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AMMONIA AND HYDROGEN SULFIDE FLUX FROM BEEF CATTLE PENS: IMPLICATIONS FOR AIR QUALITY MEASUREMENT METHODOLOGIES AND EVALUATION OF EMISSION CONTROLS

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ABSTRACT

Ammonia (NH₃) and hydrogen sulfide (H₂S) are emitted from beef cattle feedlots with NH₃ being greater by nearly three orders of magnitude. Nearly 30% of the U.S. beef cattle are fed in the High Plains of Texas. Earlier research indicates that abatement technologies may be needed to significantly reduce NH₃ emissions. To date, little is known about the appropriate measurement methods to evaluate the effectiveness of NH₃ emission controls. In this research, we determined the (a) variability of NH₃ and H₂S fluxes within a single pen and (b) the relationships between NH₃ and H₂S fluxes and manure characteristics as a part of a larger field study to determine the effectiveness of the urease inhibitor NBPT. A dynamic, flow-through chamber system was used to estimate NH₃ flux from experimental beef cattle pen with a 15.6 m²/head stocking density. The total of 27 measurements were completed within one day using a flux chamber interfaced with an on-site, mobile-instrument shelter. Manure samples from each location were analyzed for moisture content, total kjeldahl nitrogen (TKN), NH₄-N, NO₃-N, and C:N to characterize their relations with NH₃-N and H₂S-S flux. The NH₃-N flux varied by nearly 30 fold between 512 to 14,993 µg/m²-min. The H₂S-S flux varied from 0.52 to 8.07 µg/m²-min. In addition, flux from fresh urine and feces were also measured for nearly one day. The cumulative NH₃-N emissions from fresh feces were 2.5 to 13.7% of NH₃-N from urine. The apparent variation of flux within a typical pen has important implications on the selection of appropriate measurement methods for statistically significant evaluation of emission controls.

KEYWORDS. Ammonia, hydrogen sulfide, beef cattle, air quality, manure

INTRODUCTION

More than 40% of the U.S. beef cattle are fed and processed in the High Plains of Texas, New Mexico, Oklahoma, Kansas, and Colorado. To date, little is known about the extent of ammonia (NH₃) and hydrogen sulfide (H₂S) emissions from cattle feedyards in Texas. Earlier reports suggest that NH₃ is likely emitted in much larger quantities that may require reporting of releases (Baek et al., 2003; Koziel et al., 2004). Thus, research is needed on feasible abatement methods for NH₃ emissions. To date, no standard method is available to evaluate the effectiveness of NH₃ abatement at cattle feedlots. Since a considerable amount of research was completed on measuring NH₃ and H₂S emissions from cattle pens using a flux chamber (Baek et al. 2004, Koziel et al. 2004a, Koziel et al. 2004b), this apparatus was selected for use in evaluating treatment of various loads of NBPT, a urease inhibitor. During these experiments, high variability in NBPT's effectiveness was observed. These variations made treatment comparisons challenging due to the low statistical significance of the data. Thus, we set out to explore the

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reasons behind some of these variations. This manuscript is a summary of the lessons learned. The conclusions made will improve the measurement protocol for future experiments.

METHODOLOGY

Cattle Pen

This study was conducted at the West Texas A&M University's Research Feedlot in Canyon. All measurements were conducted inside one cattle pen located between 5 and 10 identical-size pens to the left and to the right, respectively. The pen was approximately 26 by 6 m, sloping 4% from the concrete feed bunk and apron to the cattle alley. The pen was stocked with 10 steers having an average weight of 485 kg 4 weeks prior to the experiment. The experiment was conducted on May 13, 2004 between 1 and 5 PM. The cloud cover was approximately 75%. High northerly winds were associated with high relative humidity.

