Ammonia and Hydrogen Sulfide Flux and Dry Deposition Velocity Estimates using Vertical Gradient Method at A Commercial Beef Cattle Feedlot

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1. **Introduction**

There are several approaches to measure and estimate trace gas emissions from surface sources, such as (1) isolation chamber and wind tunnel techniques, (2) micrometeorological vertical gradient and eddy correlation methods and (3) Gaussian dispersion and backward Lagrangian models. The surface isolation flux chamber (Baek *et al*., 2004; Koziel *et al*., 2004; Roelle, 2002; Aneja *et al*., 2001; Eklund, 1992) and wind tunnel can measure trace gases from enclosed small defined areas, such as soil landfill, water, and wastewater surfaces. However, micrometeorological and statistical dispersion methods are more appropriate for large surface sources with sufficient target source fetch distance and source uniformity (Phillips *et al*., 2004; Flesch *et al*., 2002; Oke, 1978). Due to the fact that the commercial cattle feedyard in the Texas panhandles is a large size of surface source approximately $941\times10^3 m^2$ (825m×1140m), this study conducted the vertical gradient flux method for estimating NH_3 and H_2S fluxes and dry deposition velocities.

The primary objectives of this study were to (1) compare NH_3-N and H_2S-S fluxes from a commercial feedyard in the panhandle of Texas using a micrometeorological vertical gradient flux method with previous measurements at the same sampling location using the isolation chamber method; (2) investigate the relationship of NH_3-N and H_2S-S fluxes and dry deposition velocities with meteorological variables and atmospheric stability classes.

2. Methodology

2.2 Sampling Location and Scheme

Two observations of NH_3–N and H_2S-S fluxes and dry deposition velocities using micrometeorological gradient flux method were conducted at a commercial cattle feedyard in the Texas panhandle from January 22nd to 24th 2003 and June 16th to July 6th 2004. The operation accommodated approximately 43,000 head of beef cattle. The stocking density average was 14.4 m^2/head. In this study, NH_3 and H_2S concentrations were measured continuously at 3-m and 6-m heights and profiles of wind speed (WS) and ambient temperature were measured at multiple heights (1, 2, 3, 4, 5 and 6-m) on a 10m weather tower. For the Summer 2004 event, the tower was located in the northeastern quadrant area of the

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yard to maximize fetch in the direction of prevailing southwesterly winds and to reduce the potential interferences of emission from the waste lagoon on the east side of the feedlot. For the Winter 2003 event, the tower was located in the center quadrant for the same reasons as stated above. Thus, we excluded data when the wind was from other than 180^o to 270^o. A total of 29 hourly average NH_3 and H_2S measurements were selected for the Winter 2003 experiment and a total of 83 and 122 hourly average NH_3 and H_2S measurements were selected for the Summer 2004 experiment. Wind direction with cup anemometer at 8 m, relative humidity, precipitation, manure temperature, and net radiation were also monitored at a collocated weather tower.

Ammonia concentrations were measured with a Thermo Environment Instrument (TEI) 17C chemiluminescence NH_3 analyzer (Franklin, MA) with a range of 0 to 10 parts per million by volume (ppmv). Hydrogen sulfide concentrations were measured using a TEI 45C SO_2/H_2S analyzer (Franklin, MA) with a range of 0 to 1000 parts per billion by volume (ppbv). In order to measure trace gas concentrations at two different heights, a 3-way solenoid was installed to switch gas sampling lines from one height to the other every 10 min. Due to the response time of each analyzer unit, only measured concentrations from the last 3 min out of each 10 min were averaged at each height (3-m and 6-m). Those three 3-min averages occurring every 20 min were averaged for hourly average trace gas concentrations.

