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Atmospheric transport and wet deposition of ammonium in North Carolina

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Abstract

Wet deposition and transport analysis has been performed for ammonium (NH_4^+) in North Carolina, USA. Multiple regression analysis is employed to model the temporal trend and seasonality in monthly volume-weighted mean NH_4^+ concentrations in precipitation from 1983 to 1996 at six National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites. A significant ($p < 0.01$) increasing trend beginning in 1990, which corresponds to an annual concentration increase of approximately 9.5%, is detected at the rural Sampson County site (NC35), which is located within a densely populated network of swine and poultry operations. This trend is positively correlated with increasing ammonia (NH_3) emissions related to the vigorous growth of North Carolina's swine population since 1990, particularly in the state's Coastal Plain region. A source–receptor regression model, which utilizes weekly NH_4^+ concentrations in precipitation in conjunction with boundary layer air mass back trajectories, is developed to statistically test for the influence of a particular NH_3 source region on NH_4^+ concentrations at surrounding NADP/NTN sites for the years 1995–1996. NH_3 emissions from this source region, primarily evolving from swine and poultry operations, are found to increase NH_4^+ concentration in precipitation at sites up to ≈ 80 km away. At the Scotland County (NC36) and Wake County (NC41) sites, mean NH_4^+ concentrations show increases of at least 44% for weeks during which 25% or more back trajectories are influenced by this source region.

Keywords: Ammonium; Ammonia; Multiple regression; Wet deposition; Back trajectories; Source–receptor

1. Introduction

1.1. Background

Interest in atmospheric ammonia (NH_3) has increased substantially over the past several years as its roles in both atmospheric chemistry and nutrient cycling have become better understood. Atmospheric NH_3 is an abundant alkaline responsible for the neutralization of a substantial fraction of strong acids in the atmosphere (Asman et al., 1982). The adverse effects of excess reduced nitrogen in forest systems are well documented (Nihlgard, 1985; Reuss and Johnson, 1986). Atmospheric NH_x (NH_x = ammonia + ammonium + amines) is now thought to be an important component of total atmospheric nitrogen (TAN) input to nitrogen-sensitive ecosystems such as coastal and estuarine waters (Aneja et al., 1998; Aneja, 1997). Such systems may receive nitrogen by direct wet and dry atmospheric deposition, as well as surface and ground water transport. North Carolina's Albemarle-Pamlico Sound system is one of many North American, European and Asian estuarine and coastal ecosystems impacted by atmospheric nitrogen deposition which are exhibiting advanced signs of eutrophication in the form of recurring toxic and non-toxic phytoplankton

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blooms (Paerl, 1991,1995; Paerl et al., 1993). Such phytoplankton blooms are associated with varying degrees of oxygen depletion in water and fish losses (Paerl, 1995).

Atmospheric nitrogen deposition may be responsible for a substantial amount of nitrogen input across North Carolina's Coastal Plain region, owing to NH_3 emissions from the large number of animal operations across the region. Such sources will have a local impact on NH_3 and NH_4^+ deposition, and densely populated groups of such sources may have a regional influence on NH_4^+ deposition. The purpose of this study is to investigate the temporal characteristics of wet NH_4^+ deposition across North Carolina and to investigate the possible influence of NH_3 derived from a region of Coastal Plain animal operations on wet NH_4^+ deposition across the state. The analysis presented uses multiple linear regression to estimate the seasonality and long term trend in NH_4^+ concentration in precipitation at six National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites across North Carolina. Ammonium transport analysis is performed to investigate the influence of NH_3 emissions in southeastern North Carolina, where livestock population density is the largest, on NH_4^+ concentration in precipitation across the state. This is accomplished using boundary layer air mass back trajectory analysis coupled with multiple linear regression modeling. Incorporation of a weekly *influence factor* into a linear regression model allows for a formal statistical test of this source region's influence.

1.2. Ammonia emissions

Many studies have shown domestic animals to be the largest global source of atmospheric NH_3, with emission estimates ranging from 20–35 Tg N yr^{-1} (Schlesinger and Hartley, 1992; Warneck, 1988). Nitrogen emission estimates for the state of North Carolina (NC) show domestic animals to be the largest statewide contributor of NH_3, with swine operations present as the primary domestic animal source (Wooten, 1997; Aneja, 1997). Swine operations account for approximately 48% (68,450 t yr^{-1}, NH_3–N) of all North Carolina NH_3 emissions and approximately 21% of total nitrogen emissions.

Prior to 1990, the number of hogs in the state was relatively stable at near 2.5 million, however, this number began to rapidly increase within the period 1989–1990 (NCDA, 1998). In 1996, North Carolina contained approximately 9.3 million hogs, roughly 93% of which were located in the Coastal Plain region shown in Fig. 1. Area I in this figure, designated by shading, is defined as the six individual NC counties with the largest hog population densities. This collection of counties has an average hog population density of ~ 528 hogs km^{-2}. The average county hog population density for the remaining Coastal Plain is ~ 65 hogs km^{-2}. Area I contains approximately 66% of the Coastal Plain hog population and only 17% of the total Coastal Plain land area. Area I also contains approximately 68% of the Coastal Plain's domestic turkey population. These factors make area I a region of strong NH_3 emission relative to the rest of the state. Table 1 shows estimated area I NH_3 emissions by domestic animal type. Swine operations account for 77% of total NH_3 emissions from domestic animals within area I. Animal population statistics used in this study were supplied by the North Carolina Department of Agriculture (NCDA, 1998). Emissions are based on emission factors given by Battye et al. (1994).

1.3. Atmospheric ammonia

Estimates of the atmospheric lifetime of NH_3 range from approximately 0.5 h to 5 d (Fowler et al., 1997; Aneja et al., 1998). This short lifetime is the result of rapid gas-to-particle conversion of NH_3 to NH_4^+ and deposition of NH_3 to natural surfaces, particularly wet surfaces and vegetation which have low NH_3 compensation points. Once into the atmosphere, NH_3 which is not dry deposited or scavenged by raindrops will undergo conversion to NH_4^+ aerosol. The lifetime of NH_4^+ aerosol is typically 5–10 d (Crutzen, 1983). The rate of this conversion, which is largely unknown, will have an important bearing on the regional impact of NH_3 sources or source regions such as area I in this study. If this conversion proceeds slowly, area I emissions will primarily be deposited locally; thus, less NH_4^+ will be made available for long-range transport.