Flux Chamber

A dynamic flow-through chamber was used to enclose a small fraction of the cattle pen surface, flush it with pure air, measure concentrations of NH_3 and H_2S and then estimate NH_3 and H_2S flux from the pen surface (figure 1). A similar set up was used to measure NH_3 , H_2S , VOCs and odor flux from commercial cattle feedlots (Baek et al., 2004; Koziel et al., 2004a; Koziel et al., 2004b). The chamber was an exact copy of the dynamic flow-through chamber used by Aneja and co-workers (Aneja et al, 2000; Aneja et al., 2001a; and Aneja et al. 2001b). The chamber was built from the Lexan translucent tube, 26.5 cm inside diameter and 47.2 cm high, and lined with 0.5 mm thick fluorinated ethylene propylene (FEP) foil (figure 1). Compressed zero-grade air was directed into the chamber at 24 L/min via a 6 mm PTFE tubing. Flowrate was controlled by a series of mass flow controllers (Aalborg, Orangeburg, NY). Zero air was mixed inside the chamber with the NH_3 , H_2S , and other gases emitted from the surface. A stirring paddle operating at 50 rpm provided additional mixing. The majority of the flow was exhausted. Only a small fraction of the total exhaust flow, approximately 1 L/min, was directed to the continuous NH_3 and H_2S analyzers.

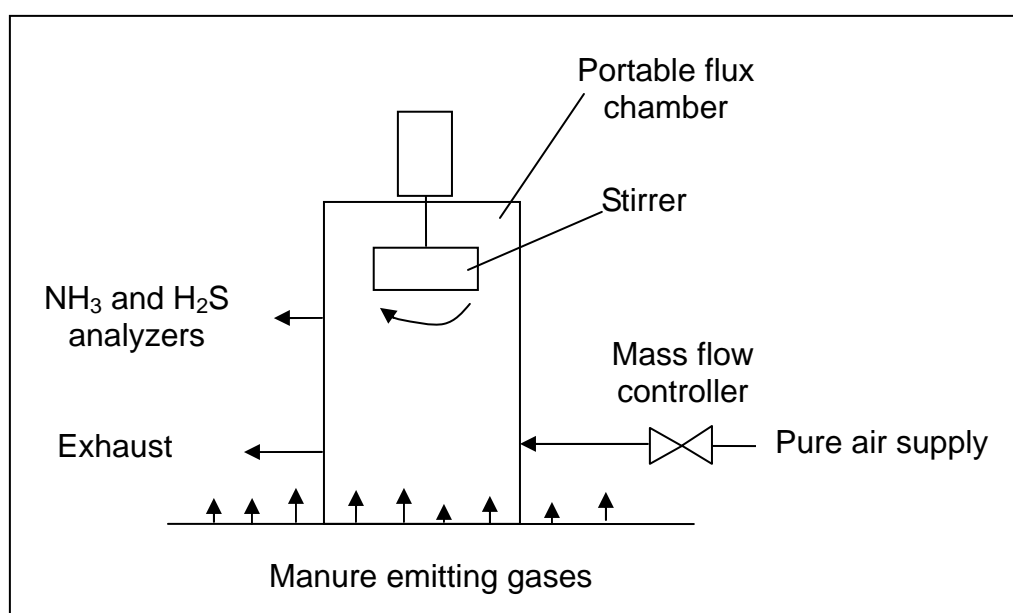


Figure 1. Schematic of a portable dynamic flow-through chamber used for measurements of ammonia and hydrogen sulfide flux.

Measurement of Ammonia and Hydrogen Sulfide Concentrations

Concentrations of NH_3 and H_2S were measured with continuous analyzers located inside a temperature-controlled instrument shelter. The TEI 17C chemiluminescence NH_3 analyzer

(Franklin, MA) with 0.5% precision of full scale and 120 sec of the 0 to 90% response time with 10 sec averaging was used to measure NH_3 concentrations inside the chamber. An NH_3 analyzer is a combination of NH_3 converter and an $\text{NO-NO}_2\text{-NO}_x$ analyzer. The analyzer was calibrated using UHP-grade air, certified standard span NH_3 gas in air (50 ppmv and 10 ppmv) and NO in nitrogen (50 ppmv) (Matheson TriGas, Montgomeryville, PA). Hydrogen sulfide concentrations inside the chamber were measured continuously by a TEI 45C $\text{SO}_2/\text{H}_2\text{S}$ analyzer (Thermo Environmental Instruments, Franklin, MA) equipped with a pulsed fluorescence SO_2 detector and a high intensity xenon lamp. Instrument precision is 1% of reading or 1 ppbv and its linearity is $\pm 1\%$ of full scale. The analyzer was calibrated daily using UHP-grade air, certified standard H_2S gas in nitrogen (2 ppmv) and SO_2 in nitrogen (1 ppmv) (AirGas Southwest, Amarillo, TX).