2.3 Vertical Gradient Flux and Dry Deposition Velocity

The micrometeorological vertical gradient method is one of the most widely used for trace gas vertical flux estimations for a large surface source. It is an analogy between molecular and turbulent exchange processes based on eddy diffusivity relations. Under assumption of the same eddy diffusivity for gaseous mass and heat, the mean vertical gradient flux (F_C) could be expressed as:

$$F_c = -K_m \frac{\partial \bar{c}}{\partial z} \cong -K_h \frac{\partial \bar{c}}{\partial z} = -\frac{kzu_*}{\phi_h}\frac{\partial \bar{c}}{\partial z} \cong \frac{ku_*}{\phi_h}\frac{\Delta \bar{c}}{\ln(z_2/z_1)}, \text{ where } \left(\frac{K_h}{kzu_*} = \frac{1}{\phi_h(\zeta)}\right) \qquad (1)$$

$$\text{and } u_* = \frac{kz}{\phi_m}\frac{\partial \bar{u}}{\partial z} \cong \frac{k}{\phi_m}\frac{\Delta \bar{u}}{\ln(z_2/z_1)} \qquad (2)$$

where $\Delta \bar{c}$ is the difference between the mean concentrations at the two different heights (z_1 and z_2). K_m and K_h are the eddy diffusivities of mass and heat involving mean gradients, respectively. Eddy diffusivities can be expressed in terms of the Monin-Obukhov (M-O) similarity functions for momentum and heat flux, $\phi_m(\zeta)$ and $\phi_h(\zeta)$, respectively. The friction velocity (u_*) is related to air-surface stress, k is the von Karman constant (assumed to be $k \cong 0.4$). Variable z is the reference height and z_m is a geometric mean height $\left(z_m = \sqrt{z_1 z_2}\right)$. $\zeta = z_m / L$ can be determined by its relationship *to the Richardson number* $R_i(z_m)$ estimated from equations 3 (equation 4). L is the M-O length, the depth of the near-surface layer in which shear effects are likely to be significant under any stability conditions. The corresponding relations between $\zeta = z_m / L$ and $R_i(z_m)$ are (Arya, 1999 and 1995) as follows:

$$R_i(z_m) = \frac{g}{T_o}\frac{\partial\bar{\theta}/\partial z}{\left(\partial\bar{u}/\partial z\right)^2} \cong \frac{g}{T_o}\frac{\Delta\bar{\theta}\ z_m}{\left(\Delta\bar{u}\right)^2}\ln\left(\frac{z_2}{z_1}\right) \qquad (3)$$

$$\zeta = R_i\,,\quad \text{for}\quad R_i < 0 \quad ; \quad \zeta = \frac{R_i}{1-5R_i}\,,\quad \text{for}\quad 0 \le R_i < 0.2 \qquad (4)$$

The empirical M-O similarity functions for momentum and heat flux are determined from micrometeorological experiments in various flat and homogeneous surfaces. The most widely used and simplest forms adapted from Businger-Dyer relations are (Arya 1995 and 1999):

$$\phi_h = \phi_m^2 = (1-15\zeta)^{-1/2}\,,\quad \text{for } -5 < \zeta < 0 \quad \text{(Unstable)} \qquad (5)$$

$$\phi_h = \phi_m = 1+5\zeta\,,\quad \text{for } 1 > \zeta \ge 0 \quad \text{(Stable)} \qquad (6)$$

The direct quantitative measurements of vertical gaseous mass flux near the surface can be also used to characterize dry deposition velocity (V_d). This velocity is commonly used in parameterization of dry deposition rate and can be expressed as:

$$v_d = -\frac{F_c}{\bar{c}} \qquad (7)$$

where $\bar{c}$ is the mean concentration at the reference height above the surface *e.g.* the canopy or roughness layer. Vertical gradient flux (F_c)is assumed to be positive when it is directed upward from a source, and dry deposition velocity is assumed to be negative as it is directed downward the surface.

3. Results and Discussion

The sampling site in this study was located at the target source area of the feedyard which resulted in upward (positive) flux and downward (negative) dry deposition velocity. These conditions are different to those typically found at downwind remote sampling locations, where dry deposition velocity is assumed to be positive and flux is assumed to be negative deposition velocity which when hourly concentration gradient were positive (Phillips *et al.*, 2004; Duyzer et al., 2987; Sutton et al., 1993). Phillips et al. (2004) observed the deposition (downward) fluxes near to the swine production facilities. It ranged from –6.6 ± 8.41 during the summer and the spring seasons to -1.2 ±1.8 μg NH_3-N/m^2/min during the winter. The highest dry deposition velocity occurred during the winter (2.41 ±1.92 cm/sec) during the winter and the lowest occurred during the summertime (3.94±2.79 cm/sec) (Phillips *et al.*, 2004). However, Erisman and Wyers (1993) observed the positive upward fluxes from dry and wet heathland in Europe.

