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Ammonia flux and dry deposition velocity from near-surface concentration gradient measurements over a grass surface in North Carolina

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Abstract

Atmospheric ammonia concentrations were measured during fall 2001, winter, spring, and summer 2002 over natural surfaces in North Carolina where animal farms and waste storage and treatment lagoons (which are known to emit ammonia) at two heights (2 and 6 m) above the surface employing an arrangement of two Thermo Environmental Instruments, Inc. Model 17C chemiluminescent nitrogen oxides (NO_X)–ammonia (NH_3) analyzers along with a solenoid for each analyzer to alternate measurements between the two elevations. Simultaneously, mean winds and temperatures are also measured at the same two heights. The micrometeorological gradient method is used in conjunction with the Monin–Obukhov similarity theory, to estimate the vertical flux and dry deposition velocity of ammonia under different meteorological conditions. Diurnal and seasonal variations of ammonia flux and dry deposition velocity were investigated under a wide range of wind and atmospheric stability conditions yielding hourly variation of NH_3 fluxes and deposition during each seasonal campaign. Fall average NH_3 concentrations were generally the highest with daytime concentrations of $7.60 \pm 6.54\,\mu g\,m^{-3}$ at 2 m, while nighttime NH_3 concentrations were $7.25 \pm 6.14\,\mu g\,m^{-3}$ at 2 m. The winter season had the lowest overall concentrations collected during each seasonal campaign with averages of $1.73 \pm 2.00\,\mu g\,m^{-3}$ (2 m) during daytime and $1.37 \pm 1.50\,\mu g\,m^{-3}$ (2 m) during nighttime. Deposition and emission occur, both on daily and seasonal scales. Summer measurements yielded the largest average daytime deposition velocity of $3.94 \pm 2.79\,cm\,s^{-1}$, whereas winter measurements gave the lowest daytime velocities with an average of $2.41 \pm 1.92\,cm\,s^{-1}$. The largest nighttime deposition velocities were estimated during the summer season with an average of $0.76 \pm 1.69\,cm\,s^{-1}$, whereas fall nighttime deposition velocities were considerably lower at $0.07 \pm 0.17\,cm\,s^{-1}$. Regression relationships between the ammonia deposition velocity and the friction velocity are obtained for different stability conditions.

Keywords: Ammonia; Dry deposition velocity; Flux; Stability; Friction velocity

1. Introduction

Until recently, reduced forms of atmospheric nitrogen, ammonia (NH_3, the most abundant alkaline component in the atmosphere), and ammonium (NH_4^+, the primary atmospheric reaction product of NH_3) ($NH_X = NH_3 + NH_4^+$) as pollutants have received little attention, in relation to their emission, transport, transformation, and deposition in the atmosphere

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(Aneja et al., 2001a). Ammonia in the atmosphere can be deposited to the surface of the earth by either wet or dry deposition. Hence, atmospheric ambient NH_3 concentrations have been arduous to accurately measure and estimate related fluxes due to its high reactivity between phases (Jaeschke et al., 1998). The rate of conversion between gas to particle (NH_3 to NH_4^+) primarily controls the spatial distribution of a specific NH_3 source's contribution to atmospheric deposition. A considerable fraction of NH_3 (20–40%) can deposit near its source resulting in a short lifetime, low source height, and relatively high dry deposition velocity (Asman and van Jaarsveld, 1992; Asman et al., 1998; Roelle, 2001). Whereas, ammonium will deposit farther downwind, away from its source due to its longer lifetime of $\tau = 1-15$ days (Aneja et al., 1998a; Chimka et al., 1997). Consequently, ammonia concentrations depend on near-surface winds (wind speed at 10 m), turbulence, atmospheric stability, surface roughness and other properties, as well as the spatial distribution of sources. A shift from deposition to emission can be caused by an increase in temperature, and/or relative humidity (Andersen et al., 1999).

Recent studies in Europe and the United States have reported increasing atmospheric concentration levels of NH_3 and NH_4^+, especially in regions of concentrated animal feeding operations (Aneja et al., 1998b). These higher concentration levels have shown to be directly related to the rapid growth of intensively managed agriculture. At present, ammonia emission and subsequent wet and dry deposition are a significant waste management problem facing animal husbandry and agriculture.

Ammonia emissions in the United States for 1998 show that livestock and fertilizer sources contribute 86% of principal source categories (USEPA, 2000). The swine population in the United States contributes approximately 10% of the NH_3-N budget (Battye et al., 1994). Likewise, for North Carolina (NC) state, estimates reveal that the swine population contributes approximately 46% of the NH_3-N emissions (NCDENR, 1999). This estimate shows a direct link to the recent growth of the swine population in NC; where small, rural family farm operations have developed into major corporate businesses clustered in limited geographic areas (e.g. eastern NC). Areas of scattered local sources contribute a wide range of NH_3 emission and dry deposition. Currently, NC is ranked second in the nation, behind Iowa, for swine production with approximately 10 million hogs in about 2500 hog farms located in eastern NC (Aneja et al., 2000; NCDA, 1998).

The primary objectives of this research are to: (1) measure vertical fluxes of ammonia and related dry deposition velocities from near-surface concentration gradient measurements over natural surfaces in eastern NC downwind of a source; (2) investigate and evaluate the variability of ammonia flux and related dry deposition velocity on a specified natural surface (i.e. grass) with respect to the time of the day, season, and meteorological factors; (3) obtain empirical relations for dry deposition velocity of ammonia. This particular area of emphasis is chosen because of the obvious lack of data and the expressed need for a better understanding of ammonia flux and dry deposition velocity in eastern NC, where ammonia sources have increased very rapidly in recent years (DAQ, 1997).

2. Methods and materials

2.1. Physiographic location, instrumentation, and sampling scheme

This study was designed to measure vertical fluxes and dry deposition velocities of NH_3 at a relatively flat, uniform, and smooth site with grass or short vegetation, which is located near a swine production facility in eastern NC, during four seasons (fall 2001, winter 2002, spring 2002, and summer 2002). Field experiments were conducted at the North Carolina State University's (NCSU) Research Farm Units, namely the Air Quality Educational Unit (USDA-ARS, 3908 Inwood Rd., Raleigh, NC), coordinates 35°44′N, 78°41′W (Fig. 1), where hourly averaged measurements of wind speeds, temperatures, and concentrations of ammonia were made at two heights (2 and 6 m) using a 7 m walk-up tower in the horizontally homogeneous atmospheric surface layer. The measurement levels were carefully chosen with appropriate considerations for the height and distribution of surface roughness elements, so that the surface-layer similarity relations could be used for estimating the vertical fluxes of momentum, heat, and

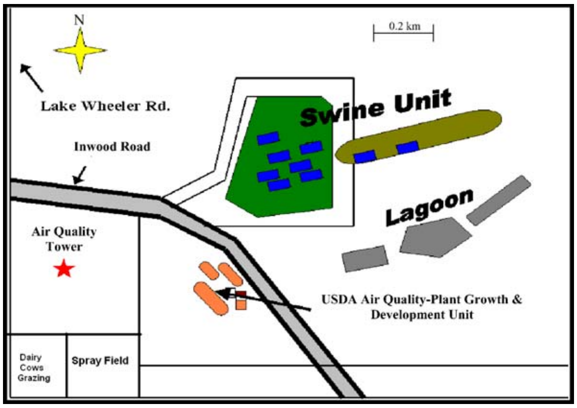

Fig. 1. North Carolina State University Air Quality Educational Unit: Field site (USDA-ARS, Inwood Rd., Raleigh, NC).

ammonia. The main objective was to accurately measure the mean gradients of ammonia concentration, air velocity, and temperature over short sampling periods of 30–60 min.