The instrument shelter was a modified 1.5 m \times 2.1 m box trailer with a 3.95 kW-h airconditioning unit. A Field Point (National Instruments, Austin, TX) data acquisition system was used to collect all measurements. A Labview-based program was written to monitor and download all measured data. Data were downloaded daily.

Selections of Sampling Location and Sampling Time

The entire pen was divided into a grid of 27 equal squares (3 m \times 3 m) grouped in 9 rows (1 through 9) and 3 columns (A through C) (figure 2).

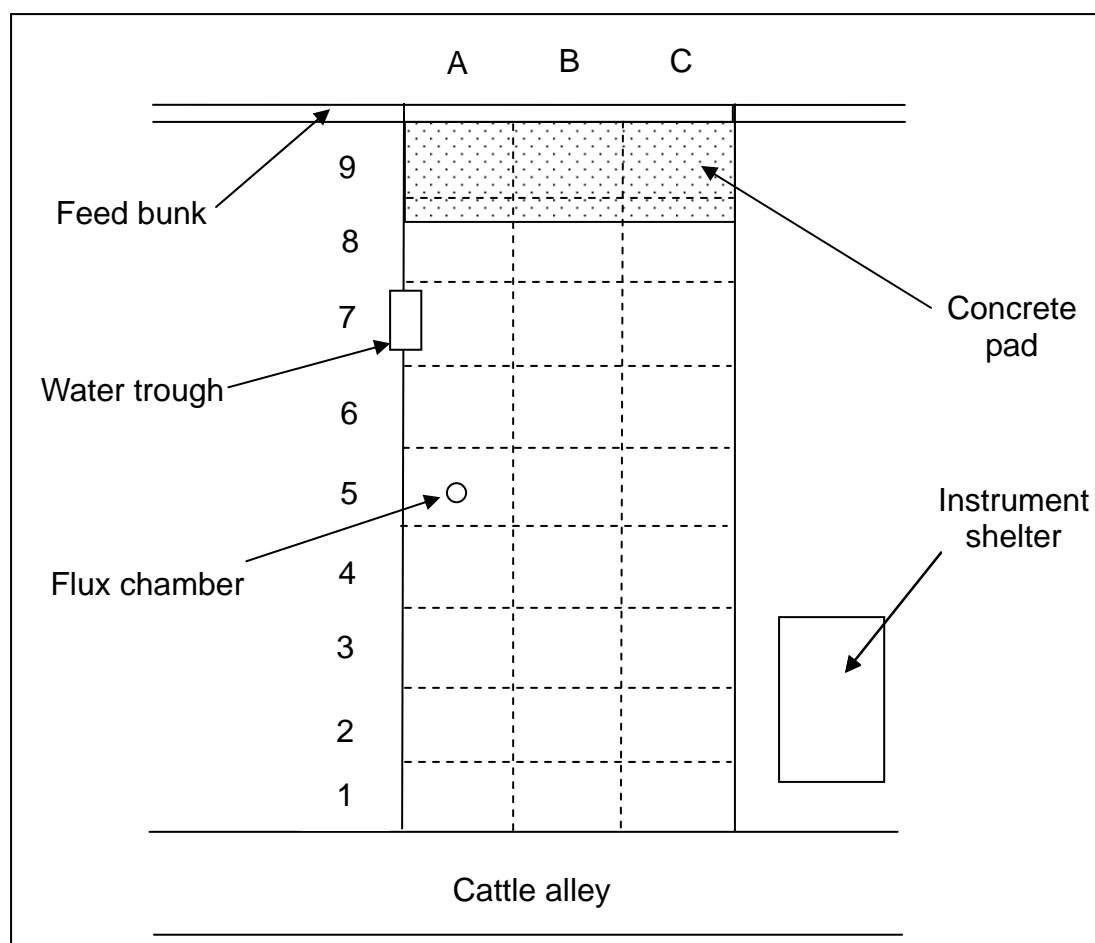


Figure 2. Schematic of beef cattle pen. Numbering of the sampling grid is consistent with results summarized in Table 1.

This grid provided means of assessing flux variations within one pen. The top row (row 9) and the fraction of row 8 had the concrete surface (apron) extending from the feed bunk. The use of concrete apron is typical in commercial feedlots. Water trough was present in square 7A. The rest of the pen surface was covered with relatively thin layer of compacted manure and dry loose manure. Fresh manure and urine spots were spread randomly over the entire pen surface. The pen surface was generally dry.

