Trends in Ammonium Concentration in Precipitation and Atmospheric Ammonia Emissions at a Coastal Plain Site in North Carolina, U.S.A.

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The temporal characteristics of annual volume-weighted average ammonium (NH_4^+) ion concentration in precipitation and local ammonia (NH_3) emissions are investigated over the period 1982−1997 at National Atmospheric Deposition Program/National Trends Network site NC35, located in Sampson County, NC. Multiple regression analysis of annual volume-weighted average values of NH_4^+ concentration in precipitation identifies a statistically significant ($p < 0.01$) 4-year cycle and increasing trend during the period. The cycle is likely a function of mean annual ambient surface temperature, which is shown to be a significant ($p < 0.01$) predictor variable for annual NH_4^+ concentrations in precipitation. Loess fitting suggests that NH_4^+ concentration in precipitation began to increase more rapidly between 1989 and 1990. An analysis of estimated population-based annual NH_3 emissions from individual sources in an intensively managed agricultural region surrounding NC35 shows that emissions from swine ($p < 0.01$), fertilizer ($p < 0.10$), turkeys ($p < 0.05$), and broilers ($p < 0.05$) are significantly greater during the period 1990−1997 than the period 1982−1989. Emissions from non-broiler chickens are significantly ($p < 0.01$) lower during the period 1990−1997. Cattle emissions are not significantly different (10% level) during the two periods. The increase in average annual swine emissions between periods accounts for ≈84% of the increase in average annual emissions from all sources between periods. Variability in local ammonia emissions from swine and mean ambient surface temperature explain approximately 90% of the variation in annual volume-weighted average NH_4^+ concentrations in precipitation at NC35 during the period 1982−1997.

1. Introduction

1.1. Background. Over the past several years, it has become apparent that North Carolina's (NC) coastal and estuarine waters are showing signs of excess nutrient input (*1*). Public awareness has grown considerably since a series of fish kills occurred in the lower Neuse River Basin (NRB) during the summers of 1995 and 1996. These and other fish kills that have occurred across the Coastal Plain region of the state are believed to be related to nitrogen (N) overenrichment and recurring outbreaks of *Pfiesteria piscicida* and *Pfiesteria*-like dinoflagellate populations. The symptoms of eutrophication in such systems include recurring toxic and nontoxic phytoplankton blooms, which have occurred in North Carolina's Albemarle-Pamlico Sound (*2*−*4*). While the direct relationship between water N levels and dinoflagellate production is still under investigation, some work suggests that inorganic nitrate indirectly supports increased production of nontoxic zoospores, which are potential precursors to toxic *Pfiesteria piscicida* and *Pfiesteria*-like dinoflagellates, by stimulating production of their algal prey (*5*). It is also likely that fish which have been weakened by conditions such as nutrient related anoxia and hypoxia are more susceptible to *Pfiesteria* (*5*).

It is estimated that only 5% of average annual N loading to the Albemarle/Pamlico Estuary is from point sources, whereas the largest fraction (45%) is attributed to nonpoint agricultural sources (*6*). The pathways by which agricultural N enters these systems include both surface and groundwater transport. Additionally, it is believed that atmospheric N deposition may contribute a significant fraction of total N loading to these systems, with estimates ranging from 35 to 60% for North Carolina Atlantic Coastal Waters (*4*).

Table 1 shows estimates of nitrogen emissions by source for the state of North Carolina. The table shows that ammonia (NH_3) accounts for about 42% of N emissions. Ammonia has a relatively short atmospheric lifetime (0.5 h to 5 days) (*11*, *7*) which is primarily a result of its rapid deposition to natural surfaces. Ammonium (NH_4^+) aerosol, which is formed by the reaction of NH_3 with acid gases such as nitric acid, sulfuric acid, and hydrochloric acid, has a longer atmospheric residence time of 5−10 days (*12*) and is therefore capable of long-range transport. In areas of high NH_3 emission, dry deposition of NH_3 will dominate overall NHx (NHx = NH_3 + NH_4^+) deposition (*13*). While the three primary sources of nitrogen oxides (NO_x) are distributed across the state, NH_3 sources are primarily concentrated in the Coastal Plain Region. Across this region, a significant fraction of the N deposited to coastal and estuarine waters may be in the form of NHx.

TABLE 1. Sources and Estimates of North Carolina Nitrogen Emissions Adapted from Aneja et. al (*7*)[a]

source	nitrogen species	estimated tons N per year	% of total nitrogen
highway mobile (1990)	NO_x	78 509	23.7
point sources (1994)	NO_x	77 798	23.6
area and nonroad mobile (1990)	NO_x	24 452	7.4
biogenic NO_x (1995)	NO_x	9926	3.0
swine (1995)	NH_3	68 540	20.6
cattle (1995)	NH_3	24 952	7.5
broilers (1995)	NH_3	13 669	4.1
turkeys (1995)	NH_3	16 486	5.0
fertilizer application (1995)	NH_3	8270	2.5
"other chickens" (1995)	NH_3	6476	2.0
NH3 point sources (1995)	NH_3	1665	0.5

[a] Nitrogen calculated from NO_x emissions assumes 100% NO_2. NO_x emissions taken from North Carolina Division of Air Quality inventories (*8*). NO_x−N tons = NO_x tons * (14/46). NH_3−N tons = 14/17(NH_3 tons). NH_3 emissions are based upon factors from Battye et al. (*9*). Livestock statistics supplied by North Carolina Department of Agriculture and Consumer Services (*10*).

