Estimations of Ammonia and Hydrogen Sulfide Fluxes from Cattle Feedlot Surfaces in Texas High Plains

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ESTIMATIONS OF AMMONIA AND HYDROGEN SULFIDE FLUXES FROM CATTLE FEEDLOT SURFACES IN TEXAS HIGH PLAINS

B.-H. Baek, J. A. Koziel, J. D. Spinhirne, D. B. Parker, and N. A. Cole

ABSTRACT

A dynamic flow-through chamber system and continuous analyzers were used for on-site measurements of ammonia-nitrogen (NH$_3$-N) and hydrogen sulfide-sulfur (H$_2$S-S) fluxes from commercial feedlot surfaces in northwestern Texas during two week period in the summer of 2002. Ambient air and air inside chamber temperatures, and manure pack temperature were measured continuously. Manure pack moisture content, pH, and TKN were measured daily to characterize its correlation with NH$_3$-N fluxes. The preliminary average NH$_3$-N flux from the feedlot surface for the entire measurement period was 1,669 ± 1,212 NH$_3$-N µg/m$^2$/min (or 1,494 ± 1,083 NH$_3$-N µg/m$^2$/min without accounting for the losses due to adsorption to chamber walls). Preliminary mean H$_2$S-S flux was estimated at approximately at 1.884 ± 1.497 H$_2$S-S µg S/m$^2$/min (1.683 ± 1.334 H$_2$S-S µg S/m$^2$/min excluding the loss due to adsorption). Manure pack temperature was found to have a weak ($R^2$ = 0.492) logarithmic relationship with NH$_3$-N flux (Log$_{10}$ NH$_3$-N flux (µg N/m$^2$/min) = 0.1308 × T$_{soil}$(°C) + 28.198). The TKN showed a weak ($R^2$ = 0.472) positive linear correlation with NH$_3$-N flux.

KEYWORDS. Ammonia, Air quality, Hydrogen sulfide, Dynamic flow through surface chamber, Flux, Continuous emissions monitoring, Area source, Open dirt cattle feedlots, Manure.

INTRODUCTION

Domestic animals are known to be a major source of global tropospheric ammonia. For the U.S. only, it was roughly estimated that the ammonia contributions from cattle account for approximately 44% of the NH$_3$-N budget in 1994 (Battye et al., 1994). 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 NH$_3$ and H$_2$S emissions from cattle feedyards in the High Plains. In this research, a dynamic flow-through chamber system was used to estimate NH$_3$-N and H$_2$S-S fluxes from commercial cattle pen surfaces. Ammonia and H$_2$S concentrations inside the chamber, air and manure pack temperature inside the chamber, and ambient air temperature were measured continuously. The air flow rate and air relative humidity were measured twice daily. Triplicate samples of manure pack were collected 2 times a day to determine the moisture content, TKN, and pH. The objectives of this research were to (1) design field measurements for NH$_3$ and H$_2$S fluxes from commercial cattle pen surfaces using dynamic flow-through chamber, (2) determine typical ranges of NH$_3$-N and H$_2$S-S fluxes from cattle pen surfaces, (3) compare these data with NH$_3$-N fluxes from other sources and species that were determined using the identical dynamic flow-through chamber, and (4) determine the effects of manure pack characteristics, and manure pack temperatures on emissions of gaseous NH$_3$ and H$_2$S emissions from cattle pens.
**METHODOLOGY**

**Sampling Site**

Ammonia-N and H2S-S flux measurements were completed at a 55,000 head, open dirt cattle feedyard located in the northwestern Texas from August 16th to 30th, 2002. One 30.5 m × 53.3 m (100 ft × 175 ft) pen on the western edge of the feedyard was selected for this study. The selection of the pen was driven by (1) the necessity to have unobstructed access to one side of pen at which the instrument shelter could be parked, and (2) access to electric power. The pen housed 112 and 116 steers on the first and the last day of the experiment, respectively. The average weight was 145 kg (320 lb) and 160 kg (353 lb) on the first and last day, respectively. This pen could be considered as representative of the dimensions, surface area, surface type, animal feed, and the stocking density to the other pens in this feedyard. The feedyard was similar to other commercial yards in this part of Texas.