Sampling location of the chamber was at the center of each square on the grid. Sampling started in square 1A, followed by 1 B and eventually ended at 9C. The sampling time for each grid was 10 min. The selection of sampling time was based from previous measurement protocol (Baek et al., 2004; Koziel et al., 2004a; Koziel et al., 2004b). This sampling time allowed for the equilibration of measured concentrations inside the chamber after placement on a new location and provided enough time for the analyzers to respond. Because of this, only the last 3 min of concentration measurement was used for averaging and estimation of the flux.

Estimation of Ammonia and Hydrogen Sulfide Fluxes

Flux of NH₃ and H₂S from cattle pen was estimated using the following equation (Baek et al., 2004; Koziel et al., 2004a; Koziel et al., 2004b):

$$J = \left(\frac{LA'}{V} + \frac{q}{V} \right) [C] \left(\frac{V}{A} \right) \quad (1)$$

where:

- C = NH₃ / H₂S concentration in the chamber (mass/volume),
- q = air flowrate through the chamber (volume/time),
- V = volume of the chamber (volume),
- J = emission flux per unit area (mass/area/time),
- A = surface area covered by the chamber (area),
- L = loss term by chamber wall per unit area (length/time), and
- A' = surface area of the chamber walls (area).

The loss term (L) in Equation 1, the sum of the losses of NH₃ or H₂S through reactions with the chamber walls and chemical reactions with existing oxidants in the carrier gas, was estimated using the method developed by Kaplan et al. (1988). In this study, the experimental mean loss in the chamber was assumed to be equal to 0.000022 m/sec based on earlier experiments.

Manure Pack Sampling and Analyses

Manure pack samples were collected immediately after the 10 min sampling period at each location. A single sample was collected consisting of three, randomly selected scoops of loose manure from the area that was covered by the flux chamber. Each composite sample was then transferred to a small polyethylene bag, sealed and refrigerated until analysis. Manure temperature was measured with a thermocouple buried 25 mm in manure near the on-side shelter (Figure 2).

All manure samples were analyzed by Servi-Tech Laboratories, Dodge City, KS, using standard methods for determination of manure pH, moisture content, total Kjeldahl nitrogen (TKN), nitrate nitrogen, ammonia nitrogen, C/N ratio, and ash content.

Measurements of NH₃ flux and emissions from fresh urine and feces

Additional experiments were conducted to compare NH₃ and H₂S emissions from fresh urine and feces. This was done to elucidate information on (a) the relative importance of urine and feces in NH₃ and H₂S emissions and (b) the variation of NH₃ and H₂S flux over extended period of time. This was accomplished by placing the flux chamber (figure 1) on a (1) fresh urine and (2) fresh feces deposited on the pen surface, and then measuring NH₃ and H₂S concentrations between 17.5 to 20.4 hrs. Immediately before the start of experiment, all steers were kept in the pen corner until one of them (1) urinated or (2) defecated. Then, the chamber was placed over the fresh spot within 1 min, and the measurement begun. The whole corner area was fenced off to protect the chamber for the duration of the experiment. The estimation of flux followed the methodology described above. Emissions were calculated based on flux.

RESULTS

Manure Characteristics and Measured NH₃ and H₂S Flux

Average values of the TKN, organic-N, ammonium-N, nitrite-N, moisture content, solid contents, organic matter content, ash content, manure pack temperature, and NH₃ and H₂S flux for each sampling location are summarized in Table 1. Average, minimum, and maximum values of TKN were slightly lower than those reported at a commercial feedlot (Baek et al., 2003; Koziel et al., 2004a). The possible explanation could be that the experimental pen was scraped before the study and was only occupied for about 4 weeks prior to the experiment. Also, the manure pack is typically older and the stocking density is higher at commercial feedlots.

Moisture content was much variable ranging from 3.8 to as high as 72.8%. Some of the locations characterized by high moisture content were annotated as those with the interferences from fresh urine, feces or water. Other measured variables and manure characteristics did not have much variability with the exception of NH₃ and H₂S flux. Manure temperature was considerably higher than the ambient air temperature. All variables were correlated with the estimates of flux. The best correlations were presented between NH₃-N flux and NH₄-N (figure 3). The presented correlation is generally consistent with the assumption that the high ammonium content results in higher potential for NH₃ emissions.