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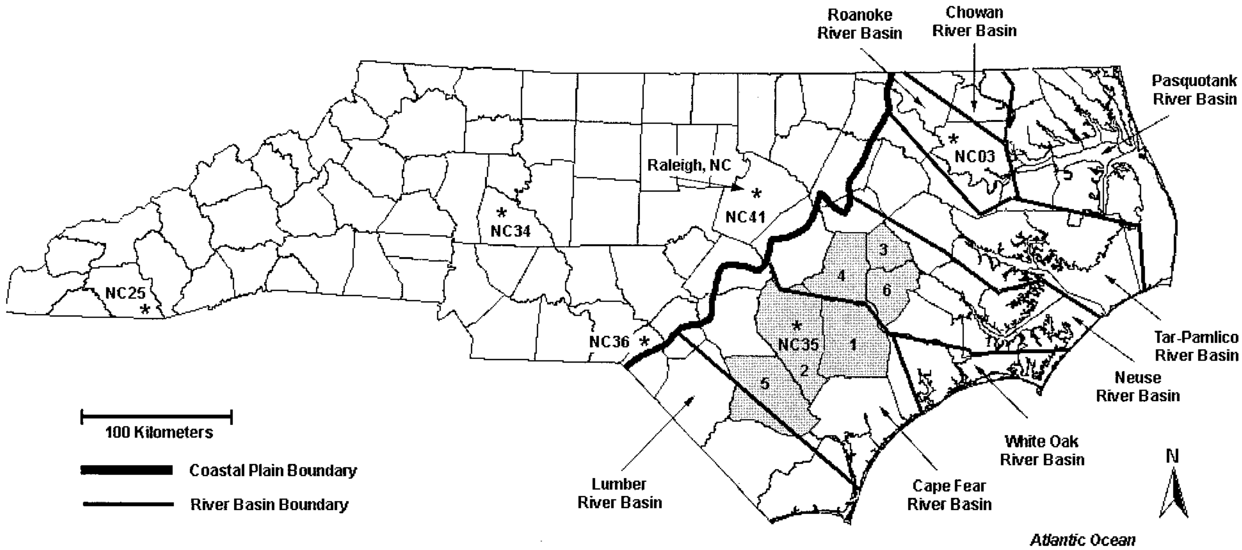

FIGURE 1. NADP/NTN sites (*), area I NH_3 source region, and Coastal Plain river basins. The shaded area represents area I, a region defined as having an average hog population density of ∼528 hogs km^{-2}. Numbers within area I represent the following individual counties with corresponding estimated 1996 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 (from ref *14*).

Table 1 shows that swine operations account for approximately 49% (68 540 tons yr^{-1}, NH_3−N) of all North Carolina NH_3 emissions and approximately 21% of total N emissions. North Carolina is presently home to approximately 16% of the U.S. hog population and is second in total number of hogs by state (*10*). Over the past 10 years, North Carolina's hog industry has experienced rapid growth. While the number of hogs in the state prior to 1990 remained relatively stable at approximately 2 million, this number began to increase rapidly beginning in 1989 to its current level of approximately 10 million (*10*). In 1996, North Carolina contained approximately 9.3 million hogs, roughly 93% of which are located in the Coastal Plain Region (*14*). Walker et al. (*14*) have previously defined a Coastal Plain NH_3 source region, characterized by elevated NH_3 emissions, based on county-scale animal population densities (Figure 1). This area (area I), composed of the six NC counties (Duplin, Sampson, Greene, Wayne, Bladen, and Lenoir) with the largest hog population densities, 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 60% of the Coastal Plain hog population and 17% of the total Coastal Plain land area. Area I also contains approximately 60% 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 2 shows estimated area I NH_3 emissions by source type (*14*). Swine operations account for 80% of total NH_3 emissions from domestic animals within area I. Furthermore, Duplin, Sampson, and Wayne Counties ranked 1, 2, and 4, respectively, in statewide total cash receipts for crops and livestock by county in 1996, making area I a region of intense agricultural activity as a whole. Ammonia emissions in this area are likely to influence the concentration of NH_4^+ in rainfall. The presence of NH_4^+ in rainfall will result from several processes which include: in-cloud and below-cloud scavenging of NH_4^+ aerosol, in-cloud and below-cloud scavenging of NH_3 followed by reaction with water to form NH_4^+, dry deposition of NH_4^+ aerosol to the open precipitation collector, and dry deposition of NH_3 to the open precipitation collector followed by reaction with water to form NH_4^+.