All of the pen surface sampling locations were located along the western fence of the pen (Figure 1). Two 3 m (10 ft) portable fence sections were installed to protect the dynamic flow-through chamber which was always placed in the geometric middle of the 3 m × 3 m × 3 m (10 ft ×10 ft ×10 ft) triangle formed by the portable fence sections and the fence of the pen (Figure 1). The chamber was moved daily (typically between 9 A.M. and 11 A.M.) to a new location that was not fenced before with the exception of the first three days and the last three days of the experiment. This was done to assure that measurements were completed on surface similar to the rest of pen. As a result, each new location roughly represented the pen for manure loads, and the weather effects, and also increased the diversity of sampling locations. First three days and last three days were dedicated to measurements from one spot to analyze the surface “aging” process without moving the dynamic chamber (Day 1 to Day 3) or with moving the chamber within one fenced area without the fresh urine and feces loads (Days 12 to Day 14). During the last three days (Day 12 – Day 14), the chamber was placed at three different locations within one fenced area to determine the aging process of feedlot surfaces without new manure loads.

![Figure 1. Schematic of the sampling site at a commercial cattle feedyard for the continuous measurements of NH3 and H2S flux using a dynamic flow-through chamber system.](image)

Manure pack samples were collected twice for each measurement day. Manure pack moisture content, pH, and Total Kjeldahl Nitrogen (TKN = organic N + NH$_3$-N+NH$_4$+-N) were analyzed at the USDA Agricultural Resource Service laboratory, at Bushland, Texas.

**Dynamic Flow-Through Chamber**

A dynamic flow-through chamber was built from the Lexan translucent tube, 26.5 cm inside diameter × 47.2 cm high, and lined with 0.5 cm thick fluorinated ethylene propylene (FEP) foil...
This chamber was an exact copy of the chamber used by Aneja and co-workers (Aneja et al., 2000, 2001a, 2001b; and Roelle, 2002). The chamber fitted inside a stainless steel collar which was driven into the manure pack to a depth of 3 to 5 cm, forming a seal with the manure pack surface and the air inside the chamber. The chamber was placed at a new location every morning with the exception of Day 1 to Day 3. Compressed zero-grade was generated by a Thermo Environment Instrument (TEI) Model 111 (Franklin, MA) generator in the instrument shelter and was directed into the chamber at 6.5 L/min using 6 mm (1/4 in) O.D. PTFE tubing. Flow rate was controlled by 10 L/min rotameter (Gilmont, Barrington, IL). Influent air mixed with NH₃, H₂S and other gases emitted from the manure pack surface. The PTFE impeller was used for mixing of air inside the chamber at constant speed at approximately 50 rpm. The chamber maintained a positive pressure throughout the experiment because the influent flow rate of zero-grade air was much higher than the effluent flow rate to the NH₃ and H₂S analyzers.

Each analyzer inside the instrument shelter drew 0.5 L/min of sampled air from the chamber via separate 6 mm (1/4 in) O.D. and 4 mm (5/32 inch) I.D. PTFE tubing. The remaining 5.5 L/min exhausted via an exhaust port. An experiment was also conducted to estimate the extent of ammonia loss due to adsorption to walls of chamber and tubing using the procedure proposed by Kaplan et al., (1988). This experiment also determined that the chamber reached steady state conditions in approximately 30 minutes after the placement on the surface.

Measurement of Ammonia and Hydrogen Sulfide Concentrations.
Ammonia concentrations inside the chamber were measured using a TEI 17C chemiluminescence NH₃ analyzer (Franklin, MA) with 0.5 % precision of full scale and 120 sec of the 0 to 90% response time with 10 sec averaging. The analyzer was calibrated daily using UHP-grade air, certified standard span NH₃ gas in air (50 ppmv) and NO in nitrogen (50 ppmv) (AirGas Southwest, Amarillo, TX).

Hydrogen sulfide concentrations inside the chamber were measured continuously by a TEI 45C SO₂/H₂S analyzer (Franklin, MA) equipped with a pulsed fluorescence SO₂ detector and a high intensity xenon lamp. Instrument precision was 1% of reading or 1 ppbv and its linearity is ±1% of full scale. The analyzer was calibrated daily using UHP-grade air, certified standard H₂S gas in N₂ (2 ppmv) and SO₂ in N₂ (1 ppmv) (AirGas Southwest, Amarillo, TX).