Conversion of NH_3 to NH_4^+ aerosol depends on the concentrations of strong acids and water vapor in the atmosphere. Ammonia reacts with sulfuric, nitric, and hydrochloric acids to form ammonium sulphate, ammonium bisulphate, ammonium nitrate and ammonium chloride aerosols (RGAR, 1997; INDTE, 1994; Finlayson-Pitts and Pitts, 1986). Ammonium aerosol formed in these reactions can exist as a solid particle or a liquid droplet depending on relative humidity (Finlayson-Pitts and Pitts, 1986). While the principal chemical transformation of NH_3 in the atmosphere is incorporation into NH_4^+ aerosol, approximately 10% is oxidized via the hydroxyl radical (OH) (Roberts, 1995).

1.4. Wet removal processes

The processes by which gases and aerosols are removed by precipitation can be divided into in-cloud and below-cloud regimes. The below-cloud processes include inertial removal by precipitation and diffusive removal on precipitation (Twomey, 1977). The in-cloud processes which govern wet deposition of aerosols and gases include inertial removal by cloud drops, nucleation, and diffusion to cloud drops (Twomey, 1977). It is generally agreed that in-cloud removal processes are more efficient

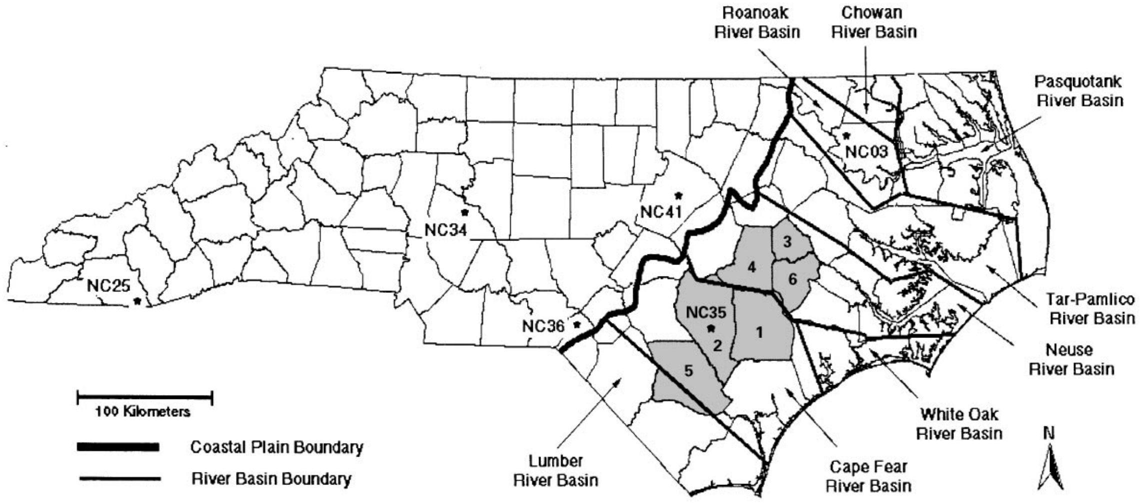

Fig. 1. NADP/NTN sites (*), area I NH_3 source region, and Coastal Plain river basins. The shaded area represents area I, a region defined as having an average hog population density of $\sim$ 528 hogs km^{-2}. Numbers within area I represent the following individual counties with corresponding estimated hog population densities (hogs km^{-2}): (1) Duplin County, 991; (2) Sampson County, 735; (3) Greene County, 503; (4) Wayne County, 349; (5) Bladen County, 316; and (6) Lenoir County, 274.

than below-cloud processes (Twomey, 1977; Asman, 1995). This is due to the large total surface area of droplets within the cloud compared to raindrops below cloud base. The contribution of below-cloud processes should not be ignored, however, especially in the case where the concentration of the compound of interest is larger in air below cloud base compared to the concentration within the cloud. It should be noted that some portion of the NH_4^+ measured in precipitation is the result of dry deposition of NH_4^+ aerosol to the precipitation collector. It is also important to point out that a fraction of the NH_4^+ measured in rainfall originates as NH_3 gas which is wet and dry deposited to the precipitation collector, resulting in the formation of NH_4^+ when NH_3 reacts with water (Warneck, 1988).

Table 1
Estimated area I NH_3–N emissions from domestic animals for the years 1996–1997[a]

Animal	NH_3–N emissions (t yr^{-1})
Hogs	47,679
Turkeys	9,585
Broilers	2,435
Cattle	2,154
All Chickens	181

[a] NH_3–N tons $= \frac{14}{17}$(NH_3 tons). Emissions calculated using emission factors given by Battye et al. (1994). Animal population statistics were provided by the North Carolina Department of Agriculture (NCDA, 1998). Calculations reflect hog population as of 1 December 1996; turkey population for 1996; cattle population as of 1 January 1997; broiler population for 1996; chicken population as of 1 December 1996. Emissions from turkeys and broilers were calculated by dividing the total population by the average number of flocks per year, 5.75 for broilers and 3.5 for turkeys.

2. Methods

2.1. Data selection

Precipitation chemistry data used in this study was provided by the National Atmospheric Deposition Program/National Trends Network, a nationwide precipitation collection network which began in 1978 and now operates over 200 sites (NADP/NTN, 1998). NADP/NTN samples are collected at 9:00 a.m. every Tuesday and sent to the Illinois State Water Survey, Central Analytical Laboratory (CAL) for chemical analysis (Peden, 1986). All samples are subject to the same field handling protocol and analytical procedures at CAL.

Only species concentrations in precipitation were used in this study. The term precipitation includes liquid, solid and mixed phase. Additionally, only samples that were considered valid and complete by NADP/NTN standards were used. Information on the data validation and completeness criteria used in this analysis can be found at the NADP/NTN website: *http://nadp.sws.uiuc.edu* (NADP/NTN, 1998). This study also employed the use of NADP/NTN daily precipitation information. The Rowan County (NC34) and Wake County (NC41) sites should be considered suburban. The remaining sites are located in rural areas. Fig. 1 shows the general location of the six NADP/NTN sites used in this study.