One objective of this paper is to investigate temporal variation in wet deposition of NH_4^+ within area I over the period 1982−1997, with the intent of defining relationships between annual estimates of NH_4^+ concentration in precipitation and NH_3 emissions (based on emission factors applied to annual livestock populations and fertilizer sales) from specific agricultural sources. A second objective is aimed at identifying additional factors which influence annual values of NH_4^+ concentration in precipitation. This paper extends the work presented by Walker et. al. (*14*) which investigates the atmospheric transport of NH_4^+ in North Carolina and temporal trend and seasonality in monthly values of NH_4^+ in precipitation across the state during the period 1983−1996. The present study uses National Atmospheric Deposition Program/National Trends Network (NADP/NTN) precipitation chemistry data (*15*), agricultural statistics from the North Carolina Department of Agriculture and Consumer Services (NCDA) (*10*), and climatological data from the North Carolina State Climate Office (NCSCO) (*16*). Statistical analyses are performed using SAS statistical analysis software.

TABLE 2. Area I NH_3−N Emissions by Animal Type[a]

	animal NH_3−N emissions (tons yr^{-1})		animal NH_3−N emissions (tons yr^{-1})
hogs	47 679	cattle	2154
turkeys	7893	non-broiler chickens	181
broilers	2005		

[a] NH_3−N tons = 14/17(NH_3 tons). Emissions calculated using emission factors given by Battye et al. (*9*). Animal population statistics are provided by the North Carolina Department of Agriculture and Consumer Services (*10*). Calculations reflect hog population as of Dec 1, 1996; turkey population for 1996; cattle population as of Jan 1, 1997; broiler population for 1996; and chicken population as of Dec 1, 1996. Emissions from turkeys and broilers are calculated by dividing the total population by the average number of flocks per year, 5.75 for broilers and 3.5 for turkeys.

1.2. NADP/NTN Data. The National Atmospheric Deposition Program/National Trends Network is a nationwide precipitation collection network which operates over 200 sites (*15*). NADP/NTN samples are collected weekly and sent to the Illinois State Water Survey, Central Analytical Laboratory (CAL) for chemical analysis (*17*). Only samples that are considered valid by NADP/NTN standards and analyzed for all major analytes are used in this study. For information on the data validation procedures used for wet samples at CAL, the reader is referred to Bowersox (*18*).

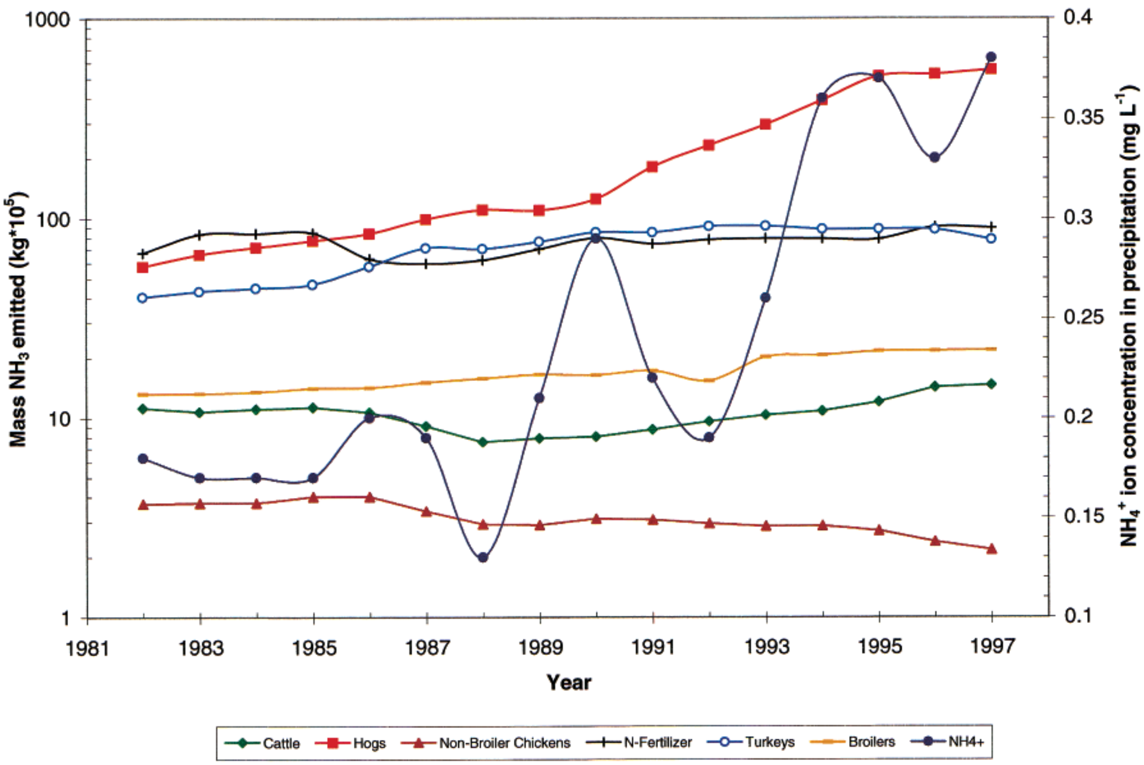

FIGURE 2. Area I NH_3 emissions by source type and annual volume-weighted average NH_4^+ concentration in precipitation at NADP/NTN site NC35 (Sampson County) during the period 1982–1997. Turkey and broiler populations for the years 1982–1991 are estimated from statewide populations.