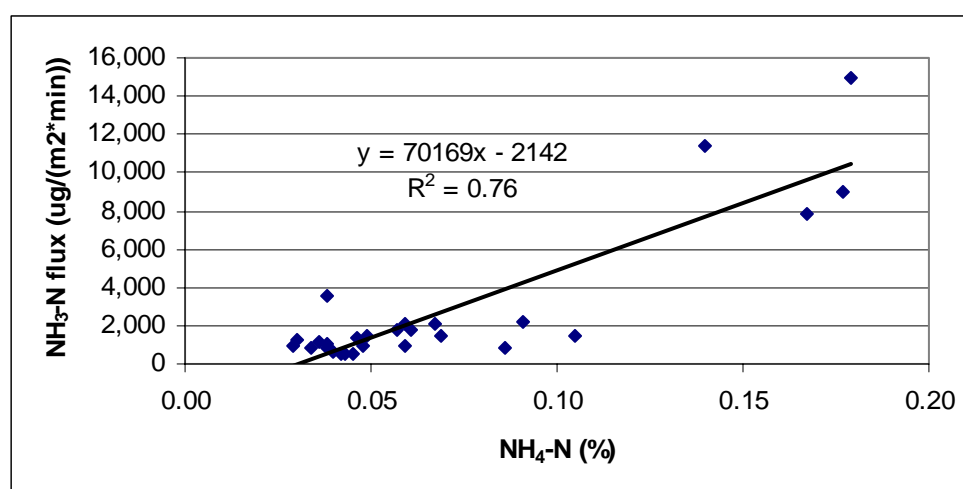


Figure 3. Correlation between NH₃-N flux and NH₄-N content in manure.

Table 1. Summary of manure characteristics and measured ammonia and hydrogen sulfide flux.

Grid	TKN	Org-N	NH ₄ -N	NO ₃ -N	M.C.	Solids	O.M.	Ash	C:N	T _{manure}	H ₂ S-S flux	NH ₃ -N flux	Notes
#	%	%	%	mg/kg	%	%	%	%	-	°C	ug/m ² /min	ug/m ² /min	
1A	1.37	1.32	0.049	2.4	6.6	93.4	36.8	56.7	14.9	26.4	1.16	1,445	
1B	1.42	1.38	0.036	2.2	5.3	94.7	33.6	61.1	13.1	27.0	1.33	1,170	
1C	1.39	1.33	0.057	1.7	6.1	93.9	34.6	59.2	13.8	26.1	1.13	1,820	
2A	1.56	1.51	0.046	2.2	5.2	94.8	41.0	53.8	14.6	25.7	0.78	1,381	
2B	1.29	1.25	0.042	1.5	5.3	94.7	34.9	59.8	15.0	26.4	0.52	536	
2C	1.48	1.44	0.043	1.4	5.0	95.0	39.8	55.3	14.9	26.0	0.75	570	
3A	1.25	1.08	0.167	2.3	31.3	68.7	31.0	37.8	13.8	24.6	1.89	7,870	wet from feces
3B	1.18	1.14	0.038	1.3	4.3	95.7	34.6	61.1	16.3	26.2	0.78	1,093	
3C	1.42	1.37	0.048	1.6	4.1	95.9	36.6	59.3	14.3	25.3	0.83	921	
4A	1.61	1.52	0.091	2.4	6.6	93.4	38.3	55.1	13.2	24.8	1.33	2,165	
4B	1.09	1.06	0.034	1.9	3.8	96.2	33.6	62.6	17.1	24.8	0.75	887	
4C	1.23	1.19	0.038	1.2	3.9	96.1	31.6	64.6	14.3	26.0	0.75	800	
5A	1.24	1.18	0.061	2.2	7.0	93.0	39.9	53.1	17.9	26.1	1.59	1,767	
5B	1.09	1.06	0.029	2.9	63.8	36.2	13.8	22.4	7.0	24.1	0.75	916	
5C	1.38	1.34	0.045	1.8	12.6	87.4	34.5	52.9	13.9	22.8	1.31	512	wet from feces
6A	1.23	1.09	0.140	1.9	10.4	89.6	39.5	50.1	17.8	24.7	2.44	11,404	wet from urine
6B	1.34	1.31	0.030	1.2	5.6	94.4	34.1	60.3	14.1	28.4	1.10	1,270	
6C	1.23	1.17	0.059	2.0	5.2	94.8	25.9	69.0	11.7	26.8	1.29	2,135	
7A	1.37	1.19	0.179	1.6	14.3	85.7	32.2	53.5	13.1	27.5	8.07	14,993	wet from urine
7B	1.43	1.39	0.038	2.7	3.9	96.1	40.6	55.5	15.8	27.1	1.20	3,545	
7C	1.48	1.41	0.067	1.5	4.7	95.3	38.9	56.3	14.6	25.4	1.38	2,118	
8A	0.58	0.54	0.040	0.6	72.8	27.2	14.8	12.4	14.3	24.6	0.97	653	wet from water trough