2.2. Trends analysis

Given the drastic increase in NH_3 emissions within area I beginning during the period 1989–1990, we hypothesize that a positive trend in NH_4^+ concentration in precipitation should be present at site NC35, located within area I, beginning in 1990 and that this trend may also be present at additional sites. To test this hypothesis, multiple linear regression is used to illustrate seasonality and trend in 14 yr worth of monthly volume-weighted mean NH_4^+ concentrations in precipitation. The 14 yr record is split into two periods. Period 1 includes the years 1983–1989 and period 2 includes the years 1990–1996. This was done in an effort to facilitate the correlation of any increasing NH_4^+ trends during period 2 with the growth of the North Carolina swine industry and the resulting increase in area I NH_3 emissions beginning in 1990. Complete analyses were performed for both periods at all sites.

Multiple linear regression analysis to investigate the temporal variation of precipitation chemistry has been widely used in the past (Buishand et al., 1988; Dana and Easter, 1987; MAP3S/RAINE, 1982). The present analysis employs the following regression model for separate analysis of both 7 yr periods at all sites:

$$Y_i = a_0 + a\cos(2\pi i/12 - \phi) + bi + cP_i + e_i,$$
$$i = 1, \ldots, 12N. \tag{1}$$

where N represents the number of years in the time series ($N = 7$). In this case, Y_i is the natural logarithm of the volume-weighted mean NH_4^+ concentration (mg l^{-1}) in precipitation for the ith month. The use of the natural log transform of concentrations has proven useful in improving the fit of parametric models such as the one above (Dana and Easter, 1987). The approximate lognormal distribution of species concentrations in precipitation has been illustrated (MAP3S/RAINE, 1982). Sirois (1991) points out that this transformation will help to achieve the regression modeling assumption of constant error variance. The term a_0 represents the intercept.

P_i represents the natural logarithm of the precipitation amount (ml) for the ith month. The inverse relationship between precipitation amount and concentration of ammonium in precipitation, which is the result of several processes occurring simultaneously, is well illustrated by Prado-Fiedler (1990). It should be pointed out that the use of volume-weighted concentrations will effectively reduce the amount of variation imposed on the concentration by precipitation amount. The precipitation term in the presently addressed regression model is included to capture remaining precipitation effects.

The term bi, where i (month) goes from 1 to $12N$, represents the monotonic trend in NH_4^+ concentration in precipitation over time. It should be pointed out that a systematic trend in precipitation amount will have some degree of collinearity with the trend term for concentration, thus the precision in the estimate of the trend magnitude will be reduced. Additionally, the assumption of a linear trend will simplify the structure of the actual trend which may have non-linear characteristics. In addressing the detectability of possible trends in the 7 yr records analyzed, emphasis was placed on the value of b in Eq. (1) for which the null hypothesis H_0: $b = 0$ is rejected with 80% probability. Buishand et al. (1988) used this approach in addressing the detectability of NH_4^+ trends in 5 yr records of monthly bulk precipitation samples.

The probability of detecting a trend, or power, is a function of degrees of freedom v, significance level (SL), and the noncentrality parameter δ where

$$\delta = b/\sigma_b. \tag{2}$$

Power increases with δ and v, though power varies minimally above $v = 30$. Power has a much stronger relationship with δ, which is a function of trend magnitude. Note that $v = n - c$ where n is the total number of observations and c is the number of regression coefficients in the model. As pointed out by Buishand et al. (1988), it is usually necessary to have at least 10 degrees of freedom in order to obtain a powerful t-test. For this reason it is advantageous to use monthly concentration values in this analysis rather than annual values. Another way to increase the power of trend detectability is to reduce the error (e_i) standard deviation. This illustrates the usefulness of adding additional explanatory variables, such as precipitation amount, to regression models designed to detect trend and seasonality. In this analysis, adding explanatory variables such as concentrations of other analytes (NO_3^- and SO_4^{2-}) resulted in a reduction of error standard deviation at the cost of severe multicollinearity among model independent variables. To avoid such multicollinearity, only the most parsimonious group of variables was chosen for the final model.

The use of a cosine or sine term to model the annual cycle in concentrations is well documented (Buishand et al., 1988; MAP3S/RAINE, 1982). The cosine term in model (1) represents the seasonal component of the variation in concentration where a is the amplitude and ϕ is the phase angle. This term achieves a maximum at $i \approx 6\phi/\pi$, thus the location of the maximum in the annual cycle of concentration can be readily identified. It should be noted that the seasonality term will have some degree of collinearity with seasonality present in the precipitation term.

To test the hypothesis that presence of seasonality and trend in precipitation amount exist, the following regression model was used for analysis of both periods at all sites:

$$P_i = a_0 + a\cos(2\pi i/12 - \phi) + bi + e_i, \quad i = 1, \ldots, 12N. \tag{3}$$

P_i represents the natural logarithm of precipitation amount and bi is the trend term. The cosine term models the seasonal cycle in precipitation amount.

2.2.1. Reparameterized models

To facilitate the estimation of the coefficients a_0, a, b, c, and ϕ following Buishand et al. (1988), the final form of model (1) becomes

$$Y_i = a_0 + \alpha\cos(2\pi i/12) + \beta\sin(2\pi i/12) + bi + cP_i + e_i,$$
$$i = 1, \ldots'' \, 12N \tag{4}$$

where $\alpha = a\cos\phi$ and $\beta = a\sin\phi$. The cosine term in Eq. (1) is thus decomposed into the cosine and sine terms in Eq. (4) to determine a and ϕ. Using the Proc Reg procedure within SAS® statistical analysis software, estimates $\hat{a}_0, \hat{\alpha}, \hat{\beta}, \hat{b}$, and $\hat{c}$ of the regression coefficients in Eq. (4) were calculated by the method of ordinary least squares (SAS Institute Inc., 1990). It follows that estimates of a and ϕ can be derived from the relations:

$$\hat{a} = \sqrt{\hat{\alpha}^2 + \hat{\beta}^2}, \tag{5}$$

$$\hat{\phi} = \begin{cases} \arctan(\hat{\beta}/\hat{\alpha}) & \text{if } \hat{\alpha} \geqslant 0, \\ \arctan(\hat{\beta}/\hat{\alpha}) + \pi & \text{if } \hat{\alpha} < 0. \end{cases} \tag{6}$$