The NADP/NTN has developed a four-component rating procedure for determining the degree to which data adequately characterize a particular summary period. The first criterion represents the percentage of the summary period for which there are valid samples and requires a value $\geq$ 74.5 for inclusion of a data point in official NADP/NTN products such as maps and summary tables. Criterion 2 is the percentage of the summary period for which precipitation amounts are available either from the collocated rain gage or from the sample volume and has a cutoff value of 89.5. Criterion 3 is the percentage of total measured precipitation associated with valid samples and has a cutoff value of 74.5. Criterion 4 is sampler collection efficiency (percentage) which is the sum of sample bucket precipitation depth during the period divided by the sum of the rain gage amounts for valid samples where both values are available. This criterion also has a cutoff value of 74.5. In this study, criteria 1, 3, and 4 are relaxed slightly to a cutoff value of 73.8. This is done so that an additional annual data point, which does not exhibit any outlier signatures, can be included at site NC35. This cutoff value reduction is much less than 1 SD for each of the relaxed criteria, which are 7.6, 10.8, and 4.1, respectively. Based on the above criteria, two annual values are omitted from the analysis.

2. Methods and Results

Figure 2 shows annual values of NH_4^+ concentration in precipitation at NADP/NTN site NC35, located in Sampson County, and NH_3 emissions by source type for area I (Figure 1) during the period 1982–1997. Ammonia emissions for livestock are calculated by applying emission factors taken from Battye et al. (*9*) to annual county-scale livestock population estimates (*10*). Ammonia emissions from fertilizer are based on total tonnage of single and multinutrient nitrogen containing fertilizers shipped into area I (*10*). Emission factors (*9*) are then used to estimate total NH_3 emissions from nitrogen fertilizers in this region.

Addressing the NH_4^+ concentration time series, an interesting feature of the plot is an apparent 4-year cycle. To determine the statistical significance of this cycle, the following multiple regression model is used:

$$Y_i = a_o + a\cos(2\pi i/X - \phi) + bi + cP_i + e_i \qquad (1)$$

$$i = 1, ..., N$$

In model 1, Y_i is the natural logarithm of the annual volume-weighted average NH_4^+ concentration value during year i. The term bi represents any monotonic trend in NH_4^+ concentration with time, and P_i is the natural logarithm of the precipitation volume during year i. It has previously been shown that weekly samples and, in some cases, monthly volume-weighted samples show an inverse relationship between NH_4^+ concentration and precipitation volume (*19*, *20*, *14*). For this reason, precipitation volume is used as an explanatory variable in the model. Finally, a_o represents the intercept of the regression line while the residual (e_i) represents the error in the point prediction of Y.

The cosine term in (1) models the cyclic pattern of the time series, with amplitude (a), period in years (X), and phase angle (ϕ). In this case, $X = 4$ represents a recurring cycle with a period of 4 years. The cosine term in model 1 is decomposed into

$$a\cos(2\pi i/X - \phi) = \alpha\cos(2\pi i/X) + \beta\sin(2\pi i/X) \qquad (2)$$

where the estimate ($\hat{a}$) of (a) is given by

$$\hat{a} = \sqrt{\hat{\alpha}^2 + \hat{\beta}^2} \qquad (3)$$

and

$$\hat{\phi} = \arctan(\hat{\beta}/\hat{\alpha}) \quad \text{if } \hat{\alpha} \geq 0$$
$$\hat{\phi} = \arctan(\hat{\beta}/\hat{\alpha}) + \pi \quad \text{if } \hat{\alpha} < 0 \qquad (4)$$

Thus, when information on the frequency of the cycle of interest is known, regression of the dependent variable (Y_i) on the sine and cosine terms on the right-hand side of (2) provides a test of the statistical significance of (a). More specifically, a t-test can be calculated under the null hypothesis that (a) is zero, which would suggest that there is no component of the cosine term in (1) at frequency $2\pi i/X$. The use of trigonometric functions in regression analysis to model sinusoidal characteristics of time series is widely used (*21*, *22*) and has specifically been used to model temporal variation in precipitation chemistry (*23*, *20*). Substituting (2) into (1) yields the final form of the regression model

$$Y_i = a_o + \alpha \cos(2\pi i/X) + \beta \sin(2\pi i/X) + bi + cP_i + e_i \quad (5)$$

$$i = 1, ..., N$$

where $N = 16$ represents the number of years in the time series. Using the Proc AutoReg (*22*) regression procedure within SAS, estimates $\hat{a}_0$, $\hat{\alpha}$, $\hat{\beta}$, $\hat{b}$, and $\hat{c}$ of the regression coefficients in (5) are calculated. Estimates of (a) and (ϕ) are then calculated using (3) and (4), respectively. Within Proc AutoReg, an autoregressive model is assigned to residuals when they are found to be correlated in time. First-order autocorrelation is assessed by using the Durbin-Watson test (*21*).

Using model 5, the apparent 4-year cycle in annual volume-weighted average NH_4^+ concentration is revealed to be statistically significant at the 1% level and explains about 20% of the variation in NH_4^+ concentration when variation due to time trend and precipitation volume are accounted for. This means that there is less than a 1% probability ($p < 0.01$) of falsely rejecting the hypothesis that (a) in model 1 is equal to zero. This test of statistical significance is valid under the assumptions that the regression model residuals are uncorrelated in time, have constant variance, and have a normal probability distribution (*21*). Precipitation volume is not a significant predictor of NH_4^+ concentration at the 10% level. The term (bi) is significant and will be discussed later.

