kjeldahl nitrogen mg/L	Ammonia-N mg/L	Total COD mg/L	Soluble COD mg/L	Total sulfide mg/L
Season								
Fall		55.2 (n=35)	8.14 (n=35)		2350 (n=35)	33700 (n=35)		1.32 (n=35)
Spring		60.3 (n=33)	7.62 (n=33)		2850 (n=33)	48800 (n=33)		43.3 (n=33)
Manure source								
Gestation	0.789 (n=12)	47.2 (n=12)	8.17 (n=10)	2150 (n=12)	1310 (n=12)	12100 (n=12)	4890 (n=12)	
Nursey	2.63 (n=11)	63.6 (n=11)	7.67 (n=11)	3600 (n=11)	2260 (n=11)	44500 (n=11)	17000 (n=11)	
Finish	3.62 (n=33)	61.3 (n=34)	7.84 (n=36)	4470 (n=34)	3220 (n=34)	54800 (n=34)	19000 (n=34)	
Wean-to-finish	3.89 (n=6)	65.5 (n=6)	7.86 (n=6)	4800 (n=6)	3820 (n=6)	49400 (n=6)	19700 (n=6)	
Farrowing	0.403 (n=5)	36.0 (n=5)	8.18 (n=5)	913 (n=5)	655 (n=5)	-392 (n=5)	760 (n=5)	
Collection type								
Flush	0.442 (n=9)	33.0 (n=9)	8.27 (n=10)	1200 (n=9)	515 (n=9)	5700 (n=9)	1130 (n=9)	
Slats	3.25 (n=54)	62.0 (n=55)	7.79 (n=55)	4240 (n=55)	3020 (n=55)	48600 (n=55)	17700 (n=55)	
Pull plug	0.905 (n=4)	54.5 (n=4)	8.41 (n=3)	1610 (n=4)	1320 (n=4)	17100 (n=4)	7690 (n=4)	
Storage type								
Deep pit	3.32 (n=52)			4310 (n=53)	3080 (n=53)			
Tank	1.56 (n=1)			2640 (n=1)	2050 (n=1)			
Earthen basin	0.630 (n=14)			1400 (n=14)	797 (n=14)			
Storage Stage								
Single		59.2 (n=57)	7.86 (n=58)		2870 (n=57)			
First		63.0 (n=7)	7.96 (n=6)		1230 (n=7)			
Second		44.7 (n=4)	8.23 (n=4)		1060 (n=4)			

Manure total sulfide showed a large difference from fall to spring; 1.32 mg/L compared to 43.3 mg/L or about a 33-fold increase. One possible explanation could be the increase of sulfur-based drugs or antibiotics (either therapeutic or sub-therapeutic) during the winter period leading into spring compared to summer. Another explanation is that cold temperature during the winter reduces microbial activity, which would reduce the formation of H_2S from various sulfur sources (amino acids, elementary sulfur, sulfates, etc.). Reduced spring pH would increase H_2S losses to the atmosphere, contraire to increased total sulfide in solution. Further investigation is needed to confirm and explain the source of this additional sulfide.

Another interesting trend is that manure associated with sows has a higher pH at about 8.2 compared to manure pH associated with market animals at about 7.8. And that the pH of the collection types of high-volume flushing and pull-plug / gravity-drain are about half a unit higher that slotted flooring with manure going into deep pits below.

Air gas and odor analysis—whole data set

For the air analysis, the overall means of all samples tested are located in Table 6.

Data collected from the micro-tunnel are air concentrations of NH_3, H_2S, TRS, and odor. To determine fluxes from the manure surface, the concentration is multiplied by a constant reflection the airflow rate and contact surface opening. This multiplication factor remained constant or the same; thus only the flux results of statistical analysis and means are reported.

Table 7 contains the results of the statistical analysis of the whole data set, or 72 air analysis collected.

Table 8 contains the means of the various air flux sorted by manure categorization for those categories that are significant.

Table 6. Overall means for whole data set of air gas concentrations and fluxes.

	Observations	Mean	Minimum	Maximum
Ammonia concentration (ppb)	71	7480	444	18,900
Ammonia flux (µg/s/m^2)	71	446	26	1110
Odor dilutions-to-threshold (DT)	70	2750	15	9980
Odor flux (OU/s/m^2)	70	217	1.2	800
Hydrogen sulfide Concentration (ppb)	68	1900	2.5	4440
Hydrogen sulfide flux (µg/s/m^2)	68	226	0.3	544
Total reduced sulfur concentration (ppb)	62	1310	5	8700
Total reduced sulfur flux (ppb/s/m^2)	62	102	0.39	675

Table 7. Statistical analysis (*p*-value) for whole data set for air constituents flux. Those gas fluxes that are significant at the *p*-value $\leq$ to 0.05 are bolded.

