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Agricultural ammonia emissions and ammonium concentrations associated with aerosols and precipitation in the southeast United States

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[1] Temporal and spatial variations in ammonia (NH_3) emissions and ammonium (NH_4^+) concentrations associated with aerosols and volume-weighted NH_4^+ concentration in precipitation are investigated over the period 1990–1998 in the southeast United States (Alabama, Florida, Georgia, Kentucky, North Carolina, South Carolina, Mississippi, and Tennessee). These variations were analyzed using an NH_3 emissions inventory developed for the southeast United States and ambient NH_4^+ data from the various Clean Air Status and Trends Network (CASTNet) and the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Results show that natural log-transformed annual NH_4^+ concentration associated with aerosols increases with natural log-transformed annual NH_3 emission density within the same county ($R^2 = 0.86$, $p < 0.0001$, $N = 12$). Natural log-transformed annual volume-weighted average NH_4^+ concentration in precipitation shows only a very weak positive correlation with natural log-transformed annual NH_3 emission densities within the corresponding county ($R^2 = 0.12$, $p = 0.04$, $N = 29$). Analysis of NH_4^+ concentration associated with aerosols at CASTNet sites revealed that temperature, precipitation amount, and relative humidity are the most statistically significant ($p < 0.05$) parameters in predicting the weekly concentrations of NH_4^+ during the period 1990–1998. Wind speed and wind direction were also statistically significant ($p < 0.05$) at several CASTNet sites, but the results were less consistent. Investigation into wet NH_4^+ concentration in precipitation consistently yielded temperature as a statistically significant ($p < 0.05$) parameter at individual sites. Trends over the period 1990–1998 revealed a slight decrease in NH_4^+ concentration at CASTNet site SPD, Claiborne County, Tennessee (2.14–1.88 $\mu g\ m^{-3}$), while positive trends in NH_4^+ concentration in precipitation were evident at NADP sites NC35, Sampson County, North Carolina (0.2–0.48 mg L^{-1}) and KY35, Rowan County, Kentucky (0.2–0.35 mg L^{-1}) over the period 1990–1998. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0330 Atmospheric Composition and Structure: Geochemical cycles; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* ammonia, ammonium, aerosols, agriculture, southeast United States, statistical model

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1. Introduction

[2] Ammonia (NH_3) plays an important role in the atmosphere, neutralizing acids formed by the oxidation of such compounds as sulfur dioxide (SO_2) and nitrogen oxides ($NO_x = NO + NO_2$) [*Aneja et al.*, 2000; *RIVM*, 1995; *Nihlgard*, 1985; *Asman et al.*, 1982]. These reactions result in ammonium (NH_4^+)-containing aerosols, which may be of concern in particulate matter (PM_{fine}) nonattainment areas. At the Earth's surface, NH_x (= $NH_3 + NH_4^+$) at low concentrations can be a valuable source of nutrient input; however, high concentrations can lead to acidification of soils, forest decline, and eutrophication of waterways [*Asman*, 1994; *Aneja et al.*, 1998]. Therefore, the spatial distribution of NH_3 emissions and parameters which control

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the fate of this specie are important in determining areas of excess nitrogen input, and will aid in the development of models to predict the transport and deposition of atmospheric NH_x.

[3] Globally, approximately 54 (22–83) Tg N-NH_3 (1 Tg $=10^{12}$ g) are emitted each year [*Bouwman et al.*, 1997; *Schlesinger and Hartley*, 1992; *Warneck*, 1988]. The largest fraction (~41%) is from domestic animal excreta, at approximately 22 Tg N-NH_3 yr^{-1}. In the United States, domestic animal waste is also the largest contributor to atmospheric NH_3 emissions, responsible for approximately 80% nationwide [*Battye et al.*, 1994]. Combined with fertilizer application to farmland, animal husbandry and agricultural practices account for ~90% of the total NH_3 emitted in the United States each year [*Battye et al.*, 1994]. Approximately 32% of the southeast United States (Alabama, Florida, Georgia, Kentucky, North Carolina, South Carolina, Mississippi, and Tennessee) is used for farming practices and agriculture and while the southeast accounts for only 12% of the total area of the continental United States, it holds 18% of the total farmland [*USDA*, 1999].

[4] Analysis of the fate of NH_3 emissions in the United States is complicated by a lack of data on gaseous NH_3 in the ambient atmosphere. NH_3 monitoring data for the United States are rare, and data on long-term ambient trends are generally not available for gaseous NH_3. However, acid deposition monitoring networks provide considerable data on NH_4^+ ion concentrations in particulate matter. The Clean Air Status and Trends Network (CASTNet) measures concentrations of particulate NH_4^+, sulfate (SO_4^{2-}), and nitrate (NO_3^-). These data can provide some insights into the fate of gaseous NH_3 emissions. Therefore the objective of this study is to investigate concentrations of NH_4^+ associated with aerosols and in precipitation and NH_3 emissions in the southeast United States over the period 1990–1998, with the intent of defining relationships between NH_4^+ concentrations, local meteorology and NH_3 emissions.

2. Methods

2.1. Data Selection

[5] To estimate NH_3 emissions, agricultural data was obtained from the 1997 Census of Agriculture [*USDA*, 1999]. The census provided a complete data set for cattle and horses (i.e., an exact number was provided for each county in each state). However, the data for poultry, swine, and sheep was incomplete. In this case, the total number of animals was based on the average farm inventory. When the statewide population was less than 5000 for a particular animal, the estimate for that animal was considered negligible and therefore excluded from the final estimates. In the case of fertilizer, data was obtained from the Association of American Plant Food Control Officials, Inc. and is based on sales made by fertilizer registrants in each state.