Temperature Measurements and Characterization of Manure Pack.
Two FW3638 thermocouples from ThermoElectric Wire and Cable, L.L.C. (Saddle Brook, NJ) were used to measure continuously the temperature of ambient air and air inside the chamber. Manure pack temperature was measured using a Campbell Scientific (Logan, UT) model 107 soil temperature probe (accuracy ± 3%) inserted 5 cm into the manure at 45 deg angle inside the
chamber. Manure pack samples were collected twice a day, i.e., before and after each measurement. Three samples from the inside of dynamic flow-through chamber were collected at the end of each 24 hr measurement and three representative samples from the outside of chamber were collected at the beginning of each day. Manure pack samples were analyzed for pH, and water content, and TKN.

The in-situ field measurements were conducted using a temperature-controlled instrument shelter. The shelter was a modified 1.5 m × 2.1 m (5 ft × 7 ft) size box trailer with a 13,500 BTU air-conditioning unit. A Campbell Scientific data logger CR23X was used as an automated data acquisition system. The system recorded 60-s rolling average concentration measurements. Data were downloaded daily.

Estimation of Ammonia and Hydrogen Sulfide Fluxes.

The following mass balance equation was used for calculating the flux of NH$_3$ and H$_2$S gas from the measured concentration in the chamber:

$$\frac{dC}{dt} = \left( \frac{q[C_{\text{in}}]}{V} \right) + \left( \frac{JA'}{V} \right) - \left( \frac{LA' + q}{V} \right)[C] - R$$

(1)

where $C$ = NH$_3$ / H$_2$S concentration in the chamber (mass/volume), $t$ = sampling time (time), $q$ = zero air flow rate through the chamber (volume/time), $C_{\text{in}}$ = NH$_3$ / H$_2$S concentration in the zero air supplied to the chamber (mass/volume), $V$ = volume of the chamber (volume), $J$ = emission flux per unit area (mass/area/time), $A'$ = manure pack surface area covered by the chamber (area), $L$ = loss term by chamber wall per unit area assumed first order in [NO] (length/time), $A'$ = surface area of the chamber walls (area), and $R$ = chemical production/destruction rate in the chamber. Zero-grade air does not contain NH$_3$ nor H$_2$S, i.e., $[C_{\text{in}}] = 0$. It is also assumed that there is no chemical production/destruction of target gases inside the chamber ($R = 0$). Thus, Equation 1 simplifies to:

$$\frac{dC}{dt} = \left( \frac{JA'}{V} \right) - \left( \frac{LA' + q}{V} \right)[C]$$

(2)

The loss term ($L$) in Equation 2, i.e., the sum of the loss of NH$_3$ or H$_2$S through reactions with the chamber walls and chemical reactions with existing oxidants can be estimated using a method developed by Kaplan et al., 1988. This method relies on changing the air flow rate and allowing the sampled gases to reach two equilibrium states (Kim et al., 1994; Aneja et al., 1995):

$$-\ln \left( \frac{C_{\text{eq}} - C}{C_{\text{eq}} - C_0} \right) = \left( \frac{LA' + q}{V} \right)t$$

(3)

$C_0$ is the NH$_3$ or H$_2$S concentration in the chamber when NH$_3$ or H$_2$S reaches the first equilibrium state at an initial flow rate and $C_{\text{eq}}$ is the NH$_3$ or H$_2$S concentration in the chamber after the flow rate is reduced and allowed to reach a second equilibrium. The linear relationship between the value of

$$-\ln \left( \frac{C_{\text{eq}} - C}{C_{\text{eq}} - C_0} \right)$$

and time ($t$) of the experiment could be plotted and the slope should be equal to
Thus, the loss term was derived by Equation 3. At this study, the experimental mean loss in the chamber was estimated to be 0.000022 m/sec based on two measurements during the experimental period. This loss term was used in Equation 4 to calculate the NH$_3$ and H$_2$S fluxes:

$$J = \left( \frac{LA'}{V} + q \right) \left( \frac{V}{A} \right)$$  

(4)

For estimating the base line of NH$_3$–N and H$_2$S–S fluxes that do not account for losses, Equation 4 could be updated with Equation 5:

$$J = \frac{q[C]}{A}$$  

(5)

**RESULTS AND DISCUSSION**

Preliminary Ammonia and Hydrogen Sulfide Fluxes.