An analysis of mean annual ambient surface temperatures, collected at a station in Sampson County (*16*), using the model

$$T_i = a_o + \alpha \cos(2\pi i/X) + \beta \sin(2\pi i/X) + bi + e_i \quad (6)$$

where T_i is the mean annual ambient surface temperature during year i, reveals a significant ($p < 0.01$) 4-year cycle which is generally in phase (within 0.08 rad or ≈20 days) with that of NH_4^+ concentration (Figure 3). The cyclic pattern associated with the sine and cosine terms in (6) explains about 40% of the variation in temperature. The trend term (bi) in (6) is not significant at the 10% level. Walker et al. (*14*) and Smith (*20*) found a significant seasonal cycle, peaking during the summer, in NH_4^+ concentration in precipitation at NADP/NTN sites across North Carolina. It follows that the influence of temperature on NH_4^+ concentration in precipitation should also exist on longer time scales, as shown in this analysis. Using the model

$$Y_i = fT_i + bi + cP_i + e_i \quad (7)$$

temperature (T_i) explains approximately 10% ($p < 0.10$) of the variation in NH_4^+ concentration at site NC35. The trend term (bi) explains approximately 65% of the variation ($p < 0.01$), and precipitation volume is found not to be a significant predictor variable ($p > 0.10$) when temperature and trend are taken into account. Analysis of annual NH_4^+ concentration in precipitation values is also performed at additional North Carolina NADP/NTN sites located in Wake (NC41), Rowan (NC34), Scotland (NC36), Bertie (NC03), and Macon (NC25) counties (Figure 1), to determine if this annual temperature effect is common among sites. Analyzing data for individual sites (model 6), a 4-year temperature cycle is detected in all cases. No sites individually show a statistically significant 4-year cycle in NH_4^+ concentration (model 5) or temperature effect (model 7). In analyzing the data for individual sites, however, several sites exhibit residuals which are autocorrelated and not distributed normally, thus the assumptions for linear regression modeling are violated. Therefore, use of the reported p-values to determine the significance of independent model variables is questionable. Normality of the residuals is assessed using the Shapiro-Wilk test (*24*). By combining the datasets for all sites except NC35 and performing the same analysis, the model assumptions are satisfied. Combining the datasets also increases the sample size from $N = 16$ for individual sites to approximately $N = 80$. The power of a statistical test, or the probability that statistical significance will be detected if indeed present, depends on test significance level, magnitude of the effect being detected, and sample size (*21*). Thus, increasing the sample size from $N = 16-80$ increases the probability of detecting the 4-year cycle in NH_4^+ concentration and temperature effect. In the combined dataset, a significant ($p < 0.01$) 4-year cycle in NH_4^+ concentration is found and is generally in phase (within 0.09 rad or ≈20 days) with the underlying significant ($p < 0.01$) temperature cycle. Finally, in the combined dataset, temperature is found to be a significant ($p < 0.10$) predictor variable for NH_4^+ concentration, explaining about 6% of the variation, while precipitation volume is not significant (10% level).

Numerous studies have reported a positive correlation between measured ambient NH_3 concentration and temperature in the atmospheric boundary layer (*25*, *26*). It follows that ambient NH_4^+ concentration, and thus the concentration of NH_4^+ in rainfall, should also display a positive correlation with temperature. In general, higher air temperatures will result in larger NH_3 emission rates from several known sources, both anthropogenic and biogenic. Livestock is the largest source of atmospheric NH_3 globally (21.7 Mt NH_3-N yr^{-1}), accounting for approximately 40% of total emissions (*27*). Ammonia is produced through the hydrolysis of urea found in animal urine, and the emission rate of NH_3 from animal waste is known to increase with temperature (*13*). Ammonia emissions from animal production facilities will therefore exhibit some degree of temperature dependence. Ammonia emission from soil occurs when the partial pressure of NH_3 in soil pores becomes greater than that of the atmosphere. The partial pressure of NH_3 in soil is positively correlated with soil solution pH, NH_4^+ concentration, and temperature (*25*). Furthermore, the production rate of soil NH_4^+ through mineralization also increases with temperature (*28*). Undisturbed ecosystems, including unfertilized soils, are believed to cumulatively emit approximately 2.4 Mt NH_3-N yr^{-1} globally (*27*). Ammonia emission from soils increases dramatically with application of nitrogen-containing fertilizers. Synthetic fertilizers and agricultural crops taken together emit approximately 12.6 Mt NH_3-N yr^{-1} or 23% of total global emissions (*27*). Other factors which may influence the ambient concentration of NH_3 at a particular site include changes in prevailing flow conditions and timing of nearby fertilizer applications. As illustrated, site NC35 is located within a densely populated region of livestock operations and croplands. The dependence of ambient NH_3 levels and resulting NH_4^+ concentrations in precipitation on temperature at this site is likely influenced by the temperature dependency of NH_3 emissions from nearby swine and poultry operations, along with fertilized soils. Direct measurements of NH_3 emissions from animal production facilities in the U.S. are limited. Researchers have shown, however, that emission of NH_3 from swine waste