During the Summer of 2004, the mean NH_3–N flux estimated using the vertical gradient flux method was 3,671 ±2,624 μg NH_3-N/m^2/min (Table 1). This flux estimate was significantly higher than NH_3–N fluxes measured during the summer 2003 at the same feedyard using the isolation chamber method (Baek *et al*., 2004; Koziel *et al*., 2004). During the summers of 2003 and 2002 the mean NH_3-N flux from the feedyard surface using the chamber method was 1,666 ± 1,642 μg NH_3-N/m^2/min and 1,681± 1,931 μg NH_3-N/m^2/min, respectively. Measured fluxes were much lower in winter. In contrast to the summer measurements, the winter measurements were conducted within the same season and were scheduled as series. During the Winter 2003 experiment, the isolation chamber method (January 8th – 21st 2003) for 13 days and vertical gradient flux method (January 22nd – 24th 2003) for 2.5 days were performed and were no any significant weather changes. The mean flux measured with the chamber method during the Winter 2003 was 289 ± 237 μg NH_3-N/m^2/min. The ammonia flux estimate using the vertical gradient flux method was 317 ± 209 μg NH_3-N/m^2/min. The difference between the ammonia-N flux estimates was only of approximately 11.6%. This difference is quite small considering how different these 2 methodologies are and the uncertainties associated with them.

Measured hydrogen sulfide concentrations and therefore the estimates of fluxes were always lower than those of ammonia, regardless of the technique used. Differences between the H_2S-S flux estimates were also much higher. The estimates using the gradient flux method were considerably higher (21.71 ± 20.71 μg H_2S-S/m^2/min) during the Summer 2004 than downward deposition flux (-0.99 ± 2.91 μg H_2S-S/m^2/min) during the Winter 2003. During the Summer 2004 experiment, there were five rain events including two thunderstorms. The significant higher H_2S fluxes were observed after the rainfalls due to active evaporation processes by manure temperature increase. It is consistent with Baek *et al*. (2004) results using the chamber method. The negative deposition flux contradicts our current knowledge about the fate of hydrogen sulfate emissions at a commercial feedyard. One explanation could be the relatively high standard deviation associated with the very low flux measurements (Table 1).

Table 1. Comparison of average NH_3-N and H_2S-S fluxes between using vertical gradient flux and isolation chamber at the commercial cattle feedyard in the Texas panhandle.

Reference	Measurement Period	Sampling Technique	Site Description	NH_3-N flux (μg/m^2/ min)	H_2S-S flux (μg/m^2/ min)
This study	Winter 2003	Vertical Gradient Flux	Commercial Cattle Feedyard, Texas	317 ± 209	-0.99 ± 2.91
	Summer 2004			3,671 ± 2,624	21.71 ± 20.71
Baek *et al*. (2004)	Summer 2002	Dynamic Isolation Flux Chamber		1,666 ± 1,642	1.28 ± 1.06
	Winter 2003			289 ± 237	0.31 ± 0.63
	Summer 2003			1,681 ± 1,931	1.22 ± 1.08

Ammonia and hydrogen sulfide flux had diurnal patterns with higher flux in daytime and lower flux in nighttime. These variations are partially controlled by changes in manure temperature and active evaporation process during daytime (Figure 1) (Baek *et al*., 2004;

Koziel *et al.*, 2004). The numbers located at each time of day in Figure 1 represent a number of hourly average data used for average point. It indicated that they are evenly distributed throughout 24 hours. Manure temperature had the similar diurnal trend as NH_3-N flux estimates and was positively correlated with NH_3-N fluxes ($R^2 = 0.56$). This finding is consistent with strong correlations between manure temperature and flux for 3 seasons reported earlier (Baek *et al*., 2004; Koziel *et al*., 2004).