Proc Reg also provides estimates of the standard errors of the above regression coefficients as well as an estimate of σ_e. Buishand et al. (1988) give the following relationships for $\hat{a}$ and $\hat{\phi}$ which are derived from a Taylor expansion of Eqs. (5) and (6):

$$\sigma^2(\hat{a}) = \operatorname{var}\hat{a} \approx (\alpha^2/a^2)\operatorname{var}\hat{\alpha} + (\beta^2/a^2)\operatorname{var}\hat{\beta}$$
$$+ 2(\alpha\beta/a^2)\operatorname{cov}(\hat{\alpha}, \hat{\beta}), \tag{7}$$

$$\sigma^2(\hat{\phi}) = \operatorname{var}\hat{\phi} \approx (\beta^2/a^4)\operatorname{var}\hat{\alpha} + (\alpha^2/a^4)\operatorname{var}\hat{\beta}$$
$$- 2(\alpha\beta/a^4)\operatorname{cov}(\hat{\alpha}, \hat{\beta}). \tag{8}$$

Estimated values of the variances and covariances of $\hat{\alpha}$ and $\hat{\beta}$ are calculated by Proc Reg. By using estimates of a, α and β on the right-hand sides of (7) and (8), the standard errors $\hat{\sigma}(\hat{a})$ and $\hat{\sigma}(\hat{\phi})$ can be calculated.

The final form of model (3) is:

$$P_i = a_0 + \alpha\cos(2\pi i/12) + \beta\sin(2\pi i/12) + bi + e_i,$$
$$i = 1, \ldots, 12N. \tag{9}$$

Model variables are defined as in model (3). Estimates of a, α, β, ϕ and b and their standard errors are obtained as in model (4).

The Student's t-statistic is used to test the statistical significance of the regression coefficients in the model under the null hypothesis (H_0) that the regression coefficient being tested is zero. Probability values (p-values) are also calculated for each coefficient. A small p-value suggests a disagreement between the data and the null hypothesis. In this study, the significance level $\mathrm{SL} = 0.1$ is chosen as the value above which a given p-value results in failure to reject H_0.

The validity of the t-test is subject to the basic assumptions of the linear regression model. These assumptions are that the errors (e_i): have constant variance; are uncorrelated with each other in time; and have a normal distribution. The Durbin–Watson test was used to test for first-order autocorrelation among the residuals. At sites where the correlation assumption was violated or considered inconclusive, a regression technique, Proc Autoreg, which accounts for correlation in residuals was used to estimate regression coefficients. The validity of the normality assumption was assessed by visual inspection of residual frequency distributions and quantile–quantile (Q–Q) plots of ordered residuals against normal quantiles. In observing Q–Q plots, a linear relationship suggests a normal population of residuals. For a more detailed treatment of residual frequency distributions and Q–Q plots, the reader is referred to *SAS® System for Statistical Graphics* (1991).

In this analysis, outliers that were not considered influential were left in the model. The level of outlier influence was estimated by using the difference in fits (DFFITS) and difference in beta (DFBETAS) statistics produced by the Proc Reg procedure. The commonly used cutoff value of 2 was used for both statistics (Bowerman and O'Connell, 1990). When the value of DFFITS exceeds 2, removing the corresponding observation from the data set substantially changes the point prediction of Y_i (model (4)). If the value of DFBETAS exceeds 2, then removing the corresponding observation from the data set substantially changes the point estimate of the corresponding regression coefficient. Those observations with DFFITS and DFBETAS values less than 2 after the initial model run were retained.

2.3. Source–receptor analysis

The source–receptor analysis developed here combines air mass back trajectory analysis with multiple linear regression to investigate the influence of area I NH_3 emissions on NH_4^+ concentration in precipitation at surrounding NADP/NTN sites. An air mass trajectory within the boundary layer which arrives at a site after having traversed any portion of area I for any duration of time is considered to possibly contain elevated concentrations of NH_3 and NH_4^+, and is consequently labeled as influenced. The distances of individual sites from the perimeter of area I are listed in Table 2. All sites in

Table 2
Distance from the perimeter of area I to NADP sites

Site	Distance (km)
NC41	56
NC03	76
NC36	60
NC34	170
NC25	387

Fig. 1 except site NC35 are included in the source–receptor analysis. This analysis uses weekly NH_4^+ concentrations in precipitation and daily precipitation information. The period of analysis includes the years 1995 and 1996.

Back trajectory models are commonly used to link receptors to source regions in wet deposition studies (Billman-Stunder et al., 1986; Moody and Samson, 1989; Henderson and Weingartner, 1982; Ruijgrok and Romer, 1993; RGAR, 1997). Such studies typically utilize chemistry data from samples collected on an event basis. This analysis uses weekly concentration values and back trajectories for days on which precipitation was measured. Therefore, a weekly sample can be comprised of a maximum of seven separate precipitation events.

Back trajectories were calculated using version 4 of the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by the National Oceanic and Atmospheric Administration's Air Resources Laboratory (NOAA/ARL). The model was accessed and run from the World Wide Web at *http://www.arl.noaa.gov/ready/hysplit4.html* (HYSPLIT4, 1997). The HYSPLIT model calculates three-dimensional trajectories from previously gridded horizontal (u and v) and vertical (ω) wind fields output and archived every 2 h from NOAA's National Center for Environmental Prediction's Nested Grid Model (NGM) (Draxler, 1997). The trajectories in this analysis used the vertical motion prescribed by the NGM and are therefore kinematic.

A single 24 h back trajectory starting at 2300 h was run for each day on which precipitation was measured at the NADP/NTN site. Given its distance from area I, 36 h back trajectories were calculated for site NC25. When initial trajectories exhibited significant curvature, additional trajectories were also run at 1800 and 1200 h. The trajectory level was chosen as 150 m. The 150 m level is expected to be within the boundary layer even during stable nocturnal conditions, when boundary layer depth is typically 100–200 m (Arya, 1998). The HYSPLIT wind fields at this level are interpolated from the nearest NGM sigma level. There are about 4 NGM sigma levels within the boundary layer (Draxler, 1996).