The experimental site is located near a swine production facility, which employs an anaerobic lagoon for disposal of swine waste. The farm consisted of seven production barns to house the swine, from the time of breeding to finishing. During each measurement period, the swine production facility averaged a total volume inventory of approximately 1200 swine.

The farm utilizes an anaerobic lagoon as means of storage for the swine waste, located 0.8 km east of the air quality tower. The bulk (60–80%) of nitrogen entering the atmosphere from anaerobic lagoons is known to escape by means of NH_3 volatilization (Sims and Wolf, 1994). In addition to the swine educational facility, the NCSU Research Farm Unit also contains a dairy, turkey and chicken educational units that are within 0.8 km proximity to the air quality measurement tower. Among these units, the dairy cattle ($\sim$35 head of cattle) graze in a field directly south/southwest, adjacent to the position of the tower.

Ammonia concentrations are measured using two Thermo Environmental Instruments Inc. (TEI), Model 17C Chemiluminescence Ambient Ammonia Analyzers (TEI, 2000). The manufacturer states that the minimum detection level of the analyzer is 1 ppb ($\sim 0.7\,\mu g\,m^{-3}$); above this threshold mean concentrations and gradients for a 1 h exposure can be resolved for estimation of NH_3 fluxes and dry deposition velocities with an estimated uncertainty of $\pm 10\%$ and $\pm 20\%$, respectively. Performance evaluations of the NH_3 analyzers were frequently conducted which included converter efficiency, relative precision, linearity across output ranges, and system error of two co-located analyzers. Due to expected low ammonia concentrations of approximately 5–15 ppbv at the field site, an ammonia low permeation wafer device (Permeation Rate: $20 \pm 0.0005\,ng\,min^{-1}$ at 30°C) was used in conjunction with a VICI Metronics Dynacalibrator Model 230. In addition, to ensure calibration precision in the lower range of 0–5 ppbv, converter efficiency was evaluated during each measurement period at multiple points across the scale of 0–50 ppbv using a periodically calibrated TEI 146 dilution/titration instrument, which ranged from 65% to 75%. Daily sampling scheme consisting of measuring diurnal ambient NH_3 concentrations were conducted consecutively 24 h a day with interruptions due only to protocol daily zero and span checks noted by the operator manuals.

Meteorological data (wind speed/wind direction, temperature) and concentration measurements are collected and recorded via a Campbell Scientific 23X Micrologger. The data acquisition system comprises a Dell laptop computer using Campbell Scientific software, which produces and records a 60 s rolling average. The two-chemiluminscence analyzers and other gas detection instruments are housed in a temperature-controlled mobile laboratory. The temperature inside the van is monitored and maintained at $\sim 21°C$.

2.2. Gradient method for determining flux

The general gradient method is used for estimating the vertical flux and the deposition velocity of ammonia (Businger, 1986; Hicks, 1986). In the absence of fast-response sensors, the general gradient method (Hansen et al., 1998; Erisman and Wyers, 1993) has been successfully used in several studies where trace gas fluxes and deposition velocities were evaluated (e.g. sulfur dioxide and ozone). The gradient method is based on the eddy diffusivity relations for the vertical turbulent fluxes of sensible heat and tracer gas. This method utilizes the following relationship:

$$\overline{w'c'} = \overline{w'\theta'}\frac{\Delta\bar{c}}{\Delta\bar{\theta}}, \tag{1}$$

which implies that eddy diffusivities of heat and tracer mass are equal. This assumption appears to be justifiable for conservable, passive tracers, but becomes somewhat questionable for fast reacting species. Here, $\Delta\bar{c}$ and $\Delta\bar{\theta}$ denote the differences between the mean concentrations and potential temperatures measured at the same two heights z_2 and z_1. The sampling time over which averages are taken should be large enough to include all the significant scales of eddy motion but smaller than the characteristic time scale of reactions involving the chemical species of interest. An assumption implied in the gradient method is that the tracer flux does not vary between the two heights. In Eq. (1), the sensible heat flux $\overline{w'\theta'}$ may be determined or estimated through the use of the gradient method and the surface-layer similarity relations which yield (see, e.g., Arya, 1995, 1999, 2001):

$$\overline{w'\theta'} = -k^2\frac{\Delta\bar{u}\Delta\bar{\theta}}{\phi_m\phi_h}\left(\ln\frac{z_2}{z_1}\right)^{-2}. \tag{2}$$

Here, $k \cong 0.4$ is the von Karman constant, $\Delta\bar{u}$ is the difference in wind speeds between the two heights, and ϕ_m and ϕ_h are the dimensionless wind shear and potential temperature gradient at the geometric mean height $z_m = (z_1 z_2)^{1/2}$.

According to the Monin–Obukhov (M–O) similarity theory, ϕ_m and ϕ_h are unique functions of the M–O similarity parameter z/L (see Eqs. (7) and (8)), where L is the M–O length. Their functional forms have been determined empirically from previous micrometeorological experiments. The similarity theory also relates z/L to the more easily measured gradient Richardson number. In particular, Richardson number at z_m can be estimated from

$$Ri(z_m) = \frac{g}{T_o} \frac{\Delta\bar{\theta} z_m}{(\Delta\bar{u})^2} \ln \frac{z_2}{z_1}, \tag{3}$$

from which z_m/L can easily be determined from its unique relationship to $Ri(z_m)$ (e.g. $\zeta = Ri = z_m/L$, implying that ϕ_m and ϕ_h are unique functions of $\zeta = z_m/L$) (Arya, 1995, 2001).

Likewise, the gradient method can also be used to obtain the following expression for the vertical flux of tracer:

$$\overline{w'c'} = -\frac{kzu_*}{\phi_h} \frac{\partial\bar{c}}{\partial z} \cong \frac{ku_*}{\phi_h} \frac{\Delta\bar{c}}{\ln(z_2/z_1)}, \tag{4}$$

where u_* is the friction velocity, z is the reference height, and ϕ_h is to be evaluated at z_m/L. The friction velocity can be estimated from the M–O similarity relations as

$$u_* = -\frac{kz}{\phi_m} \frac{\partial\bar{u}}{\partial z} \cong \frac{k}{\phi_m} \frac{\Delta\bar{u}}{\ln(z_2/z_1)}. \tag{5}$$

The total vertical flux of tracer

$$F_c = \overline{w'c'} + \bar{w}\bar{c} \tag{6}$$

includes the mean vertical transport term which can usually be neglected close to a flat and homogeneous surface (however, see Businger, 1986). In this study, we use the empirical expressions of the M–O similarity functions ϕ_m and ϕ_h, for the atmospheric surface layer proposed by Arya (2001) for unstable and moderately stable conditions and by Beljaars and Holtslag (1991) for very stable conditions. In particular, for $Ri \geqslant 0.14$ and $\zeta > 1$, we have used

$$\phi_m = 1 + [a + b(1 + c - d\zeta)\exp(-d\zeta)]\zeta, \tag{7}$$

$$\phi_h = 1 + [a\left(1 + \tfrac{2}{3}a\zeta\right)^{1/2} + b(1 + c - d\zeta)\exp(-d\zeta)]\zeta, \tag{8}$$

where $a = 1$, $b = 0.667$, $c = 5$, and $d = 0.35$ (Beljaars and Holtslag, 1991; Ding et al., 2001).