Table 1 summarizes preliminary daily mean values of ammonia-nitrogen (NH$_3$–N, where NH$_3$–N = 14/17 × NH$_3$) and hydrogen sulfide-sulfur (H$_2$S–S, where H$_2$S–S = 32/34 × H$_2$S) fluxes, and manure pack characteristics for measurements conducted from August 16th to 30th 2002. Two rainfall events occurred on August 20th and August 29th, 2002. Increases in NH$_3$ and H$_2$S fluxes were observed on Day 6 (8/21/2002) and Day 7 (8/22/2002), i.e., next two days after the first rain event. The second rain event did not have an apparent effect on flux in the last day of measurements. The second rain event occurred when measurements were conducted within one fenced area and no fresh manure loads were added to the surface for at least 2 days prior to the last day of measurement. The H2S measurements were concluded on 8/23/2002 due to the failure of the analyzer.

<table>
<thead>
<tr>
<th>Date</th>
<th>NH$_3$-N Flux w/o Loss Term (µg/m$^2$/min)</th>
<th>NH$_3$-N Flux w/ Loss Term (µg/m$^2$/min)</th>
<th>H$_2$S Flux w/o Loss Term (µg/m$^2$/min)</th>
<th>H$_2$S Flux w/ Loss Term (µg/m$^2$/min)</th>
<th>Soil Temperature (°C)</th>
<th>Manure Pack Characteristics</th>
<th>pH</th>
<th>H$_2$O (%)</th>
<th>TKN (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/16/</td>
<td>1.84 ± 0.58</td>
<td>2.05 ± 0.76</td>
<td>6 ± 0.648</td>
<td>32.0 ± 8</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8/17/</td>
<td>1.91 ± 1.35</td>
<td>2.15 ± 1.43</td>
<td>1.525 ± 0.56</td>
<td>31.4 ± 5.4</td>
<td>A A</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8/18/</td>
<td>1.71 ± 1.27</td>
<td>1.91 ± 1.58</td>
<td>1.433 ± 0.57</td>
<td>4 ± 0.7</td>
<td>9 6.5</td>
<td>4</td>
<td>18.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8/19/</td>
<td>1.10 ± 0.65</td>
<td>1.23 ± 0.71</td>
<td>0.736 ± 0.58</td>
<td>29.7 ± 3.9</td>
<td>8 1</td>
<td>9</td>
<td>18.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8/20/</td>
<td>1.16 ± 1.91</td>
<td>1.30 ± 1.33</td>
<td>2.134 ± 1.34</td>
<td>21.5 ± 1.9</td>
<td>6 6 6</td>
<td>6</td>
<td>26.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8/21/</td>
<td>1.02 ± 0.56</td>
<td>0.66 ± 0.62</td>
<td>0.736 ± 0.18</td>
<td>22.7 ± 1.9</td>
<td>7.5 59 25.85</td>
<td>4 0 4</td>
<td>27.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8/22/</td>
<td>0.95 ± 0.18</td>
<td>1.06 ± 0.20</td>
<td>0.204 ± 0.28</td>
<td>28.5 ± 6.3</td>
<td>7.8 48</td>
<td>27.45</td>
<td>9 5 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>02</td>
<td>1 1 8 8 3 3 2</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
During the first (8/16/2002 to 8/18/2002) and the second (8/27/2002-8/29/2002) manure pack “aging” process experiments, the NH$_3$-N concentrations significantly decreased (Table 1). This is consistent with the fact that there was only a limited amount of N in manure pack that could be released over time. Preliminary average of NH$_3$-N flux from the feedlot surface including the loss term effects (Equation 4) was 1,669 ± 1,212 NH$_3$-N µg/m$^2$/min. The same estimate without the loss term (Equation 5) was 1,494 ± 1,083 NH$_3$-N µg/m$^2$/min. For H$_2$S, the average H$_2$S-S flux excluding the loss term was estimated at 1.683 ± 1.334 H$_2$S-S µg/m$^2$/min and 1.884 ± 1.497 H$_2$S-S µg/m$^2$/min (including the loss term).