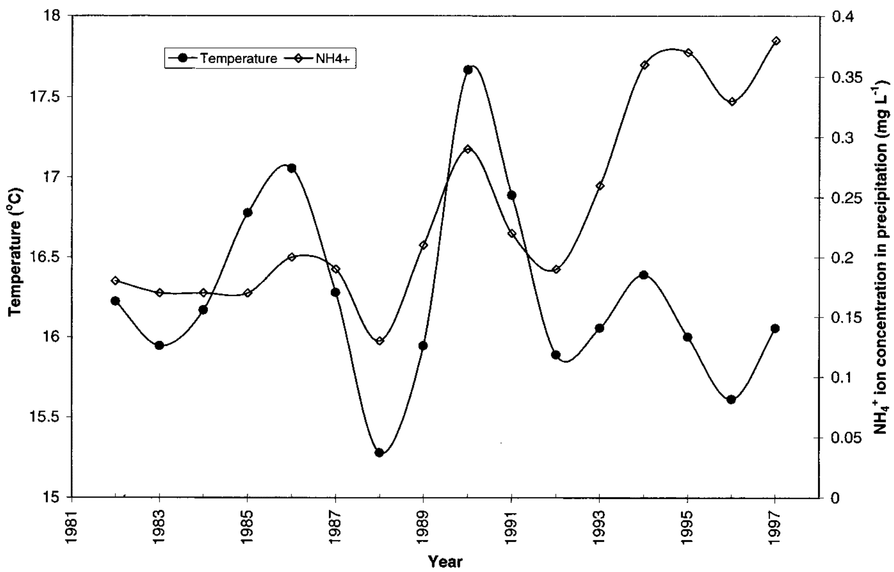

FIGURE 3. Mean annual temperature and annual volume-weighted average NH_4^+ concentration in precipitation at NADP/NTN site NC35 (Sampson County) during the period 1982−1997.

treatment lagoons has a positively correlated exponential relationship with lagoon water surface temperature (*29, 30*).

In previous studies, it has been shown that a loss of NH_4^+ from a precipitation sample may occur post-collection due to microbial consumption and volatilization (*31, 32*). This effect may impose an underestimate in average annual values of NH_4^+ concentrations in precipitation. Conversely, it should be noted that a fraction of the NH_4^+ measured in the sample represents NH_3 and NH_4^+ which is dry deposited to the precipitation collector, acting to impose a positive bias (*33*). Both of the above biases are likely to be positively correlated with temperature, and it is, unfortunately, impossible to assess the net effects on the results of this study.

The cause of the 4-year temperature cycle in Figure 3 is difficult to discern, but may arise at least partly from synoptic scale meteorological influences such as the El-Nino Southern Oscillation (ENSO) and the North Atlantic Oscillation (NAO). The ENSO refers to an oscillation in the surface pressure between the southeastern tropical Pacific Ocean and the Australian-Indonesian regions. During an ENSO event, the waters of the eastern Pacific are warmer than normal, causing a sea level pressure drop in the eastern Pacific and an increase in the west. The NAO refers to an oscillation in the normal surface pressure field over the Atlantic Ocean. The redistribution of Northern Hemispheric precipitation and temperature patterns associated with NAO and ENSO is well documented (*34, 35*). Over the southeast U.S., ENSO events are generally associated with cooler than normal temperatures (*36*), while the opposite is true for NAO events (*37*).

Monthly values of the Southern Oscillation Index (SOI) for the period 1982−1997 were obtained from the East Anglia Climate Research Unit (*38*). The monthly SOI is based on the normalized pressure difference between Tahiti and Darwin, with negative values indicating an ENSO event. For details on the SOI calculation, the reader is referred to Ropelewski and Jones (*39*). Hurrell's monthly values of the NAO Index (*35*) were obtained from the Climate Analysis Group, University of Reading (*40*). The monthly NAO Index is based on the difference of normalized sea level pressures between Ponta Delgada, Azores and Stykkisholmur/Reykjavik, Iceland. For information on the calculation of the NAO Index, the reader is referred to Hurrell and van Loon (*37*). For the analysis presented here, winter (Jan−Feb) and summer (Jul−Aug) values of both indices are calculated, along with annual averages, for each year.

Multiple regression analysis suggests that annual average temperature for all sites across the state is positively correlated ($p = 0.095$, $R^2 = 0.15$) with the annual NAO Index. Annual temperature and SOI values are not correlated at the 10% significance level. Furthermore, it is found that winter temperatures are strongly correlated winter NAO Index values ($p = 0.003$, $R^2 = 0.46$), while summer temperatures are not correlated with summer NAO Index values at the 10% level. Finally, annual temperature values are more strongly correlated with winter temperatures ($p = 0.07$, $R^2 = 0.31$) than summer temperatures ($p = 0.39$) during the period of analysis. This evidence suggests that the NAO is potentially a source of variation in annual temperature values across the state and is, therefore, through the temperature dependence of ambient NH_3 concentrations, a potential source of variation in annual NH_4^+ concentration in precipitation. A more sophisticated and thorough statistical analysis than presented here is warranted to further test this hypothesis. Further detailed analysis is also needed to identify additional sources of variation in the temperature time series shown in Figure 3.