The main difficulty that is encountered in the gradient method is that the average concentration $\bar{c}$ has to be measured with a precision of $\pm 10\%$ in order to adequately resolve the difference $\Delta\bar{c}$ or the gradient $\partial\bar{c}/\partial z$. First, an inter-comparison of concentration measurements by the two TEI-17C analyzers, sampling at the two heights with the same instrument on the tower, is made to determine their accuracy and suitability for gradient measurements. A scatterplot and linear regression of the measured hourly average NH_3 concentrations during daytime and nighttime periods of the first measurement intensive (fall, 4–14 September 2001) by the two chemiluminescent analyzers showed some scatter, but good agreement, with strong correlations during both daytime (2 m: $R^2 = 0.84$; 6 m: $R^2 = 0.70$) and nighttime (2 m: $R^2 = 0.87$; 6 m: $R^2 = 0.91$) periods (Phillips, 2003). There was only a slight bias between the two analyzers on the average, but significant differences between their individual hourly concentration measurements at the same height indicated that small concentration gradients between the two heights cannot be accurately determined by using two separate instruments. For this reason, ammonia concentrations are measured at two heights (2 and 6 m) above the surface employing an arrangement of two identical TEI-Model 17C chemiluminescence analyzers, and a solenoid for each analyzer to alternate measurements between the two elevations. A switching frequency of 10 min between the two heights allows hourly gradient measurements of three 10-min intervals for each height. An average of the last 6 min of concentration data is considered in order to minimize measurement errors related to the analyzer's response time (~2–3 min) including the length of sampling tubing (6.35 mm o.d. FEP Teflon) for both analyzers (~7 m). The instrument and measurement technique have been described elsewhere where measurements of NO_X soil fluxes/soil emissions were determined (Aneja and Murthy, 1994; Aneja et al., 1998c; Roelle et al., 1999).

3. Dry deposition velocity

The dry deposition velocity can be estimated from its conventional definition as a ratio of vertical flux of a material at or near the surface of the earth to mean concentration at a reference height:

$$v_d = -F_c/\bar{c} \tag{9}$$

in which the negative sign is introduced because, in micrometeorology, the flux is considered positive when it is directed upward. Dry deposition processes include molecular diffusion, transport by turbulent eddies, gravitational settling of particulate matter, and inertial impaction or absorption at the surface (Aneja and Murthy, 1994). One can also define a transfer velocity for heat as

$$v_{t\theta} = -\overline{w'\theta'}/(\bar{\theta} - \bar{\theta}_o) \tag{10}$$

and similarly for mass (ammonia) transfer (Businger, 1986), where θ_o is potential temperature at $z = z_o$.

A widely used parameterization or expression for deposition velocity of a gaseous substance is

$$v_d = (r_a + r_s + r_t)^{-1}, \tag{11}$$

where r_a is the aerodynamic resistance to transfer through the turbulent surface layer, r_s is the resistance associated with the molecular sublayer adjacent to the depositing surface, and r_t represents the combined resistance of the surface and transfer to the substrate (Arya, 1999; Andersen et al., 1999). Although this expression does not take into account estimates of compensation point (however considering stability parameters) it has been widely and successively used to estimate dry deposition of surfaces where emission is negligible. Expression of r_a is determined utilizing the Reynolds analogy between the mass and momentum transfers to the surface:

$$r_a = \frac{\overline{u_r}}{u_*^2}, \tag{12}$$

where $\overline{u_r}$ is the mean velocity at the reference height z_r for deposition velocity and u_* is the friction velocity. An approximate expression for r_s is

$$r_s = \frac{c}{u_*} \tag{13}$$

in which the empirical constant, c, is estimated to lie between 5 and 6.5 (Asman, 1998; Wesley and Hicks, 1977). Noting that $r_a \gg r_s$, it is apparent that turbulence primarily influences the maximum possible deposition velocity (v_{max}) or emission rate (Andersen et al., 1999). Assuming that the gas is readily absorbed at the surface, $r_t = 0$. While any deviation in v_d from v_{max} will be reflected when $r_t > 0$, exhibiting absorption/uptake at the surface (Andersen et al., 1999). Estimating only the aerodynamic resistance, r_a, Wyers and Erisman (1998) defined the maximum possible deposition velocity (v_{max}) and the maximum possible flux (F_{max}) as

$$v_{max} = \frac{1}{r_a} = \frac{u_*^2}{\overline{u_r}}, \tag{14}$$

$$F_{max} = -v_{max}\overline{c_r} = -u_*^2 \frac{\overline{c_r}}{\overline{u_r}}. \tag{15}$$

However, we also apply a relaxed criteria to this assumption of v_{max} (where a transfer velocity for heat transfer (Eq. (10)) may be larger than v_{max} by a factor of two) accounting for the possibility supported by considerable experimental evidence (Arya, 1977, 2001) of heat and mass being transferred more efficiently than momentum under unstable and convective conditions.

4. Results

4.1. Seasonal ammonia concentrations: comparison with meteorological conditions

A series of seasonal field measurements of ammonia concentrations were conducted over a grass surface at NCSU Air Quality Educational Unit, in which two TEI Model-17C chemiluminescence analyzers were utilized in conjunction with a solenoid for each analyzer to alternate measurements between two elevations (2 and 6 m). Meteorological conditions such as wind speed, wind direction, and temperature were also measured at the same two heights (2 and 6 m) as NH_3 concentrations. However, due to instrument and calibration errors suspected within thermocouple sensors during the fall and winter seasons, meteorological data (wind speed, wind direction, and temperature at 2 and 10 m) from the State Climate Office of North Carolina (SCO-NC) (2002) AgNet tower, which is located 45 m from the air quality tower were used. The instruments used to measure temperature and wind speed/direction at the AgNet tower were similar to the instruments used in this field study. Since, the upper AgNet measurement height (10 m) is different than the upper height of NH_3 concentration measurements (6 m); this difference was taken into account in the computation of ammonia flux using the micrometeorological gradient technique with NH_3 concentrations collected. Seasonal statistics of NH_3 concentrations are presented in Table 1(a).

The winter season had the lowest overall concentrations collected during each seasonal campaign with averages of $1.73 \pm 2.00\,\mu g\,m^{-3}$ at 2 m during daytime and $1.37 \pm 1.50\,\mu g\,m^{-3}$ during nighttime (Table 1(a)). Accordingly, winter season had the largest overall wind speeds: daytime wind speeds at the 10 m height ranged from 8.0 to $0.90\,m\,s^{-1}$ ($3.94\,m\,s^{-1}$ average) and nighttime 10 m wind speeds ranged from 6.20 to $0.10\,m\,s^{-1}$ ($2.50\,m\,s^{-1}$ average).