Figures 3 and 4 shows the mean 24-hr profiles of NH$_3$-N and H$_2$S-S flux. Each hourly data point represents mean of hourly NH$_3$-N and H$_2$S-S flux values over the number of observation days and vertical bars represent the ±1 standard deviations. The dotted line represents the NH$_3$-N and H$_2$S-S flux values that exclude the loss term effects that were estimated using Equation 5. Daytime maximum of NH$_3$-N and H$_2$S-S flux occurred between 2:00 and 4:00 PM, usually the warmest time of the day. A nighttime minimum for both gases developed between 5:00 to 7:00 AM, typically the coolest time of the day. This indicates that manure pack temperature of the feedlot is one of the major factors regulating the loss of NH$_3$-N and H$_2$S-S from the feedlot surfaces.

![Mean NH$_3$-N Flux Diurnal Variation](image)

**Figure 3.** Daily trend of hourly mean NH$_3$-N flux. Error bars represent standard deviation of each hour mean value during the selected periods.
Figure 4. Daily trend of hourly mean H$_2$S-S flux. Error bars represent standard deviation of each hour mean value during the selected periods.

Table 2 shows comparison of the average NH$_3$-N flux from other different sources (Aneja et al., 2001b; Roelle, 2002). This study showed that the average NH$_3$-N flux during summer period from the feedlot surfaces is approximately 60% less than NH$_3$-N flux value during summer period from the swine anaerobic lagoon surfaces estimated by Aneja et al. (2001b).

Relationship between Ammonia Emissions, Manure Pack Temperature and TKN.

Figure 5 shows hourly mean NH$_3$-N flux versus the mean hourly manure pack temperature for Days 4 to 11. In this study, we found that manure pack temperature (T$_{soil}$) has a weak logarithmic relationship with NH$_3$-N flux [Log$_{10}$ NH$_3$-N flux (µg N/m$^2$/min) = 0.1308 $\times$ T$_{soil}$($^o$C) + 28.198, where $R^2 = 0.492$]. Previous research (Bunton, 1999; Chauhan, 1999, Dewes, 1996) showed that the temperature of animal waste is a major factor in controlling the release of NH$_3$ into the atmosphere. Roelle (2002) also indicated that soil temperature had a logarithmic dependence with NH$_3$-N flux from intensively managed agricultural soils. Figure 6 shows the NH$_3$-N flux as a function of TKN. The NH$_3$-N flux was weakly ($R^2 = 0.472$) proportional to the TKN. Figure 6 excludes rainfall and aging process events.

<table>
<thead>
<tr>
<th>Studies</th>
<th>Measurement Period</th>
<th>Site Description</th>
<th>NH$_3$-N flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>Summer</td>
<td>Feedyard Surface w/o Loss Term</td>
<td>1,494 ± 1,083 µg N/m$^2$/min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feedyard Surface with Loss Term</td>
<td>1,169 ± 1,212 µg N/m$^2$/min</td>
</tr>
<tr>
<td>Roelle, 2002</td>
<td>Spring</td>
<td>Corn Crop, pre-fertilization</td>
<td>0.038 to 0.271 µg N/m$^2$/sec</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>No Crop Planted</td>
<td>0.063 to 0.026 µg N/m$^2$/sec</td>
</tr>
<tr>
<td>Aneja et al., 2001b</td>
<td>Spring</td>
<td>Anaerobic Lagoon Surface</td>
<td>1,706 ± 552 µg N/m$^2$/min</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td></td>
<td>4,017 ± 987 N/m$^2$/min</td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td></td>
<td>3,05 ± 154 µg N/m$^2$/min</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td></td>
<td>4,017 ± 987 N/m$^2$/min</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Ammonia-N and H₂S-S fluxes from commercial feedlot surfaces in northwestern Texas were monitored by a dynamic flow-through chamber system and continuous analyzers during the experimental period (8/16/2002 – 8/30/2002). Preliminary mean NH₃-N flux from the feedlot pen surface including the loss term effects was 1,669 ± 1,212 NH₃-N µg/m²/min (1,494 ± 1,083 NH₃-N µg/m²/min excluding the loss due to adsorption to walls of sampling system). Preliminary mean H₂S-S flux was estimated at approximately at 1.884 ± 1.497 H₂S-S µg S/m²/min (1.683 ± 1.334 H₂S-S µg S/m²/min excluding the loss due to adsorption). The average NH₃-N flux was approximately 60% less than NH₃-N flux from the swine anaerobic lagoon surfaces estimated by Aneja et al. (2001b). Manure pack temperature and TKN showed weak correlations with the NH₃-N flux.

Acknowledgements

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