8B	1.47	1.41	0.059	2.1	4.8	95.2	40.8	54.4	15.4	24.3	1.27	894
8C	1.64	1.57	0.069	2.1	6.0	94.0	42.2	51.8	14.3	24.7	0.75	1,514
9A	1.79	1.61	0.177	3.0	7.5	92.5	43.6	48.9	13.5	24.6	1.70	8,944
9B	1.63	1.53	0.105	3.1	6.5	93.5	40.1	53.4	13.7	26.6	0.82	1,420
9C	1.64	1.55	0.086	2.4	4.9	95.1	46.9	48.3	15.9	25.9	0.75	857
Avg	1.36	1.29	0.07	1.97	11.8	88.2	35.3	52.9	14.4	25.7	1.39	2,726
Std	0.23	0.22	0.04	0.59	16.9	16.9	7.4	11.7	2.0	1.2	1.38	3,587
Min	0.58	0.54	0.03	0.60	3.8	27.2	13.8	12.4	7.0	22.8	0.52	512
Max	1.79	1.61	0.18	3.10	72.8	96.2	46.9	69.0	17.9	28.4	8.07	14,993

Note: Grid = sample location consistent with Figure 2; Org-N = organic N, NH₄-N = ammonium-N; NO₃-N = nitrite-N; M.C. = moisture content; O.M. = organic matter; C:N = carbon-to-nitrogen ratio; Avg = mean; std = standard deviation around the mean; Min = minimum; Max = maximum.

Correlation between the manure moisture content and measured NH₃ flux was weak ($R^2 = 0.0007$). When four data points (8A as wet from water trough, 3A and 5C as wet from feces, and 5B as an “outlier”) were removed, however, the whole correlation improved. The new correlation is shown on figure 4.