In our analysis it is assumed that most of the NH_3 emitted at ground level within area I will likely arrive at surrounding NADP/NTN sites, aside from NC25, via transport within the boundary layer. We are, by consequence, characterizing flow conditions which result in the wet deposition of area I NH_3 and NH_4^+ at a site via below-cloud mechanisms. Only when the cloud-level trajectory is the same as the 150 m level will we describe those conditions which result in wet deposition of NH_3 or NH_4^+, which has originated from area I, by both in-cloud and below-cloud mechanisms.

The methodology presented here also assumes that the 150 m trajectory characterizes the general flow of the boundary layer. Within the well-mixed daytime boundary layer, trajectories at different levels should not deviate from each other significantly. Arya (1988) points out that wind direction across the moderately unstable and convective boundary layer typically changes by less than 15°. Under stable conditions, the horizontal deviation of trajectories at different heights in the boundary layer will be greater. The largest change in trajectory imposed by diurnal variation in boundary layer stability may take place in the transition from unstable daytime conditions to more stable nighttime conditions. In this case however, the layers that begin to form and fan out as stratification proceeds will roughly have the same concentration of NH_3 or NH_4^+, a result of the uniform concentration within the well-mixed daytime boundary layer.

During the time required for transport from area I to NC25, a considerable amount of NH_4^+ may make it out of the boundary layer and into clouds associated with precipitating systems transported by synoptic scale flow. For this reason, a 2000 m trajectory was calculated in addition to the 150 m trajectory.

In order to facilitate the use of daily back trajectories with weekly NADP samples, an influence factor (I) is introduced. I is defined as the ratio of the number of influenced trajectories during week i to the total number of trajectories during week i. Note that $I = 1$ when all the trajectories during a week are considered influenced. The maximum possible number of trajectories for a week is 7.

We hypothesize that area I NH_3 emissions may be influencing NH_4^+ concentrations at NADP sites surrounding area I. To set up this hypothesis, we first use the non-parametric Wilcoxon Rank Sums (WRS) test to compare the average concentration for weekly samples where $I \geqslant 0.25$ to the average concentration of those weeks where $I < 0.25$. $I \geqslant 0.25$ represents a week during which 25% or more of all back trajectories were considered to be influenced. H_0 for the WRS test is that the means of the groups being compared are equal. The WRS test is also performed to test for the equality of mean precipitation amounts of the two I groups. If the two group mean precipitation amounts are equal, then the physical meaning of different group mean NH_4^+ concentrations is maximized with respect to the dependence of concentration on I. Using the information gained in this means comparison as the foundation for our hypothesis, we then use regression analysis to conduct a formal hypothesis test.

In order to formally test for a statistically significant influence of area I NH_3 emissions on NH_4^+ concentration in precipitation collected at sites other than NC35, the influence factor (I) is incorporated into the following source–receptor regression model:

$$Z_i = a_0 + \alpha\cos(2\pi i/52) + \beta\sin(2\pi i/52) + dP_i + fI_i + e_i\ ,\quad i = 1, \ldots, 52N. \tag{10}$$

In this model, Z_i represents the natural logarithm of NH_4^+ concentration in precipitation ($\mathrm{mg\,l^{-1}}$) for the ith week, P_i is the precipitation amount (ml) for the ith week, and I_i represents the influence factor for the ith week. The sine and cosine terms model the annual cycle which may be present in the weekly concentration values. Coefficients α, β, and corresponding phase angle ϕ are described in Section 2.2.1. $N (N = 2)$ represents the number of years present in the time series. This model was used to perform separate analyses at each site for the entire 2 yr period. Tests for regression coefficients, recognition of model assumptions and treatment of outliers are described in Section 2.2.1.

3. Results and discussion

3.1. Trends analysis

Table 3 summarizes the results of the trends analysis [model (4)]. The average R^2 for all sites is 0.45, meaning that the collection of variables in the regression model explains about 45% of the variation in the monthly volume-weighted mean NH_4^+ concentrations in precipitation. Mean observed concentration values for time period 1 range from 0.16 to 0.28 $\mathrm{mg\,l^{-1}}$, and from 0.15 to 0.31 $\mathrm{mg\,l^{-1}}$ for period 2. Mean predicted concentrations for time period 1 range from 0.11 to 0.24 $\mathrm{mg\,l^{-1}}$, and from 0.11 to 0.26 $\mathrm{mg\,l^{-1}}$ during period 2. The two highest concentration values, both observed and predicted, for period 1 are found at the two suburban sites, NC34 and NC41. It should be noted that NH_4^+ concentrations at NC34 and NC41 are likely influenced by NH_3 emissions from local livestock throughout both periods. The highest value for period 2 is shared by site NC35, located within area I, and NC41. The mean predicted value is an average of 0.045 $\mathrm{mg\,l^{-1}}$ lower than the corresponding mean observed value at all sites during both periods. Precipitation amount is a significant predictor variable at several sites.

Table 3 shows a statistically significant (SL = 0.01) seasonal cycle at all sites, with maximum NH_4^+ concentrations in precipitation occurring in the summer, except for a spring maximum at site NC25 during period 1. Figs. 2 and 3 illustrate the typical seasonal cycle. Standard deviations of the phase angle, which illustrate the accuracy of $i_{\max}$, range from 6.6 to 16.6°, or approximately 1 to 2.5 weeks (Table 3).

The increased ambient concentration of NH_4^+ during summer comes partly from the fact that mineralization in soil, which drives natural production of NH_3, is governed partially by temperature dependent microbial activity. A 10°C increase in soil temperature approximately doubles the rate of ammonification (Addiscott, 1983). As pointed out by Davies et al. (1986,1991), seasonality in

Table 3
Estimated regression coefficients in model (4), multiple coefficients of determination (R^2), and mean volume-weighted monthly NH_4^+ ion concentrations in precipitation for all sites. Time period 1: 1983–1989. Time period 2: 1990–1996. The value $i_{\max}$ is the month corresponding to the seasonal maximum ($i_{\max} = 1$ corresponds to January). The phase angle $\hat{\phi}$ and its standard deviation (SD) are in degrees. $\hat{y}$ and y represent predicted and observed concentrations ($\mathrm{mg\,l^{-1}}$), respectively

