8.2 MEASUREMENT AND MODELING OF AMMONIA FLUX AND DEPOSITION VELOCITY OVER NATURAL SURFACES IN EASTERN NORTH CAROLINA

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1. INTRODUCTION

Recent studies in Europe and the United States have reported increasing atmospheric concentration levels of ammonia (NH_3) and ammonium (NH_4^+), especially in regions of concentrated animal feeding operations (Aneja et al., 1998). 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. In NC, estimates reveal that the swine population contributes approximately 46% of the NH_3-N emissions. This estimate shows a direct link to the recent growth of the swine population in NC. NC is ranked second in the nation for swine production with approximately 10 million hogs in about 2500 hog farms located in eastern North Carolina (Aneja et al., 2000). Areas of scattered local sources (small, rural family farm operations) contribute a wide range of NH_3 emission and dry deposition. Likewise, many environmental problems result from atmospheric ammonia deposition, e.g., particulate matter formation, aquatic and terrestrial eutrophication, and odor emanation.

The primary objectives of this research are: (1) to measure vertical fluxes of ammonia and related dry deposition velocities from near-surface concentration gradient measurements over natural surfaces in eastern North Carolina 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; (4) quantify the fate of atmospherically deposited nitrogen during summer season in North Carolina terrestrial ecosystems (water and land); and (5) evaluate model assessments of atmospheric inputs (loading) into the Neuse River Estuary North Carolina allowing abatement strategies the means to address the reduction of nitrogen 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 North Carolina, where ammonia sources have increased very rapidly in recent years (DAQ, 1997).

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2. METHODS and MATERIALS

A series of seasonal field experiments of ammonia concentrations were conducted at the North Carolina State University Air Quality Educational Unit (USDA-ARS, Raleigh, NC). This site is a relatively flat, uniform and smooth site with grass or short vegetation, which is located near a small swine production facility. Two chemiluminescent analyzers, TEI Model 17C (TEI, 2004), were utilized in conjunction with a solenoid for each analyzer to alternate measurements between two elevations (2m and 6m). Hourly-averaged measurements of wind speed, wind direction and temperature were also measured at the same two heights (2m and 6m) using a 7m walk-up tower in the horizontally-homogeneous atmospheric surface layer. The general gradient method is used for estimating the vertical flux and the deposition velocity of ammonia (Businger, 1986; Hicks, 1986) (see Phillips et al., 2002; Phillips et al., 2004)).

3. RESULTS

3.1 *Seasonal NH_3 Concentrations: comparison with meteorological conditions*

The seasonal NH_3 concentrations reveal that the largest NH_3 concentrations were during the fall measurement campaign, while the highest maximum NH_3 concentration was observed in summer at 2m (41.71 μg m^{-3}). The larger fall average concentrations are due to the lagoon irrigation practices used and relatively warm temperatures (25.11 $\pm$ 3.09 ^{o}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. A relatively small difference of 1.0-0.65 μg m^{-3} exists between spring and summer average NH_3 concentrations during day and nighttime at the two heights (2m and 6m). The winter season had the lowest overall concentrations collected during each seasonal campaign with averages of 1.73 $\pm$ 2.00 μg m^{-3} at 2m during daytime; and 1.37 $\pm$ 1.50 μg m^{-3} during nighttime.

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 to 70%. Likewise, a diurnal relationship between temperature and NH_3

concentrations became apparent reflecting typical near-surface diurnal inversion patterns in which as temperature increases (decreases), NH_3 concentrations also increases (decreases). During the fall measurement period, not only were the northeast and southeast wind directions dominant during daytime but also, higher concentrations of NH_3 occurred in the eastern wind sector due to the transport of NH_3 from a swine lagoon located east of the air quality tower. The correlation between greater frequencies of NH_3 concentrations with winds southwest and west of the tower were observed during the winter, spring, and summer suggesting 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.

3.2 *Seasonal NH_3 Deposition Fluxes*

Seasonal averages and ranges of negative deposition fluxes calculated by the gradient method are presented, which occurred when hourly concentration gradients $\left(\partial \bar{c} / \partial z\right)$ were positive and detectable (Phillips et al., 2004). Since, the level detection limit (LDL) defined by the TEI Model 17C manual is 1 ppb (~0.7 μg 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 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 Phillips et al., 2004) 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. 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 ~0 μg-NH_3 m^{-2} s^{-1} and an overall average of -0.02 $\pm$ 0.03 μg-NH_3 m^{-2} s^{-1}. Spring and summer season-averaged deposition fluxes are about the same (-0.11 $\pm$ 0.15 μg-NH_3 m^{-2} s^{-1}), while the average of hourly fall fluxes of NH_3 is -0.14 $\pm$ 0.19 μg-NH_3 m^{-2} s^{-1}. The minimum (maximum deposition) fluxes in these seasons ranged from -1.16 to -0.90 μg-NH_3 m^{-2} s^{-1}.