The fall season had the highest average NH_3 concentrations during daytime ($7.60 \pm 6.54\,\mu g\,m^{-3}$ at 2 m), as well as nighttime ($7.25 \pm 6.54\,\mu g\,m^{-3}$ at 2 m) (Table 1(a)). Spring and summer average concentrations were comparable and fell between the fall and winter averages.

Studies have shown strong correlations between air temperatures and ammonia concentration (Duyzer et al., 1989), suggesting temperature to be an important variable in influencing NH_3 volatilization from animal waste (Aneja et al., 2000, 2001b; Sommer, 1997; Aarnink et al., 1995). Fig. 2a displays the comparison of diurnal temperatures and NH_3 concentrations on a particular day (9 September 2001) during the measurement period. Overall, the diurnal relationship between temperature and NH_3 concentrations reflects typical near-surface diurnal inversion patterns in which as temperature increases (decreases), NH_3 concentrations also increases (decreases). During this measurement period frequent changes in the sign of NH_3 concentrations gradient and, hence, flux in the afternoon and night were observed, which are the result of the impact of multiple meteorological variables: temperature variation, wind speed variation from 0.90 to $5.0\,m\,s^{-1}$, wind direction variation from north to northeast, to east, and to southeast, and relative humidity variation between 98% and 70%. Likewise, a diurnal relationship between temperature and NH_3 concentrations became apparent throughout the measurement period in summer with NH_3 concentrations increasing with temperature, as shown in Fig. 2b, for one particular day representing the summer season.

Fig. 3 features a regression analysis between hourly averaged temperatures and NH_3 concentrations for all the seasons (measurement periods). This power

Table 1
Seasonal statistical analysis: (a) [NH_3] ($\mu g\,m^{-3}$) measured at two heights, 2 and 6 m; (b) average seasonal NH_3 deposition fluxes and estimated deposition velocity after limiting criteria applied (see Section 3); (c) average seasonal stability classification for estimated deposition velocity (where N = number of sampling days; n = number of measurements)

(a)

	Summer season (9–31 July 2002) [NH_3] ($\mu g\,m^{-3}$)		Spring season (26 April–16 May 2002) [NH_3] ($\mu g\,m^{-3}$)		Fall season (4–14 September 2001) [NH_3] ($\mu g\,m^{-3}$)		Winter season (4–5, 12–25 February 2002) [NH_3] ($\mu g\,m^{-3}$)	
	$N = 23$, $n = 292$		$N = 20$, $n = 225$		$N = 11$, $n = 109$		$N = 15$, $n = 124$	
	2 m	6 m	2 m	6 m	2 m	6 m	2 m	6 m
Daytime								
Average	4.69	4.90	5.69	5.53	7.60	8.44	1.73	1.63
Median	3.54	4.23	4.07	4.01	6.06	5.89	0.98	1.04
Standard deviation	4.75	3.75	4.71	4.59	6.54	7.45	2.00	1.69
Minimum	0.39	0.21	0.73	0.61	0.02	0.49	0.0	0.03
Maximum	41.71	27.45	35.82	39.87	34.30	34.31	10.79	8.65

	$N = 23$, $n = 187$		$N = 21$, $n = 164$		$N = 11$, $n = 80$		$N = 16$, $n = 135$	
	2 m	6 m	2 m	6 m	2 m	6 m	2 m	6 m
Nighttime								
Average	2.76	3.17	3.41	3.88	7.25	7.73	1.37	1.42
Median	1.88	2.32	2.59	2.92	5.11	5.48	0.91	0.94
Standard deviation	2.43	2.60	2.62	2.60	6.14	6.69	1.50	1.39
Minimum	0.50	0.34	0.0	0.74	0.0	0.46	0.02	0.04
Maximum	14.30	19.13	13.89	17.56	24.72	26.89	9.52	8.75

(b)

Season	NH_3 deposition fluxes[a] ($\mu g\ NH_3\,m^{-2}\,s^{-1}$)	NH_3 deposition velocity ($cm\,s^{-1}$)	
	Daily	Day	Night
Summer	−0.11 (±0.14) $N = 23$, $n = 135$	3.94 (±2.79) $N = 16$, $n = 85$	0.76 (±1.69) $N = 18$, $n = 50$
Spring	−0.11 (±0.15) $N = 21$, $n = 88$	2.85 (±2.01) $N = 11$, $n = 37$	0.62 (±1.04) $N = 15$, $n = 51$
Fall	−0.14 (±0.19) $N = 11$, $n = 57$	2.82 (±1.98) $N = 8$, $n = 34$	0.07 (±0.17) $N = 10$, $n = 23$
Winter	−0.02 (±0.03) $N = 15$, $n = 71$	2.41 (±1.92) $N = 9$, $n = 30$	0.19 (±0.27) $N = 12$, $n = 41$

(c)

	Stability classification for deposition ($cm\,s^{-1}$)			
	Summer	Spring	Fall	Winter
Unstable ($Ri < 0$)	4.42 (±2.65) $N = 12$, $n = 72$	3.03 (±1.66) $N = 6$, $n = 23$	3.58 (±1.59) $N = 5$, $n = 26$	3.00 (±1.87) $N = 8$, $n = 22$
Moderately stable ($0 \leqslant Ri < 0.14$)	2.37 (±2.32) $N = 12$, $n = 22$	2.14 (±1.95) $N = 9$, $n = 30$	0.88 (±0.60) $N = 3$, $n = 4$	0.50 (±0.54) $N = 12$, $n = 24$
Very stable ($Ri \geqslant 0.14$)	0.07 (±0.11) $N = 17$, $n = 41$	0.09 (±0.10) $N = 13$, $n = 35$	0.03 (±0.03) $N = 10$, $n = 27$	0.07 (±0.09) $N = 10$, $n = 25$

[a] Negative flux is depositing downward.

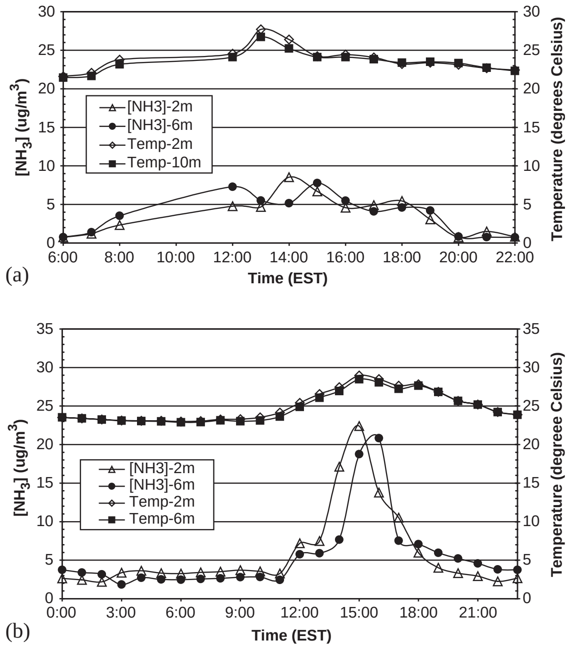

Fig. 2. Comparison of diurnal temperature pattern and diurnal NH_3 concentrations (a) fall season on 9 September 2001, which experienced dew and overcast skies during morning; (b) summer season on 14 July 2002, which experienced rain and overcast skies during morning with partly cloudy skies during afternoon.