Site	Period	$\hat{a}$	SD $\hat{a}$	$\hat{\phi}$	SD $\hat{\phi}$	$i_{\max}$	$\hat{b}$	$\hat{c}$	R^2	mean $\hat{y}$	$\bar{y}$
NC03	1	0.748[a]	0.108	189	8.3	6	– 0.0023	– 0.59[a]	0.47	0.13	0.18
	2	0.712[a]	0.082	181	6.6	6	0.0009	– 0.41[a]	0.54	0.16	0.21
NC34	1	0.708[a]	0.088	181	6.9	6	0.0005	– 0.58[a]	0.62	0.24	0.28
	2	0.545[a]	0.077	213	7.9	7	0.0050[b]	– 0.17	0.49	0.23	0.27
NC41	1	0.489[a]	0.134	201	16.4	7	0.0062	– 0.37[a]	0.27	0.22	0.27
	2	0.433[a]	0.071	194	9.6	7	0.0018	– 0.46[a]	0.47	0.26	0.31
NC35	1	0.407[a]	0.122	183	16.6	6	– 0.0003	– 0.23	0.16	0.16	0.19
	2	0.516[a]	0.068	187	7.7	6	0.0079[a]	– 0.32[a]	0.53	0.26	0.31
NC36	1	0.820[a]	0.163	244	11.6	8	0.0008	– 0.53[a]	0.57	0.11	0.16
	2	0.487[a]	0.088	263	10.7	9	0.0012	– 0.46[a]	0.45	0.16	0.20
NC25	1	0.780[a]	0.130	161	8.7	5	– 0.0012	– 0.22	0.41	0.13	0.17
	2	0.658[a]	0.111	198	9.9	7	0.0003	– 0.29[b]	0.41	0.11	0.15

[a] Significant at the 1% level.
[b] Significant at the 5% level, but not at the 1% level.

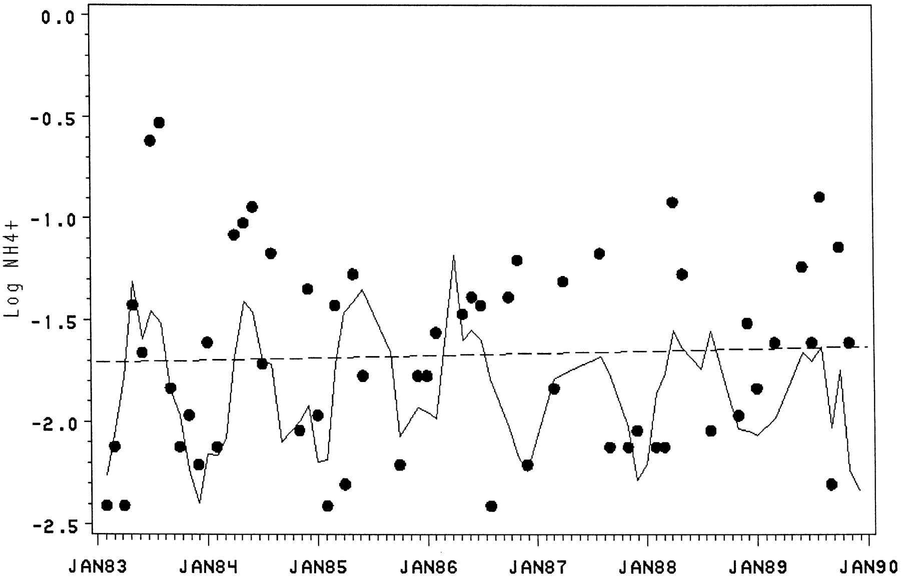

Fig. 2. Seasonality and insignificant trend ($p > 0.10$) in the natural log (log NH_4^+) of monthly volume-weighted NH_4^+ concentration in precipitation (mg l^{-1}) at Sampson County site NC35 during period 1. Solid dots (●) represent observed values. The solid and dashed lines respectively represent predicted values and estimated trend given by model (4).

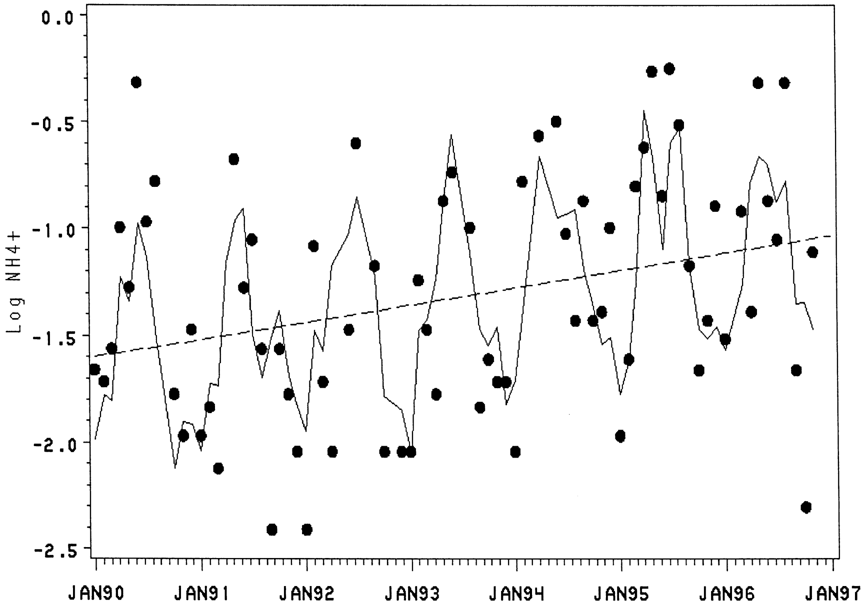

Fig. 3. Seasonality and significant trend ($p < 0.01$) in the natural log (log NH_4^+) of monthly volume-weighted NH_4^+ concentration in precipitation (mg l^{-1}) at Sampson County site NC35 during period 2. Solid dots (●) represent observed values. The solid and dashed lines respectively represent predicted values and estimated trend given by model (4).

synoptic scale meteorological conditions may also influence the seasonal pattern of NH_4^+ concentration in precipitation. This may involve a seasonal redistribution of upwind sources due to changing prevailing flow regimes and seasonal changes in precipitation characteristics such as intensity and duration.