Temperature is shown to be a significant predictor variable for annual volume-weighted average NH_4^+ concentrations at sites across the state. This is further evidence (*41*) that air quality models should account for the temperature dependence of NH_3 emissions when using standard NH_3 inventories based on livestock populations and fertilizer tonnage.

The second feature of the NH_4^+ time series is an apparent positive trend. Model 5 shows a statistically significant positive trend (*bi*) which explains approximately 65% of the variation in annual NH_4^+ concentrations when precipitation and temperature effects are taken into account. To detect any changes in this trend across time, a locally weighted regression (*loess*) curve is fit through the time series (Figure 4). This loess procedure uses a tricube weighting function and local linear regression (*42*). The smoothing parameter is chosen by selecting the number of observations in a local regression interval which minimizes the generalized cross validation mean square error (*42, 43*). This loess curve shows a slight increase in NH_4^+ concentrations prior to 1989 followed by a greater increase with time after 1989. Walker et al. (*14*), using multiple regression analysis of monthly volume-weighted average concentration values, revealed a significant ($p < 0.01$) positive trend over the period 1990−1996 and lack of a significant ($p > 0.10$) trend during the period 1983−1989

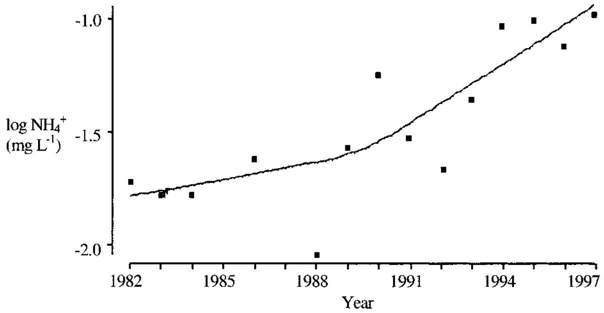

FIGURE 4. Nonparametric loess curve showing the change with time of the trend in natural-log transformed values of annual volume-weighted average NH_4^+ concentration in precipitation during the period 1982−1997 at NADP/NTN site NC35 (Sampson County).

at this site. Walker et al. (*14*) report that no trends are detected during either period at sites NC03, NC25, NC36, or NC41. An increasing trend was observed at site NC34 during the period 1990−1996, but is not thought to be related to area I NH_3 emissions. During the period 1990−1997 analyzed in the present study, there is no increasing trend in temperature at NC35 which, if present, may help to impose an increasing trend in concentration of NH_4^+ in precipitation. It is hypothesized that the positive trend in NH_4^+ concentration in precipitation at NC35 after 1989 (period 2) is related to increasing local NH_3 emissions.

To investigate temporal changes in area I population-based NH_3 emissions estimates between periods 1 (1982−1989) and 2 (1990−1997), linear regression is used to test for statistically significant differences in period-averaged NH_3 emissions for each source. To facilitate this test, a regression model of the form

$$S_i = bY_i + e_i \tag{8}$$

is used where S_i is the natural logarithm of estimated NH_3 emission (kg) during year i. The variable Y is defined as 0 for $i < 1990$ and 1 for $i > 1989$. In this regression framework, a positive value of $\hat{b}$ suggests that average emissions are higher during period 2. This method is used to compare emissions between the two periods because traditional tests of period mean emissions are deemed inappropriate due to first-order autocorrelation in the data. The above regression procedure, performed using Proc AutoReg, accounts for this autocorrelation.

Using this method, period-average atmospheric NH_3 emissions from hogs are significantly ($p < 0.01$) greater during period 2; that is, $\hat{b}$ is positive and has a p-value < 0.01. Atmospheric NH_3 emissions estimates from non-broiler chickens are significantly ($p < 0.01$) lower during period 2. Period-averaged cattle emissions estimates are not significantly different (10% level) during the two periods. Fertilizer emissions estimates showed a slight average increase during the second period that is statistically significant at the 10% level.

County-scale populations for turkeys and broilers are only available beginning in 1992. An effort has been made, however, to estimate their annual area I populations for the years 1982−1991 based on statewide population estimates which are available for the entire analysis period. Taking the total statewide annual population of turkeys for the years 1992−1997, the percentage of that population residing in area I during each of the years 1992−1997 is calculated. The average fraction of turkeys in the state residing in area I during the years 1992−1997 is 0.60 with a standard deviation of 0.008. Assuming that this fraction is constant across the period 1982−1997, population-based area I NH_3 emissions from turkeys are estimated for the missing years 1982−1991 using

TABLE 3. Summary of Area I Mean NH_3 Emissions (Tons NH_3 yr^{-1}) by Source for the Periods 1982−1989 (Period 1) and 1990−1997 (Period 2)[a]

source	period 1 mean	period 2 mean	% difference	% contribution to net increase in av yearly total emissions from all sources between periods[b]
hogs	9319.5	38729.5	+315.6	85.4
fertilizer	7892.0	8954.4	+13.5	3.0
cattle	1091.9	1213.5	+11.1	0.3
turkeys[c]	6202.3	9576.6	+54.4	10.0
broilers[c]	1587.9	2127.9	+34.0	1.6
non-broiler chickens	390.7	303.9	−22.2	NA