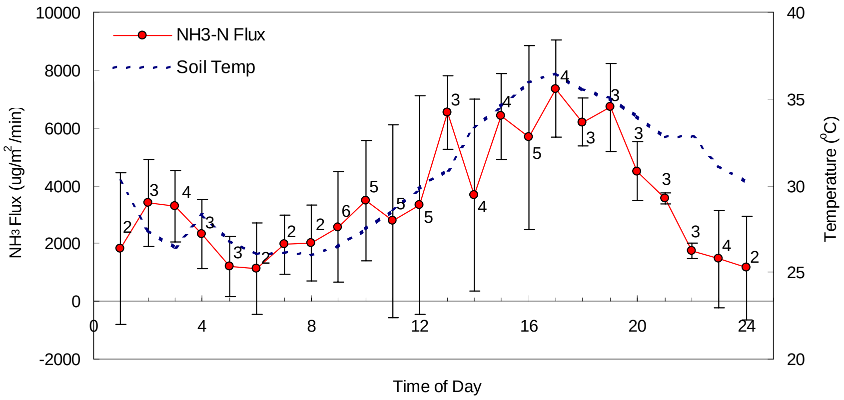

Figure 1. Diurnal variations of NH_3–N and manure temperature during the Summer 2004.

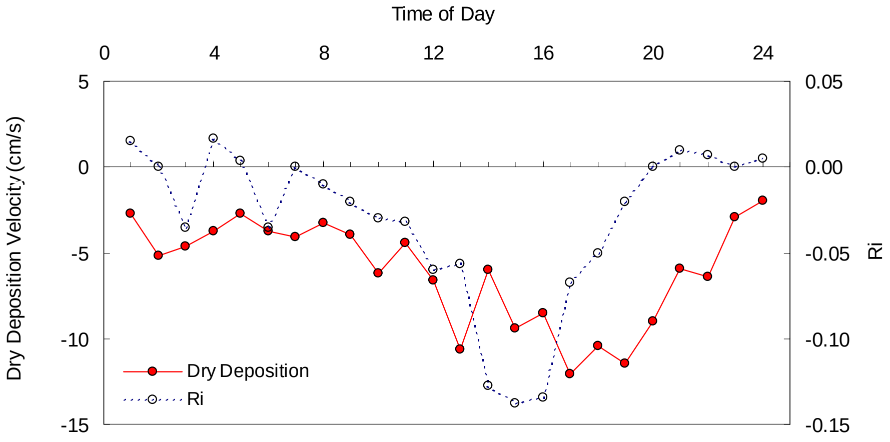

Figure 2. Diurnal variations in NH_3–N dry deposition velocity (V_d) and stability class Richardson number (R_i) during the Summer 2004.

Dry Deposition Velocity and Atmospheric Stability

Atmospheric stability during experiments was determined by the Richardson number (R_i) and M-O stability parameter $\zeta = z_m / L$. During the Winter 2003 and Summer 2004 experiments, most hourly stability conditions ranged from unstable to very unstable ($R_i < 0$). Mean R_i values from summer and winter in this study were –0.04 ±0.07 during the Summer 2004 (maximum = 0.06) and –0.03 ±0.03 during the Winter 2003 (maximum = -0.01). Deposition velocity was calculated here as the ratios of the flux to mean concentrations measured at 3-m (Equation 7). Mean dry deposition velocity (V_d) for NH_3-N and H_2S-S during the Summer 2004 were –6.27 (± 4.47) cm/sec and –7.32 (± 5.34) cm/sec, respectively. The diurnal variations in ammonia V_d and stability R_i during the Summer 2004 had similar patterns (Figure 2). The highest average V_d occurred during daytime under very unstable atmospheric conditions and the lowest during nighttime under neutral and stable atmospheric conditions. There was a strong correlation between V_d and R_i ($R^2 = 0.74$ for NH_3–N flux; $R^2 = 0.55$ for H_2S-S flux).

4. Conclusion

Mean ammonia flux estimated using the gradient flux method was approximately 3,671 (±2,624) μg NH_3-N/m^2/min during the Summer 2004 and 317 (±209) μg NH_3-N/m^2/min during the Winter 2003. Hydrogen sulfide flux was 21.71 (±20.71) μg H_2S-S/m^2/min during the Summer 2004 and –0.99 (±2.91) μg H_2S-S/m^2/min during the Winter 2003. Ammonia and H_2S-S flux had general diurnal patterns with the highest fluxes in daytime and lowest fluxes in nighttime that correlated to manure temperature changes and active evaporation process during daytime. The highest average deposition velocities also occurred during daytime with unstable atmospheric conditions and the lowest during nighttime with very stable conditions.

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