As mentioned above, area I is believed to be a significant source of atmospheric NH_3 in the North Carolina Coastal Plain region. Harper and Sharpe (1997) have shown that volatilization of NH_3 from waste lagoons has a positive correlation with lagoon surface temperature, thus such sources will have peak emission strengths during summer. This may contribute to the summertime maximum NH_4^+ concentration in precipitation at sites such as NC35 which are located within a dense population of swine operations. These sources are randomly located among croplands, thus increased concentrations of NH_4^+ in rainfall during summer may also be related to emissions of NH_3 resulting from summer fertilizer application.

It is hypothesized that seasonal patterns in precipitation may have some influence on NH_4^+ concentration in precipitation. The use of regression model (9) to detect seasonal patterns in precipitation amount revealed statistically significant ($SL = 0.05$) annual cycles during period 1 at all sites except NC25. Maximum values of precipitation amount occurred during the summer in all cases. Significant annual cycles during period 2 were found at NC36, NC35 and NC03. Maximum precipitation amounts were again found during the summer at all sites. The inverse relationship between precipitation amount and NH_4^+ concentration in precipitation suggests that the summer maximum in NH_4^+ concentration is unrelated to the seasonal pattern in precipitation amount.

As stated earlier, the hypothesis behind the trends analysis is that increasing NH_3 emissions in area I may be imposing a positive trend in NH_4^+ concentrations in precipitation at site NC35, located within area I, and that this trend may also be present at additional sites. The trends should follow the temporal pattern of NH_3 emissions related to the NC hog industry growth which was generally stable within the period 1983–1989 (period 1) and has experienced drastic growth during the period 1990–1996 (period 2). Regression analysis shows a highly significant ($SL = 0.01$) increasing trend present at Sampson County site NC35 during period 2 (Table 3) and lack of trend during period 1. Figs. 2 and 3 show predicted value trendlines for both periods at NC35. The estimated monthly increase in NH_4^+ concentration in precipitation during period 2 corresponds to an annual increase of approximately 9.5%. The location of site NC35 among such a large number of animal operations and the correlation of the NH_4^+ trend with hog population growth suggests that the increasing magnitude of local NH_3 emission is the most likely explanation for the positive NH_4^+ trend. Furthermore, Cornelius (1997) showed that hog population density may be a significant predictor of NH_4^+ concentration in precipitation for sites within densities > 140 hog mi^{-2} such as area I. Site NC35 is specifically included in his analysis. It is important to realize that the trend model addressed here and the analytical methods employed by Cornelius (1997) do not identify sources of NH_4^+ in precipitation. This analysis illustrates the apparent correlation between the increasing trend in NH_4^+ concentration in precipitation at site NC35 and the increase in local NH_3 emissions resulting from rapid growth in the number of neighboring swine operations. A less significant ($SL = 0.1$) trend is found at site NC34 for period 2 (Table 3) and is most likely related to the increase in NH_3 emissions associated with a 33% countywide (Rowan County) increase in the cattle population for the period. The remaining sites, NC03, NC41, NC36, and NC25 do not show significant temporal trends during either period (Table 3).

Buishand et al. (1988) show that $\delta = 2.85$ for an 80% chance of rejecting H_0: $b = 0$ where $v > 30$ (two-sided test at the 5% level). In this analysis, $v = n - 5$, where the average n for all sites is ≈ 69. It follows from Eq. (2) that $b_{80} = 2.85\sigma_{\hat{b}}$. Using this relationship, the estimate of b for site NC34 during period 2 falls slightly below $b_{80} = 0.006$. At site NC35 for period 2, $b_{80} = 0.005$ and $b_{90} = 0.007$, indicating that the estimated trend ($b = 0.0079$) was detected with 80 and 90% probability.

In this analysis it is found that precipitation volume has a statistically significant inverse relationship with monthly volume-weighted NH_4^+ concentration at some sites. Any trend in precipitation volume over time may then impose a trend of opposite sign in NH_4^+ concentration. Regression model (9) was used to test the hypothesis of no trend in precipitation amount at each site. A single significant ($p < 0.05$) positive trend at site NC41 was found during period 2. This trend was not strong enough to impose a significant decreasing trend in NH_4^+ concentration in precipitation during the period. No other trends were detected at any site during either period.

During the analyses of concentrations [model (4)] and precipitation amount [model (9)], no departures from normality were detected in residuals. The number of influential outliers was less than 5 in all cases.

3.2. Source–receptor analysis

Table 4 shows the results of the Wilcoxon rank sums (WRS) test. At site NC36, the mean NH_4^+ concentration in precipitation for weeks where $I \geqslant 0.25$ is approximately $0.08\ mg\,l^{-1}$ or 44% higher than the mean value for weeks where $I < 0.25$. The WRS test suggests that these means are significantly different at $SL = 0.10$. It is important to understand that the difference between these means could be entirely due to differences in group mean precipitation amounts. However, the WRS test for equality of mean precipitation amounts fails to show unequal means for the two I groups at the 10% level. This suggests that the difference in mean NH_4^+ values is likely not arising simply from a difference in group mean precipitation amounts. At site NC41, the mean NH_4^+ concentration in precipitation for weeks where $I \geqslant 0.25$ is approximately $0.17\ mg\,l^{-1}$ or 50% higher than the

Table 4
Group means for weekly NH_4^+ ($mg\,l^{-1}$) concentrations in precipitation and precipitation amount (ml) and p-values (Prob. $> |Z|$) for the Wilcoxon Rank Sums test. $\mu_{1NH_4^+}$ is the mean of the observed weekly NH_4^+ values for which $I < 0.25$. $\mu_{2NH_4^+}$ is the mean of the observed weekly NH_4^+ values for which $I \geqslant 0.25$. p-value$_A$ is the probability of falsely rejecting H_0 for the WRS test for equality of $\mu_{1NH_4^+}$ and $\mu_{2NH_4^+}$. μ_{1P} is the mean observed precipitation amount of weekly samples with $I < 0.25$. μ_{2P} is the mean observed precipitation amount of weekly samples with $I \geqslant 0.25$. p-value$_B$ is the probability of falsely rejecting H_0 for the WRS test for equality of μ_{1P} and μ_{2P}

Site	$\mu_{1NH_4^+}$	$\mu_{2NH_4^+}$	p-value$_A$	μ_{1P}	μ_{2P}	p-value$_B$
NC03	0.24	0.31	0.1600	1608	2437	0.1525
NC36	0.18	0.26	0.0586[a]	2033	2395	0.6411
NC41	0.34	0.51	0.0747[a]	1560	2337	0.0621[a]

[a] Significant at the 10% level, but not at the 5% or 1% levels.