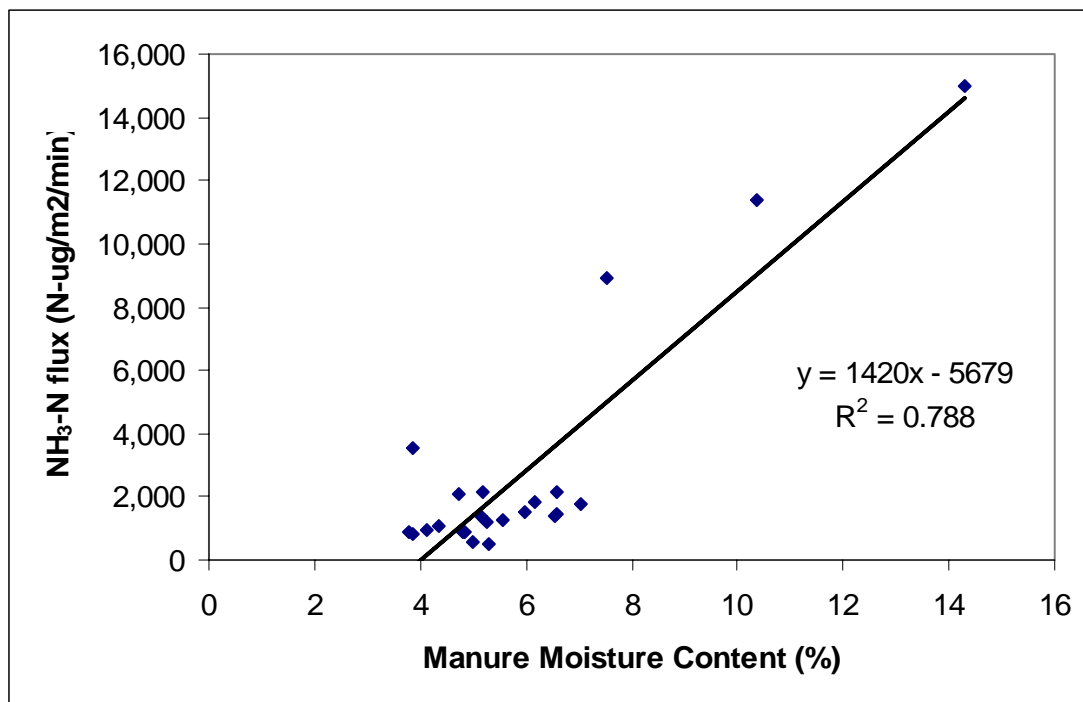


Figure 4. Correlation between NH₃-N flux and the moisture content in manure pack.

Correlation between NH₃-N and H₂S-S flux is presented in figure 5. Measured NH₃ flux was generally 3 orders of magnitude higher than the H₂S flux, *i.e.*, the average measured flux was 2,726 NH₃-N ug/m²-min and 1.39 H₂S-S ug/m²-min, respectively. These averages were consistent with the typical Spring/Summer season fluxes measured at a commercial feedlot (Koziel et al., 2004a). Ammonia and H₂S fluxes were highly variable. Ammonia flux varied from 512 to 14,993 NH₃-N ug/m²-min, a nearly 30-fold difference. Hydrogen sulfide flux varied from 0.52 to 8.07 H₂S-S ug/m²-min, a nearly 16-fold difference. This is an important observation suggesting that a larger pen area should be considered when emission abatement treatments are compared. Relatively small, enclosed area under the flux chamber may preclude detection of statistically significant differences between control and treatment pens. This conclusion is consistent with our experimental observations. No statistically significant differences could be measured between the flux on treated (with NBPT urease inhibitor) and non-treated pens for a multi-week study conducted at the same feedlot.

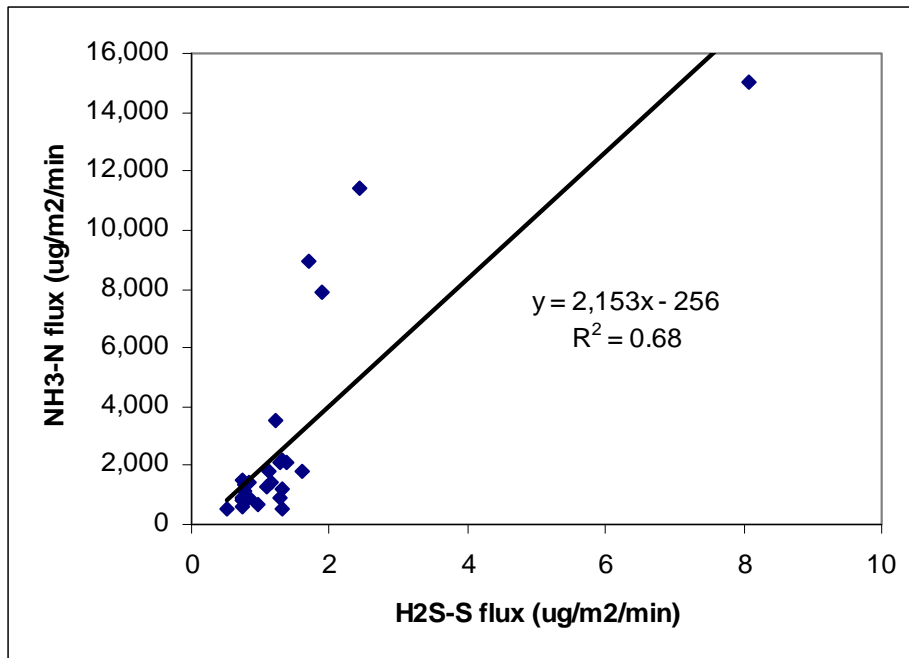


Figure 5. Correlation between NH₃-N and H₂S-S flux from cattle pen.

NH₃-N Flux and Emissions from Fresh Urine and Feces

The estimates of NH₃-N flux based on long-term measurement from two fresh urine spots and one fresh feces spot are presented in figure 6. Trends of fluxes were consistent with those reported earlier (Baek et al., 2003; Koziel et al., 2004a). Maximum flux was always measured in the afternoon hours (16 CST) while the minimum flux was observed in early morning. The time of day plays an important role in controlling flux due to manure surface temperature changes.