[a] $N = 8$ for each mean. [b] The net change in average total yearly emissions for all sources between periods is +34421.5 tons NH_3 yr^{-1}. The average yearly emission for all sources during period 1 is 26484.3 tons, while the mean for period 2 is 60 905.8 tons. [c] Populations for the years 1982−1991 are estimated from statewide populations assuming that the fraction of statewide turkeys and broilers residing in area I during the period 1982−1997 is constant.

statewide populations. Applying model 8 to these data then reveals that average estimated emissions from turkeys are significantly ($p < 0.05$) higher within area I during period 2. As depicted in Figure 2, however, the majority of growth in the turkey population occurred during period 1. A similar prediction process is carried out for broiler emissions. The average annual fraction of broilers in the state residing in area I during the years 1992−1997 is 0.11 with a standard deviation of 0.007. Again, a data set of area I annual NH_3 emissions for the period 1982−1997 is constructed from predicted broiler population values (1982−1991) and actual population values (1992−1997). Applying model 8 to this data set reveals that average estimated broiler emissions of NH_3 are significantly ($p < 0.05$) higher within area I during period 2. In interpreting the results of this exercise it is important to keep in mind the assumptions made in estimating NH_3 emissions from turkeys and broilers during the period 1982−1991. For comparison, it should be noted that throughout the entire period (1982−1997) the percentage of statewide cattle and chicken populations residing in area I experienced a net change of approximately +1.5 and −3%, respectively, while hogs experienced a net change of +30%.

From the above discussion, it is evident that the trend in NH_4^+ concentration in rainfall at NADP/NTN site NC35 may be the result of increasing NH_3 emissions from a combination of sources. Table 3 gives the population-based average yearly emissions estimates by source for each period and their respective percent changes between periods. The most dramatic difference in period means is seen in hog emissions, which experienced a positive change of 316%. Turkey emissions are found to be 54% higher during period 2. Table 3 also shows the percent contribution of individual source increases to the net increase in average yearly emissions from all sources between periods. The average total emission during period 1 is approximately 26484.3 tons, while the average during period 2 is approximately 60 905.8 tons, reflecting an increase of 34421.5 tons. The increase in average hog emissions contributes approximately 85% of the increase in total emissions, while turkeys contribute about 10% of the increase.

This atmospheric emissions analysis suggests that, if indeed NH_4^+ concentration in precipitation at site NC35 is affected by local NH_3 sources, the positive trend in concentration is likely a response to increasing NH_3 emissions from fertilizer, broilers, turkeys, and hogs, with the major contributor being hog emissions.

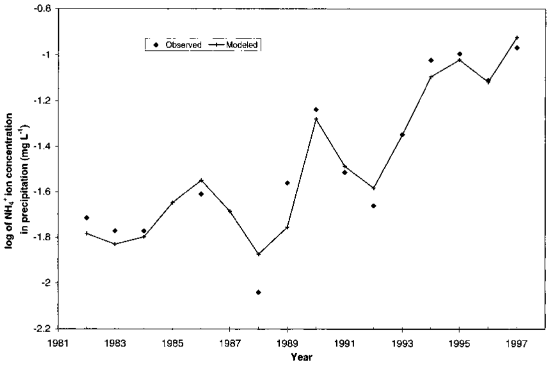

FIGURE 5. Observed and predicted (model 9) natural-log transformed values of annual volume-weighted average NH_4^+ concentration in precipitation at NADP/NTN site NC35 (Sampson County) during the period 1982−1997.

This analysis shows that temperature is consistently a significant predictor variable for annual volume-weighted average NH_4^+ concentration in precipitation at NC35 and other sites across the state. A significant increasing trend in NH_4^+ concentration is observed at NC35 beginning near 1989, which is correlated with higher average NH_3 emissions from turkeys, broilers, fertilizer, and hogs during period 2. Hogs are the dominant contributor to the total emissions increase. Precipitation volume is in general not a significant source of variation in annual volume-weighted average NH_4^+ concentration in precipitation at NC35 and other sites across the state. Based on these observations, the following model is constructed for site NC35

$$\log(NH_4^+) = -10.59 + 0.14^* \beta_1 + 1.786E - 8^* \beta_2 + e \quad (9)$$

where $\log(NH_4^+)$ is the natural log of the annual volume-weighted average NH_4^+ concentration in precipitation, β_1 is annual average ambient temperature (°F), β_2 is annual area I swine NH_3 emission (kg) for the corresponding year, and e is the model error. Using this model, temperature explains about 15% of the variation in NH_4^+ concentration, while population-based NH_3 emissions from hogs explain about 75% of the variation. Cornelius (*44*) also found hog population within Sampson County to be a significant predictor variable for NH_4^+ concentration at NC35. Model 9 explains about 90% of the overall variation in annual volume-weighted average NH_4^+ concentration in precipitation at NC35 during the period 1982−1997 (Figure 5). The general form of this model should be applicable to other sites within areas densely populated by livestock. It may provide information on the potential impact of increasing livestock populations on wet NH_4^+ deposition to nitrogen-sensitive ecosystems. This statistical model may also be a useful comparative tool for air quality model evaluation.

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