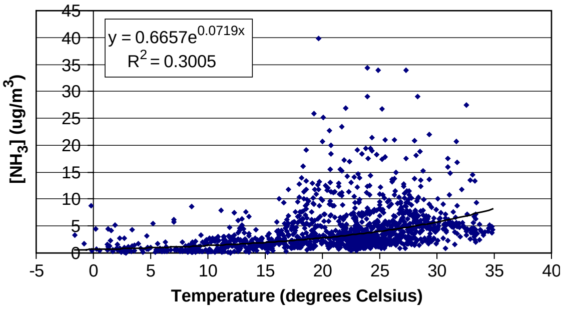

Fig. 3. Regression analysis between NH_3 concentrations ($\mu g\,m^{-3}$) at 6 m and temperature (degrees Celsius), yielding correlation coefficient $R^2 = 0.30$.

regression ($R^2 = 0.30$) reveals supporting evidence of temperature as a significant variable in influencing NH_3 volatilization from animal waste (Aneja et al., 2000, 2001a, b; Sommer, 1997; Aarnink et al., 1995); however, it is noted that the correlation coefficient is relatively low due to the various agricultural and environmental influences including motor vehicle exhaust from a nearby road (~0.32 km) surrounding the field site already discussed. Likewise, at higher temperatures the NH_3 concentrations are increasing, however displaying larger scatter, which could be a result of emission occurring at increasing temperature or the partitioning between aerosol and gas changes with temperature, or changes in Henry's Law coefficient. This analysis was further segregated into two sectors based on wind direction predominance with NH_3 concentrations: (1) northeast–southeast sector (45–135°) and (2) southwest–northwest sector (225–315°). The northeast–southeast sector displayed an increase in $R^2 = 0.38$ (supporting the influence of the swine lagoon effect), while the southwest–northwest sector showed a slight decrease in $R^2 = 0.29$. Regression analyses of daytime and nighttime ammonia concentrations and atmospheric conditions (wind speed, temperature, and relative humidity) during fall, winter, spring, and summer revealed statistically significant ($p < 0.001$) positive correlations, but with small R^2 values. Similarly, even when including autocorrelation in the regression model the other meteorological parameters were insignificant. These insignificant correlations between meteorological parameters and NH_3 concentrations are a result of a mixture of agricultural and environmental impacts surrounding the field site. Interaction between abrupt changes in wind direction in conjunction with wind speed and NH_3 concentrations are possible sources resulting in low correlations between ammonia concentrations and meteorological conditions.

The seasonal ammonia concentrations reveal that the largest average NH_3 concentrations were during the fall measurement campaign (Table 1(a)), while the highest maximum NH_3 concentrations were observed in summer at 2 m (41.71 $\mu g\,m^{-3}$) (Table 1(a)). The larger fall average concentrations are due to the lagoon irrigation practices used and relatively warm temperatures (25.11 ± 3.09 °C), whereas, lagoon irrigation was not applied during the other seasonal measurement campaigns. Based on the animal waste management plan used by the Dairy Educational Unit at the measurement filed site, lagoon liquid irrigation was applied to a field southeast of the air quality tower where a small grain overseed (wheat) was cultivated (see spray field, Fig. 1). A relatively small difference of 1.0–0.65 $\mu g\,m^{-3}$ exists between spring and summer average NH_3 concentrations during daytime and nighttime at the two heights (2 and 6 m).

In addition, since swine lagoons and housing barns were considered as dominant sources of ammonia gas at the research study site with respect to the prevailing winds, measurements were conducted during different wind directions. Although, wind directions fluctuated within each sampling intensive, predominant wind sectors became apparent in regards to NH_3 concentrations during daytime and nighttime conditions. During the fall measurement period, not only were the northeast and southeast wind directions dominant during daytime but also higher concentrations of ammonia occurred in

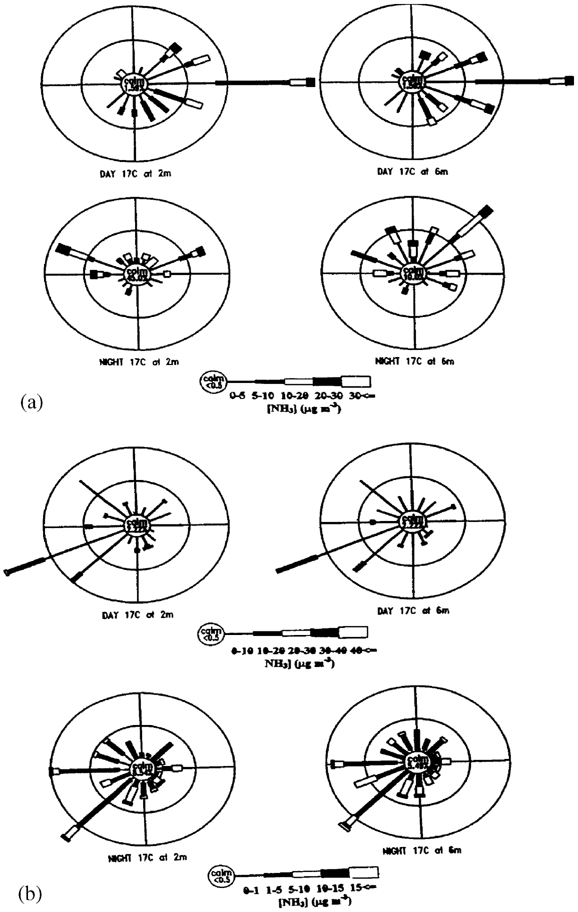

Fig. 4. Frequencies of ammonia concentration regime by wind direction during daytime and nighttime conditions for (a) fall season and (b) spring season.

the eastern wind sector due to the transport of NH_3 from a swine lagoon located east of the air quality tower (Fig. 4a). Conversely, during nighttime (fall) the higher ammonia concentrations occurred during the predominant northwest and northeast wind directions. During winter, the southwest wind direction was dominant with higher concentrations during daytime, while nighttime ammonia concentration frequencies dominated during southwest, west and northwest wind directions. Southwest and west wind directions display predominance in correlation with NH_3 concentrations during spring daytime and nighttime (Fig. 4b). Furthermore, summer measurement periods revealed southwest and west wind direction predominance in correlation with ammonia concentrations. The correlation between greater frequencies of NH_3 concentrations with winds southwest of the tower suggest the effects of environmental conditions (grazed fields as a result of dairy cows located south and southwest of the measurement site), while west wind directions show the effects of horse and chicken farms west of the tower.