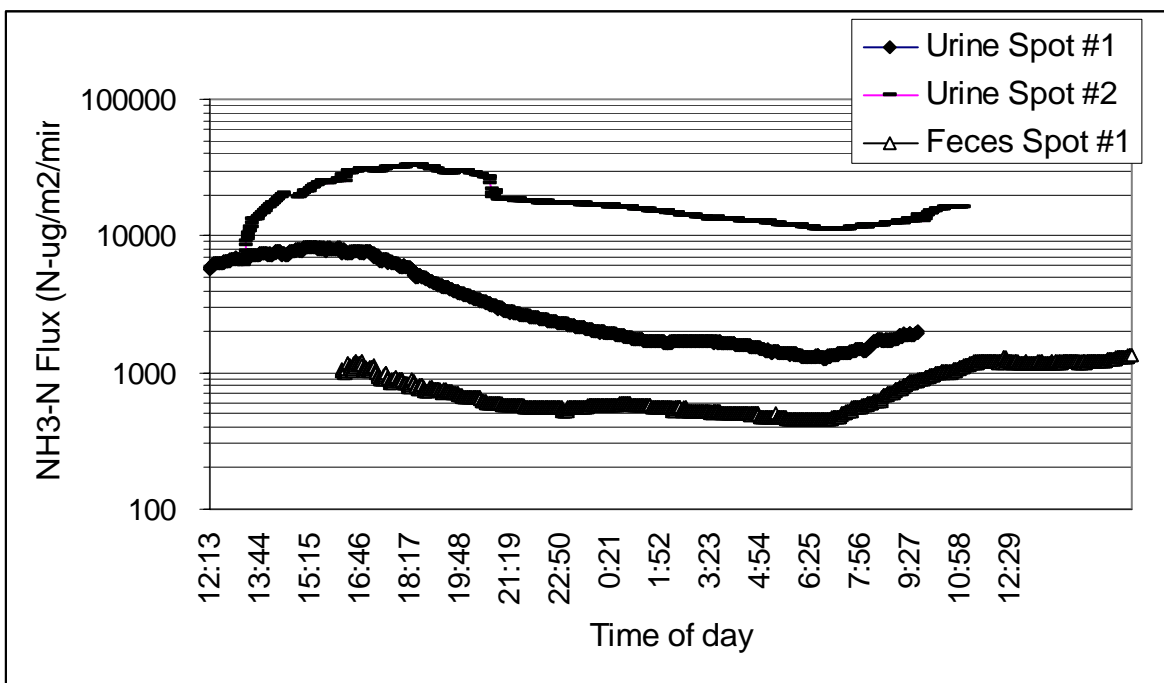


Figure 6. NH₃-N flux from fresh urine and feces.

The absolute maximum for NH₃ flux occurred in the first few hours after urination for both cases (spot #1 and spot #2). The difference between absolute maximums for Spot #1 and Spot #2 was nearly 4-fold, *i.e.*, 8,355 and 32,300 NH₃-N ug/m²-min. There was no distinguished maximum for the feces spot, *i.e.*, 1,206 NH₃-N ug/m²-min in Day 1 and 1,354 NH₃-N ug/m²-min for Day 2. The cumulative NH₃-N emissions were much higher for urine spots (1,515 kg and 0.277 kg, for

Spot #2 and Spot #1, respectively) than emissions from feces (0.0381 kg). Ammonia emissions from feces were 2.5% and 13.7% of those from urine. Ammonia emissions from urine Spot #2 appear to be very high. The preliminary assessment of this data may be conflicting with how much N a typical urination releases. The reason for this is not known. While urine contains considerable fraction of N, it may likely be in insufficient quantities to cause such high emissions. Possible explanation could be that the moisture in urine causes activation of the dry manure pack (evaporation effects from manure pack corresponding to surface temperature) and release of additional NH₃ from the manure pack. This hypothesis needs further exploration.

CONCLUSION

Several conclusions stem from these experiments:

1. Ammonia and H₂S flux from one pen significantly varied. The difference between maximum and minimum flux measured was approximately 30 and 16 for NH₃ and H₂S fluxes, respectively.
2. Flux chambers with small footprints may not be appropriate to evaluate the effectiveness of emission abatement approaches for large treatment areas.
3. The major fraction of NH₃ is caused by urine. Feces are responsible for only a small fraction of total NH₃ emissions.

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