Table 5
Influence factor regression coefficients ($\hat{f}$) and multiple coefficients of determination (R^2) for model (10). Number of influenced trajectories and percent of total back trajectories (BT) labeled as influenced for the entire period are included for each site

Site	$\hat{f}$	R^2	No. influenced BT	% influenced BT
NC03	0.441[a]	0.52	53	22.0
NC25	− 1.475[b]	0.32	11	4.0
NC34	− 0.579[a]	0.39	29	9.0
NC36	0.495[b]	0.56	56	27.0
NC41	0.323[a]	0.44	89	38.0

[a] Significant at the 10% level, but not at the 5 or 1% levels.
[b] Significant at the 5% level, but not at the 1% level.

mean value for weeks where $I < 0.25$. Here the group mean concentrations are again deemed significantly different at SL = 0.10. The mean precipitation amounts are also significantly different at SL = 0.10. The higher mean precipitation value for $I \geqslant 0.25$ shows that in spite of the inverse relationship between precipitation amount and concentration, the concentration for those weeks where $I \geqslant 0.25$ is still greater than those weeks where $I < 0.25$. At NC03, the mean NH_4^+ concentration for weeks where $I \geqslant 0.25$ is approximately $0.07\,mg\,l^{-1}$ or 29% higher than the mean value for weeks where $I < 0.25$. In this case the results were not statistically significant (SL < 0.20). The mean precipitation amounts for this site where not shown to be significantly different (SL = 0.10). It should be noted that first order autocorrelation between NH_4^+ concentration and I was found at both NC41 and NC36 ($\rho < 0.24$ in both cases). For this reason the p-values used to test H_0 in the WRS test should be used with caution, since the WRS test assumes independence in the data. The WRS was chosen here for its resistance to outliers in comparing means.

Table 5 summarizes the results of model (10) in the source–receptor analysis. The average R^2 is 0.45, meaning that precipitation amount and boundary layer air mass transport explain approximately 45% of the variation in weekly NH_4^+ concentration in precipitation. The influence of precipitation amount is highly significant ($p < 0.01$) at all sites. Statistically significant ($p < 0.01$) annual cycles are also found at all sites. The cycles reach a maximum during the summer at all sites, showing good agreement with the cyclic pattern predicted by the trends model for monthly values. An important result from this analysis is the sitewise estimates of f. Statistically significant ($p < 0.10$) positive values of $\hat{f}$ are found for NC03, NC36 and NC41. A positive value of $\hat{f}$ suggests that NH_4^+ concentration in precipitation increases with the percentage of influenced trajectories during a week. These results suggest that transport of NH_4^+ and or NH_3 originating from area I is detected for distances up to approximately 80 km. The influence of area I NH_3 emissions on NH_4^+ concentration in precipitation at sites greater than approximately 80 km away was not detected. We do not wish to suggest that the spatial extent of wet deposited NH_3 and NH_4^+ originating from area I is limited to 80 km. A larger data set is needed to provide more information for sites NC34 and NC25. The average number of observations used in this analysis for all sites is 80. Q–Q plots and frequency distributions of residuals suggest that the normality assumption was satisfied at all sites.

4. Conclusions

In this study, multiple linear regression has been used to illustrate the temporal characteristics of NH_4^+ concentration in precipitation at six North Carolina NADP/NTN sites. Seasonality, with maximum concentrations during warm months, is observed at all sites. A significant ($p < 0.01$) increasing trend in NH_4^+ concentration in precipitation beginning in 1990 is found at site NC35. This trend, which corresponds to an average annual increase in NH_4^+ concentration in precipitation of 9.5%, is correlated with the increasing number of local swine operations since 1990. A less significant trend at Rowan County site NC34 is found, which is also likely the result of increasing local NH_3 emissions and not the result of increasing area I emissions.

A source–receptor relationship has been developed for five NADP/NTN sites surrounding an area of strong NH_3 emission located over southeast North Carolina. For this analysis, boundary layer air mass back trajectories based on daily precipitation information are used in conjunction with weekly NH_4^+ concentrations in precipitation. This information is incorporated into a source–receptor regression model to test for the dependence of weekly NH_4^+ concentration in precipitation on the percentage of back trajectories during a week which are possibly influenced by this area of strong NH_3 emission.

Results show that NH_4^+ concentration in precipitation is positively correlated with the percentage of influenced trajectories during a week at sites up to approximately 80 km away. For those weeks during which 25% or more boundary layer air mass trajectories traversed area I, NH_4^+ concentration in precipitation at Scotland County site NC36 is approximately 44% higher than other weeks. At Wake County site NC41, NH_4^+ concentration in precipitation is at least 50% higher for those weeks during which 25% or more trajectories traversed area I.

Results from this analysis show that NH_3 emitted from area I is being transported over distances which would allow direct wet deposition as NH_4^+ or NH_3 to nitrogen sensitive coastal and estuarine waters. This also suggests that NH_3 emitted from area I is being wet deposited as NH_4^+ or NH_3 to all river basins in the North Carolina Coastal Plain region.

The swine industry accounts for roughly 21% of all NC nitrogen emissions and 93% of the total hog population resides in the Coastal Plain region of the state. The fraction of TAN being deposited to NC coastal and estuarine waters which can be attributed to agricultural NH_3 emissions over the southeast part of the state may therefore be significant. This study points to the need for broader regulations governing nitrogen emissions. As Paerl (1995) points out, atmospheric nitrogen emissions have increased in a largely unregulated manner globally over the last four decades. In the US, nitrogen emission restrictions primarily consist of NO_x regulations. Over the past several years it has become apparent that excess nitrogen can have acute and chronic detrimental effects on coastal and estuarine ecosystems. In coastal states such as North Carolina, whose NH_3 emissions represent a significant portion of overall nitrogen emissions, regulations on primary NH_3 sources, in addition to NO_x restrictions, may be warranted. In the future, it may be possible for us to mitigate the influence of ammonia emissions through chemical or physical process controls.

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