4.2. Seasonal ammonia deposition fluxes

In this section, we present the seasonal averages and ranges of negative deposition fluxes calculated by the gradient method, which occurred when hourly concentration gradients ($\partial\bar{c}/z$) were positive and detectable. Since, the level detection limit (LDL) defined by the TEI Model 17C manual is 1 ppb ($\sim 0.7\,\mu g\,m^{-3}$); measurements collected and gradients calculated using ammonia concentrations below this LDL value have been excluded from estimated NH_3 seasonal fluxes and deposition velocities. Table 1(b) presents the statistical analysis (average and standard deviation) of seasonal NH_3 deposition fluxes (after limiting criteria based on v_{max} was applied to estimates of deposition velocities, see Section 3) based on hourly averaged fluxes, where N equals the number of sampling days and n equals the number of sampling hours, and negative flux implies downward flux or deposition. The direction and magnitude of flux change hourly, diurnally and seasonally, suggesting the effect of environmental, meteorological, and stability conditions, as well as irrigation applications (e.g. fall season). Nevertheless, consistently throughout each season, deposition mostly occurred during the late afternoon, evening, and the early morning hours (Fig. 5). It should be noted during the hours of 8:00–10:00 a.m., deposition is not reported due to daily span checks of the instruments, and therefore the number of samples during this time interval was relatively small and biased compared to the other measurement hours within each day. The results of the seasonal statistical analysis show smallest average negative fluxes in winter 2002, with hourly averaged deposition fluxes ranging from -0.14 to $\sim 0\,\mu g\,NH_3\,m^{-2}\,s^{-1}$ and an overall average of $-0.02 \pm 0.03\,\mu g\,NH_3\,m^{-2}\,s^{-1}$. Winter season was influenced by windy, cold, and dry conditions, which resulted in a large loss of

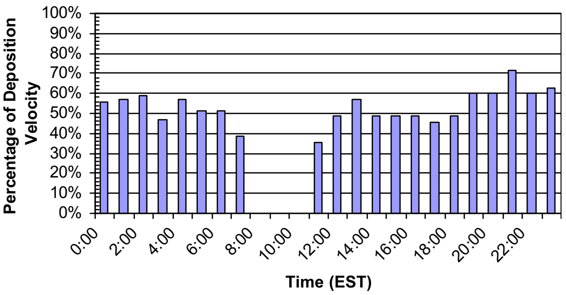

Fig. 5. Percentage of sampling days with deposition occurring as a function of time of day during all seasons (fall 2001, winter, spring, and summer 2002). Total number of sampling days equals 70.

samples restricted by the LDL. Spring and summer season-averaged deposition fluxes are about the same ($-0.11 \pm 0.15\,\mu g\ NH_3\,m^{-2}\,s^{-1}$), while the average of hourly fall fluxes of NH_3 is $-0.14 \pm 0.19\,\mu g\ NH_3\,m^{-2}\,s^{-1}$. The minimum (maximum deposition) fluxes in these seasons ranged from -1.16 to $-0.90\,\mu g\ NH_3\,m^{-2}\,s^{-1}$. Our estimated range is consistent with studies conducted in Europe where emission and deposition fluxes were estimated (Duyzer et al., 1987, 1992; Sutton et al., 1993, 1994). Among these, Erisman and Wyers (1993) observed NH_3 emission fluxes of 0–0.50 $\mu g\ NH_3\,m^{-2}\,s^{-1}$ during dry conditions and deposition fluxes of 0.0–0.45 $\mu g\ NH_3\,m^{-2}\,s^{-1}$ during wet conditions over two heathland sites located close to an extensive livestock production facility. Similarly, Duyzer et al. (1987) reported NH_3 fluxes in the range of –0.19 to –0.03 $\mu g\ NH_3\,m^{-2}\,s^{-1}$ over dry heathland.

4.3. Seasonal ammonia deposition velocities

Under a wide range of wind and atmospheric stability conditions gradient measurements were made at two heights (2 and 6 m) over a natural grass surface near an intensively managed swine production facility. The method used for estimating dry deposition velocity is described in Section 3. Estimating only the aerodynamic resistance, r_a, the maximum possible deposition velocity ($v_{max} = r_a^{-1}$) has been used to validate estimated deposition velocities with measured meteorological conditions, where $-v_{max}$ is the maximum possible emission rate (Wyers and Erisman, 1998). However, this is based on the questionable assumption that the resistance for the transfer of ammonia is identical to that of momentum. Therefore, we applied a relaxed criterion as an alternative to the assumption of $v_d < v_{max}$, where we consider from the bulk transfer method and considerable experimental evidence (Arya, 1977, 2001) of heat and mass being transferred more efficiently than momentum under unstable and convective conditions. Our relaxed criterion for acceptable values of v_d is that $v_d \leqslant 2v_{max}$ under unstable and convective conditions and $v_d \leqslant v_{max}$ under stable conditions. Seasonal assessments of v_{max} for all hourly samples of deposition flux show seasonal variations in the v_{max} values due to seasonal influences on wind speed and stability.

Estimates of v_d that did not meet the above relaxed criterion were considered to have large uncertainty in the estimated v_d, and excluded from any further analysis. Overall, the numbers of hourly flux and deposition velocity estimates retained for each season are given in Table 1(b). They meet our relaxed criterion based on v_{max} and are considered to be more reliable than those excluded. It is possible that larger fluxes and deposition velocities represented in the latter category were subjective to other environmental factors, possibly atmospheric chemical reactions. However, deposition velocities were calculated based on a conserved species approach and not atmospheric chemical reactions involving gases such as HNO_3, HCl, and acidic aerosols (Duyzer et al., 1994; Andersen et al., 1999; Pryor et al., 2001).

Seasonal averages shown in Table 1(b) represent an average of all hourly NH_3 deposition velocities over the number of observation days and are further divided into average daytime and nighttime deposition velocities. Day and night hours were based on sunrise and sunset times within each season. Summer measurements yielded the largest average daytime deposition velocity of $3.94 \pm 2.79\,cm\,s^{-1}$ while winter season gave the lowest $v_d = 2.41 \pm 1.92\,cm\,s^{-1}$. The average values for daytime v_d during spring and fall seasons are about the same ($2.8 \pm 2.0\,cm\,s^{-1}$). Conversely, nighttime estimates of v_d are much smaller, especially during fall ($0.07 \pm 0.17\,cm\,s^{-1}$) and winter ($0.19 \pm 0.27\,cm\,s^{-1}$) seasons. These daytime and nighttime differences are largely due to different stability conditions. The highest average deposition velocities were generally observed during unstable and near-neutral conditions and lowest values during very stable conditions (Table 1(c)).

4.4. Turbulence and stability effects

Micrometeorological variables including wind speed at 10 m or friction velocity, atmospheric stability, surface heat flux, and moisture flux affect turbulence transfer through the surface layer. Friction velocity, a measure of mean wind shear and shear-generated turbulence near the surface in both the canopy layer and above the canopy homogeneous surface layer is noted to be well correlated with dry deposition velocity and one of the most important variables (Arya, 1999). A regression analysis reveals that a strong relationship exists between friction velocity and estimated deposition velocities. The results of this procedure are plotted in Fig. 6 based on the combination of seasonal data stratified with respect to stability (unstable, moderately stable, and very stable categories) with corresponding regression equation and R^2 values. All seasons display strong correlations with R^2 values of 0.74, 0.54, and 0.86 based on power regression curves for unstable, moderately stable, and very stable conditions, respectively. The forms of these power regression relations are given in Fig. 6 for the three stability regimes, where y represents deposition velocity in $m\,s^{-1}$ and x represents friction velocity in $m\,s^{-1}$. Note that deposition velocities are much smaller during very stable conditions.