3.3 Seasonal Ammonia Deposition Velocities

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 $v_d \leq 2\ v_{max}$ under unstable and convective conditions and $v_d \leq v_{max}$ 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. Seasonal averages shown in Table 2 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. They meet our relaxed criterion based on v_{max} and are considered to be more reliable than those excluded.

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 2).

	NH_3 Deposition Fluxes* (μg-NH_3 m^{-2} s^{-1})	NH_3 Deposition Velocity (cm s^{-1})	
Season	***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

* Negative flux is depositing downwards.

Table 1. Average seasonal NH_3 deposition fluxes and estimated deposition velocity where N=number of sampling days; n=number of measurements]..

3.4 Turbulence and Stability Effects

Micrometeorological variables including wind speed at 10m 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 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.

	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≤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≥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

Table 2. Average seasonal Stability Classification for estimated deposition velocity [where N=number of sampling days; n=number of measurements].

3.5 Comparisons between Observations and Model Predictions: Concentration and Dry Deposition

In this study we utilize the United States Environmental Protection Agency's Models-3/Community Multiscale Air Quality (CMAQ) modeling system on a regional scale for North Carolina for predicting concentration amounts, and deposition of nitrogen species. Although, modeled concentrations were less than observed concentrations (except for NO_Y), a diurnal trend appeared for each species with consistent peaks featured over the diurnal period. Moreover, a linear regression analysis and corresponding R^2 values displayed a strong correlation between CMAQ simulations and observations. A process budget analysis (production and removal evaluation) of NO, NO_2, and NO_Y was conducted employing CMAQ. Model evaluations depicted the model's capabilities to describe vertical concentration profiles and physical/chemical vertical exchange processes effectively.

The nitrogen species production and removal mechanisms were evaluated to quantify the total nitrogen budget (dry and wet deposition processes) for North Carolina. CMAQ predicted NO and NO_2 (cumulatively) to contribute approximately 20.0 $\mu g\ N\ m^{-2}\ hr^{-1}$, and NH_3 to contribute 34.2 ± 57.9 $\mu g\ N\ m^{-2}\ hr^{-1}$. HNO_3 contributed the largest dry deposition of nitrogen in NC, 35.2 ± 16.0 $\mu g\ N\ m^{-2}\ hr^{-1}$. The average wet deposition fluxes were 37.3 ± 19.7 $\mu g\ N\ m^{-2}\ hr^{-1}$ and average NO_3^- deposition rates were estimated at 40.6 ± 11.8 $\mu g\ N\ m^{-2}\ hr^{-1}$. NH_3 contributed 38% of the total dry deposition component and NH_4^+ contributed 48% of the total wet deposition component. The distributions of deposition among wet and dry were generally equal with 46% wet deposition and 53% dry deposition. Approximately 50% of NH_X or NO_3^- is due to dry and wet processes occurring during the summer season in NC.

In addition, model assessments of atmospheric inputs (nitrogen loading) into the Neuse River Estuary in North Carolina revealed NH_3 was the largest contributor to dry deposition fluxes in the Neuse River basin, making up approximately 47% of the total. This large NH_3 deposition contribution is consistent with increasing intensively managed agriculture (swine and poultry facilities) in eastern NC. Future research should consider regional air quality models, with suitable modifications incorporating ammonia chemistry, for simulating some interesting episodes of transport, transformation and deposition of ammonia in eastern North Carolina. Such simulations will be useful for assessing the possible impacts of ammonia sources on the spatial variation of ammonia concentration and deposition flux, and their role in overenrichment of North Carolina water bodies (rivers and estuaries). Likewise, a credible extrapolation of dry deposition velocities of ammonia could be developed for forest areas which cover a substantial portion of eastern North Carolina.

The second largest dominant chemical species is HNO_3, contributing an average of 36.0 ± 16.1 $\mu g\ N\ m^{-2}\ hr^{-1}$, followed by NO_2 (17.1 ± 7.32 $\mu g\ N\ m^{-2}\ hr^{-1}$) and NO (5.6 ± 3.75 $\mu g\ N\ m^{-2}\ hr^{-1}$). The mean total dry deposition was calculated to be 111.2 $\mu g\ N\ m^{-2}\ hr^{-1}$ (1750 $kg\ N\ hr^{-1}$; 15,340 $Mg\ N\ yr^{-1}$). This dry deposition estimation shows a relative contribution of 50% to the total (wet + dry) nitrogen deposition when compared to Whitall and Pearl's (2001) estimation of wet deposition annual mean total (956 $mg\ N\ m^{-2}\ yr^{-1}$; 15,026 $Mg\ N\ yr^{-1}$).

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