	Ammonia	Odor	Hydrogen sulfide	Total reduced sulfur
Season	0.974	0.156	**0.0170**	**<0.0001**
Manure source	**0.0056**	0.565	0.219	0.384
Collection type	**0.0028**	**0.0002**	**0.0103**	**0.0335**
Storage Type	0.110	0.342	0.915	0.956
Storage State	0.506	0.455	0.459	0.998
Treatment	0.123	0.536	0.202	0.708

Odor statistical analysis based on logarithmic transformation
Total reduced sulfur measured by Jerome® meter

Table 8. Means for whole data set of air flux for those parameters that were significant at *p*-value $\leq$ to 0.05. Blank cells indicate non-significance.

	Ammonia $\mu g/s/m^2$	Odor $OU/s/m^2$	Hydrogen sulfide $\mu g/s/m^2$	Total reduced sulfur $ppb/s/m^2$
Season				
Fall			179 (n=34)	206 (n=27)
Spring			274 (n=34)	21.8 (n=35)
Manure source				
Gestation	281 (n=12)			
Nursey	403 (n=11)			
Finish	517 (n=36)			
Wean-to-finish	614 (n=7)			
Farrowing	205 (n=5)			
Collection type				
Flush	157 (n=10)	80.2 (n=10)	111 (n=10)	5.30 (n=9)
Slats	508 (n=57)	235 (n=56)	251 (n=54)	124 (n=49)
Pull plug	299 (n=4)	317 (n=4)	178 (n=4)	49.9 (n=4)

Note that H_2S and TRS fluxes contradict each as one increased in the spring, while the other decreased in spring. The TRS pattern might follow the manure total sulfide concentrations in that reduced fluxes would match increased sulfide concentrations during the spring testing. Or this increase could come from non-hydrogen sulfide gases that the Jerome® meter measures such as mercaptans, methyl sulfides, thiocresol, etc.

In reviewing the manure source data, NH_3 fluxes were about half in the gestation and farrowing facilities compared to NH_3 fluxes from manure collected from nursery, finishing, and wean-to-finishing facilities. Also note that only NH_3 flux was significantly affected by manure source. This is probably the result of being able to accurately measure NH_3 flux with lower variability when compared to H_2S or odor fluxes. This indicates that measuring H_2S and odor needs additional work to accurately measure or that more observations (data) are needed to bring about significant differences.

Air gas and odor analysis—deep-pit finishing barns

The data set was re-organized to only include observations from deep-pit finishing barns, about half of the observed data. Table 9 contains the results of the statistical analysis of this reduced data set. And Table 10 contains the means of the various air flux sorted by manure categorization for those categories that are significant.

With this limited data set, the TRS fluxes observed in the spring were only about 4% of that observed in the fall. And that treatment additives to deep pits reduced odor fluxes by about 30%.

Table 9. Statistical analysis (*p*-value) for only deep-pit finishing barns air flux (n=33). Those gas fluxes that are significant at the *p*-value $\leq$ to 0.05 are bolded.

	Ammonia	Odor	Hydrogen sulfide	Total reduced sulfur
Season	0.757	0.664	0.0572	**<0.0001**
Manure source	0.863	0.305	0.345	0.322
Treatment	0.879	**0.0399**	0.168	0.691

Odor statistical analysis based on logarithmic transformation
Total reduced sulfur measured by Jerome® meter

Table 10. Means of air flux for only deep-pit finishing barns for those parameters that were significant at *p*-value ≤ to 0.05. Blank cells indicate non-significance.

	Odor OU/s/m^2	Total reduced sulfur ppb/s/m^2
Season		
Fall		316 (n=11)
Spring		13.3 (n=18)
Treatment		
None	280 (n=25)	
Additive	187 (n=8)	

Pearson Correlation Coefficients

A correlation matrix was performed comparing the four air flux properties with eight manure characteristics (table 11). The most positive correlation is between manure ammonia-N concentration and ammonia flux at 0.65. This really indicates that not one manure characteristics can predict fluxes, but possibly multiple manure characteristics or characteristics or constituents that have not been measured.

Table 11. Pearson correlation coefficients of gas fluxes from manure surface and manure characteristics.

	Ammonia	Hydrogen sulfide	Total reduced sulfur	Odor
Total solids	0.448	0.0966	-0.0315	0.149
Total volatile solids	0.374	0.125	0.0181	0.381
pH	0.110	-0.154	0.298	-0.228
Total Kjeldahl nitrogen	0.539	0.218	0.0648	0.279
Ammonia-N	0.647	0.321	0.0619	0.352
Total COD	0.254	0.0124	-0.200	0.107
Soluble COD	0.56	0.174	-0.0686	0.255
Total sulfide	0.00697	0.0546	-0.233	0.059

Predictive Models

An attempt was made to develop predictive models of gas fluxes based on characteristics of the manure. The best and simplest model was for predicting ammonia flux:

$$NH_3F = -1830 + 240\ pH + 0.150\ NH_3\text{-}N$$
$$r^2 = 0.522$$

Where:

NH_3F = Ammonia flux ($\mu g/s/m^2$) from manure surface
pH = pH of the manure
NH_3-N = total ammonia-N concentration in manure (mg/L)

Better fitting models can be found for ammonia flux and the other gases (hydrogen sulfide, total reduced sulfur, and odor), but they are more complicated with lower coefficients of determination.

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