Andersen et al. (1999) utilized the term *relative net deposition* to facilitate any incongruity between the quantification of high and low deposition velocities. Relative net deposition is the ratio of the measured net deposition velocity to the maximum estimated deposition velocity, i.e. v_d/v_{max}. A relative deposition velocity

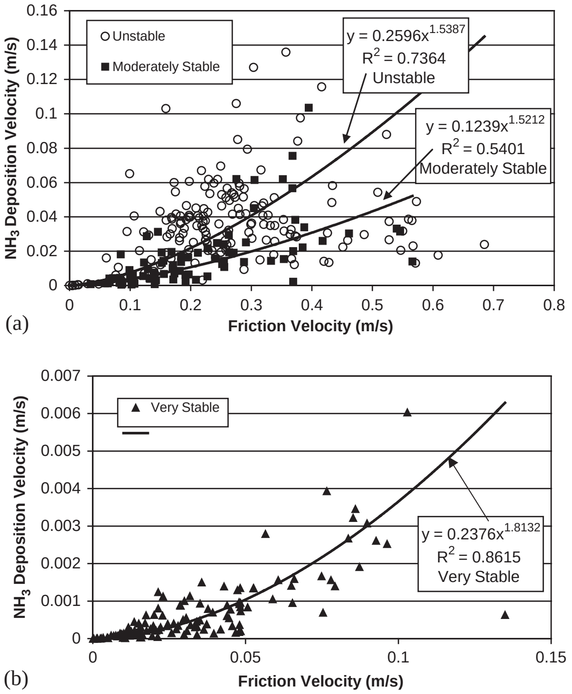

Fig. 6. Regression relationship between NH_3 deposition velocity (v_d) and friction velocity (u_*) based on stability classes: (a) unstable, moderately stable, and (b) very stable.

near zero would signify a high surface resistance value of r_c, whereas a relative deposition velocity near one or larger would signify a low r_c, since v_d is large. Diurnal (day and night) and seasonal dependence of the ratio v_d/v_{max} as a function of u_* was investigated. Most nighttime values are clustered between friction velocities of 0–0.3 $m\,s^{-1}$, while the distribution of daytime ratios is scattered over a larger range of $u_* = 0.7\,m\,s^{-1}$. However, the ratio v_d/v_{max} does not appear to depend on u_* and more values larger than one occur during daytime in warm seasons, because of the relaxed criterion $v_d \leqslant 2v_{max}$ used for unstable conditions (Phillips, 2003).

5. Conclusions

Measurements of near-surface concentration gradient are used to estimate ammonia fluxes and dry deposition velocities utilizing the micrometeorological gradient method over a natural grass surface on an animal farm site over a wide range of meteorological conditions encountered during different seasons. Diurnal and seasonal variations of ammonia flux and dry deposition velocity are investigated, using data from four seasonal campaigns. Deposition and emission occur, both on daily and seasonal scales.

Fall average NH_3 concentrations were generally the highest with little difference between daytime (7.60 $\mu g\,m^{-3}$) and nighttime (7.25 $\mu g\,m^{-3}$) average values at 2 m. The winter season had the lowest average concentrations with some difference between daytime (1.73 $\mu g\,m^{-3}$) and nighttime (1.37 $\mu g\,m^{-3}$) values at 2 m. Average NH_3 concentrations during spring and summer seasons show much larger differences between daytime (5.69 and 4.69 $\mu g\,m^{-3}$) and nighttime (3.41 and 2.76 $\mu g\,m^{-3}$) average values. A maximum hourly averaged concentration of 41.71 $\mu g\,m^{-3}$ occurred during the summer.

Frequencies of NH_3 concentrations by wind direction were also investigated. During the fall measurement period, northeast and southeast wind directions became dominant during daytime, but higher concentrations of ammonia occurred in the eastern wind sector due to the transport of NH_3 from a swine lagoon located east of the air quality tower. During nighttime (fall) higher NH_3 concentrations occurred during the predominant northwest and northeast wind directions. Furthermore, winter, spring, and summer measurement periods revealed southwest and west wind direction predominance in correlation with NH_3 concentrations. The correlation between greater frequencies of NH_3 concentrations with winds from southwest of the tower suggest the effects of environmental conditions (grazed fields as a result of dairy cows located south and southwest of the measurement site), while west wind directions show the effects of horse and chicken farms west of the tower.

The direction and magnitude of fluxes change diurnally and seasonally, suggesting the effect of environmental, meteorological, and stability conditions, as well as irrigation applications (e.g. fall season). Throughout each season the majority of upward fluxes occurred mid-day (11:00 a.m.–3:00 p.m.), while deposition occurred during the afternoon, evening, and the early morning hours. Seasonal statistical analysis shows that the largest average deposition flux occurred in the fall 2001 measurement campaign, reflecting the lagoon spray/irrigation practices used during that period.

Deposition velocity is defined here as the ratio of the deposition flux to mean concentration at 2 m. Summer measurements estimate the largest average daytime deposition velocity of $3.94 \pm 2.79\,cm\,s^{-1}$. Nighttime summer season estimates of v_d are slightly larger ($0.76 \pm 1.69\,cm\,s^{-1}$) than spring nighttime estimates ($0.62 \pm 1.04\,cm\,s^{-1}$). Fall nighttime average deposition velocities ($0.07 \pm 0.17\,cm\,s^{-1}$) are considerably lower than other seasonal estimates. The highest average deposition velocities were generally observed during unstable conditions while very stable conditions (low-level turbulence) yield the lowest average deposition velocities. A nonlinear regression analysis revealed a strong relationship between ammonia dry deposition velocity (v_d) and the friction velocity (u_*), reiterating related research findings of friction velocity as the most important variable affecting dry deposition velocity. The regression relation between v_d and u_*, however, depends on the stability regime. The findings of this research can be used for parameterizing dry deposition of ammonia on natural surfaces in practical applications of atmospheric dispersion, and deposition modeling to eastern North Carolina and, possibly, eastern United States.

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References

Aarnink, A.J.A., Keenm, A., Metz, J.H.M., Speelman, L., Verstegen, M.W.A., 1995. Ammonia emission patterns during the growing periods of hogs housed on partially slatted floors. Journal of Agricultural Engineering Research 62, 105–116.

Andersen, H.V., Hovmand, M., Hummelshoj, P., Jensen, N.O., 1999. Measurements of ammonia concentrations, fluxes and dry deposition velocities to a spruce forest 1991–1995. Atmospheric Environment 33, 1367–1383.

Aneja, V.P., Murthy, A.B., 1994. Monitoring deposition of nitrogen-containing compounds in a high-elevation forest canopy. Journal of the Air and Waste Management Association 44, 1109–1115.

Aneja, V.P., Murray, G.C., 1998a. An overview of program GNATS (GEOPONIC Nutrient and Trace Gas Study). Proceedings of the First International Nitrogen Conference, Noordwijkerhout, The Netherlands, 23–27 March.

Aneja, V.P., Murray, G.C., Southerland, J., 1998b. Atmospheric nitrogen compounds: emissions, transport, transformation, deposition, and assessment. Air and Waste Management Association's Magazine for Environmental Managers (EM), 22–25 April.

Aneja, V.P., Murthy, A.B., Battye, W., Battye, R., Benjey, W.G., 1998c. Analysis of ammonia and aerosol concentrations and deposition near the free troposphere at Mt. Mitchell, NC, U.S.A. Atmospheric Environment 32, 353–358.

Aneja, V.P., Chauhan, J.P., Walker, J.T., 2000. Characterization of atmospheric ammonia emissions from swine waste storage and treatment lagoons. Journal of Geophysical Research 105, 11535–11546.

Aneja, V.P., Roelle, P.A., Murray, G.C., Southerland, J., Erisman, J.W., Fowler, D., Asman, W.A.H., Patnif, N., 2001a. Atmospheric nitrogen compounds II: emissions, transport, transformation, deposition and assessment. Atmospheric Environment 35, 1903–1911.

Aneja, V.P., Bunton, B., Walker, J.T., Malik, B.P., 2001b. Measurement and analysis of atmospheric ammonia emissions from anaerobic lagoon. Atmospheric Environment 35, 1949–1958.

Arya, S.P., 1977. Suggested revisions to certain boundary layer parameterization schemes used in atmospheric circulation models. Monthly Weather Review 105, 215–227.

Arya, S.P., 1995. Atmospheric boundary layer and its parameterization. In: Cermak, J.E., Davenport, A.G., Plate, E.J., Viegas, D.X. (Eds.), Wind Climate in Cities. Kluwer Academic Publishing, Dordrecht, The Netherlands, pp. 41–66.

Arya, S.P., 1999. Air Pollution Meteorology and Dispersion. Oxford University Press, New York, NY.

Arya, S.P., 2001. Introduction to Micrometeorology 2nd Edition. Academic Press, San Diego, CA.

Asman, W.A.H., 1998. Factors influencing local dry deposition of gases with special reference to NH_3. Atmospheric Environment 32, 415–421.

Asman, W.A.H., van Jaarsveld, J.A., 1992. A variable-resolution transport model applied for NH_X in Europe. Atmospheric Environment 26A, 445–464.

Asman, W.A.H., Sutton, M.A., Schjorring, J.K., 1998. Ammonia: emission, atmospheric transport and deposition. New Phytologist 139, 27–48.

Battye, R., Battye, W., Overcash, C., Fudge, S., Benjey, W.G., 1994. Development and selection of ammonia emission factors. Final Report prepared for US Environmental Protection Agency Office of Research and Development, Washington, DC.

Beljaars, A.C.M., Holtslag, A.A.M., 1991. Flux parameterization over land surfaces for atmospheric models. Journal of Applied Meteorology 30, 327–341.

Businger, J.A., 1986. Evaluation of the accuracy with which dry deposition velocity can be measured with current micrometeorological techniques. Journal of Applied Meteorology 25, 1100–1124.

Chimka, C.T., Galloway, J.N., Cosby, B.J., 1997. Ammonia and the Chesapeake Bay Airshed. Stac Publication 97-1, pp. 1–49.

Ding, F., Arya, S.P., Lin, Y.-L., 2001. Large-eddy simulations of the atmospheric boundary layer using a new subgrid-scale model. II. Weakly and moderately stable cases. Environmental Fluid Mechanics 1, 49–69.

Division of Air Quality (DAQ), 1997. Assessment plan for atmospheric nitrogen compounds: emissions, transport, transformation, and deposition. Draft Report, N.C. Department of Environment, Health and Natural Resources.

Duyzer, J., Bouman, A.M.H., Diederen, H.S.M.A., Van Aalst, R.M., 1987. Measurement of dry deposition velocities of

NH_3 and NH_4^+ over natural terrains. Report R 87/273. MT-TNO, Delft, The Netherlands.

Duyzer, J.H., Verhagen, H.L.M., Erisman, J.W., 1989. The deposition of acidifying substances at the Asselsche Heide. MT-TNO Report R 89/029, Delft, The Netherlands (in Dutch).

Duyzer, J.H., Verhagen, H.L.M., Westrate, J.H., Bosveld, F.C., 1992. Measurement of the dry deposition flux of NH_3 on to coniferous forest. Environmental Pollution 75, 3–13.

Duyzer, J.H., Weststrate, J.H., Beswick, K., Gallagher, M., 1994. Measurements of the dry deposition flux of sulphate and nitrate aerosols to the Speuderbos using micrometeorological methods. TNO Report R 94/255, Delft, Holland.

Erisman, J.W., Wyers, G.P., 1993. Continuous measurements of surface exchange of SO_2 and NH_3: implications for their possible interaction in the deposition process. Atmospheric Environment 27A, 1937–1949.

Hansen, B., Nornberg, P., Rasmussen, K.R., 1998. Atmospheric ammonia exchange on a heathland in Denmark. Atmospheric Environment 32, 461–464.

Hicks, B.B., 1986. Measuring dry deposition: a reassessment of the state of the art. Water, Air, and Soil Pollution 30, 75–90.

Jaeschke, W., Dierssen, J.P., Gunther, A., Schumann, M., 1998. Phase partitioning of ammonia and ammonium in a multiphase system studied using a new vertical wet denuder technique. Atmospheric Environment 32, 365–371.

North Carolina Department of Agriculture (NCDA), 1998. Livestock Report, Raleigh.

North Carolina Department of Environment and Natural Resources (NCDENR), (1999). Division of air quality. Status Report on Emissions and Deposition of Atmospheric Nitrogen Compounds from Animal Production in N.C., Raleigh, NC, 7 June 1999.

Phillips, S.B., 2003. Measurements, modeling, and analysis of fluxes of nitrogen compounds. Ph.D. Dissertation, Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC.

Pryor, S.C., Barthelmie, R.J., Sorensen, L.L., Jensen, B., 2001. Ammonia concentrations and fluxes over a forest in the Midwestern USA. Atmospheric Environment 35, 5645–5656.

Roelle, P.A., Aneja, V.P., O'Connor, J., Robarge, W., Kim, D.S., Levine, J.S., 1999. Measurement of nitrogen oxide emissions from an agricultural soil with a dynamic chamber system. Journal of Geophysical Research 104, 1609–1619.

Roelle, P.A., 2001. Oxidized and reduced biogenic nitrogen compound emissions into the rural troposphere: characterization and modeling. Ph.D. Dissertation, Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC.

Sims, J.T., Wolf, D.C., 1994. Poultry waste management: agricultural and environmental issues. Advances in Agronomy 52, 1–83.

Sommer, S.G., 1997. Ammonia volatilization from farm tanks containing anaerobically digested animal slurry. Atmospheric Environment 31, 863–868.

State Climate Office of North Carolina, 2002. AgNet (Lake Wheeler) Horticultural Crops Research Station, www.nc-climate.ncsu.edu/.

Sutton, M.A., Fowler, D., Mocrieff, J.B., 1993. The exchange of atmospheric ammonia with vegetated surfaces I. Unfertilized vegetation. Quarterly Journal of the Royal Meteorological Society 119, 1023–1045.

Sutton, M.A., Asman, W.A.H., Schjorring, J.K., 1994. Dry deposition of reduced nitrogen. Tellus 46B, 255–273.

Thermo Environmental Instruments (TEI) Inc., 2000. Instruction Manual Model 17C: Chemiluminescence NH_3 Analyzer. http://www.thermoei.com/.

United States Environmental Protection Agency, 2000. National Air Pollutant Emission Trends Report. Document 454/R-00-002.

Wesley, M.L., Hicks, B.B., 1977. Some factors that affect the deposition rates of sulfur dioxide and similar gases on vegetation. Journal of the Air Pollution Control Association 27, 1110–1116.

Wyers, G.P., Erisman, J.W., 1998. Ammonia exchange over coniferous forest. Atmospheric Environment 32, 441–451.