[6] Data on NH_4^+ concentration associated with aerosols was obtained from the Clean Air Status and Trends Monitoring Network [*CASTNet*, 1998]. CASTNet was designed to be a rural monitoring network collecting data to establish site-specific measurements of total deposition and is considered the nation's primary source for estimates of dry acidic deposition and rural ozone (O_3) concentrations [*CASTNet*, 1998]. The network consists of 51 monitoring sites located across the United States, most of which have been operational since 1987. Continuous measurements of meteorological data including temperature, relative humidity, solar insolation, precipitation, wind speed, and wind direction are taken at each site and atmospheric concentrations of NH_4^+ are obtained from weekly filter pack measurements [*Holland et al.*, 1999].

[7] The CASTNet monitoring network [*USEPA*, 1998] measures weekly average ambient concentrations of particulate NH_4^+ [*Lawrence et al.*, 2000; *Sickles et al.*, 1999; and *Clarke et al.*, 1997]. The network also measures concentrations of particulate SO_4^{2-}, NO_3^-, base cations, O_3, SO_2, and nitric acid (HNO_3). NH_4^+ in the particulate, which is collected on a Teflon filter, is measured on a weekly basis by colorimetry. The CASTNet network was not designed to measure NH_3 gas. Ten CASTNet sites chosen for this study were selected based on location and availability of data. All of the sites, excluding CKT (located in Morgan County, KY), have more than 290 weekly NH_4^+ measurements from 1990 to 1998 making them suitable for long-term trend analysis. For more information regarding CASTNet data analysis and validation procedures, see the studies of *Clarke et al.* [1997] and of *USEPA* [1998].

[8] Data on NH_4^+ concentration associated with precipitation were obtained from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) [*NADP/NTN*, 1999]. NADP/NTN began monitoring in 1978 and currently operates over 200 sites nationwide. The purpose of the network is to collect data on the chemistry and amount of precipitation for monitoring spatial and temporal long-term trends. The precipitation at each station is collected weekly from AeroChem Metrics wet–dry deposition samplers according to strict clean-handling procedures. The precipitation sample is then sent to the Central Analytical Laboratory in Illinois, where it is analyzed for hydrogen (acidity as pH), SO_4^{2-}, NO_3^-, NH_4^+, chloride, and base cations (such as calcium, magnesium, potassium, and sodium) (NADP/NTN). Data validation procedures used at the laboratory are described by *Bowersox* [1984].

[9] It should be noted that both positive and negative biases in NH_4^+ concentration in precipitation have been measured. A positive bias may result from the deposition of NH_3 gas to the open precipitation collector [*Jensen and Asman*, 1995]. This bias will, on average, be greatest in agricultural areas and will likely be positively correlated with ambient temperature. A negative bias, as large as 40% in some cases, has been shown to result from postcollection incorporation of NH_4^+ into microbial biomass [*Ramundo and Seastedt*, 1990; *Lamb and Comrie*, 1993]. This bias is also expected to be larger under warm temperatures. Unfortunately, it is not possible to quantify the net result of these biases. While this source of error may reduce the amplitude of season cycles, due to a net reduction of summer values at most sites, it should not greatly effect the magnitude of long-term trends. At agricultural sites, the competing biases may result in a relatively small net error.

[10] In order to assess the temporal variability in NH_4^+ concentrations associated with aerosols and precipitation across the southeast United States over the period 1990–1998, 10 CASTNet sites and 10 corresponding NADP sites were chosen based on location (distance between CASTNet and NADP sites) and availability of weekly data. For this

Table 1. CASTNet and NADP Sites Used in Weekly and Monthly Analyses of NH_4^+ in Ambient Air and Precipitation[a]

CASTNet Sites					Corresponding NADP Sites					Distance Between Sites (km)
State	County	Identifier	Lat./Long. (°)	Elevation (m)	State	County	Identifier	Lat./Long. (°)	Elevation (m)	
KY	Morgan	CKT	37.92/83.07	455	KY	Rowan	KY35	38.12/83.55	204	47.3
NC	Montgomery	CND	35.26/79.84	198	NC	Rowan	NC34	35.70/80.62	219	86.0
NC	Macon	COW	35.06/83.43	686	NC	Macon	NC25	35.06/83.43	686	0
MS	Yalobusha	CVL	34.00/89.80	134	MS	Yalobusha	MS30	34.00/89.8	134	0.1
GA	Pike	GAS	33.18/84.40	270	GA	Pike	GA41	33.18/84.41	270	0.2
KY	Washington	MCK	37.70/85.05	353	KY	Washington	KY03	37.70/85.05	293	0.1
NC	Avery	PNF	36.10/82.04	1219	NC	Yancey	NC45	35.73/82.12	1987	46.6
AL	Dekalb	SND	34.29/85.97	352	AL	DeKalb	AL99	34.29/85.97	349	0.2
TN	Claiborne	SPD	36.47/83.83	361	TN	Anderson	TN00	35.96/84.29	341	70.0
FL	Liberty	SUM	30.11/84.99	14	FL	Gadsden	FL14	30.55/84.60	60	62.0
					NC	Sampson	NC35	35.02/78.27	41	

[a] KY = Kentucky, NC = North Carolina, MS = Mississippi, GA = Georgia, AL = Alabama, TN = Tennessee, FL = Florida.

time series analysis, an additional NADP site was included (NC35, Sampson County, North Carolina) based on its location within an agricultural region, though this site does not have a corresponding CASTNet site. Table 1 summarizes the CASTNet and NADP sites used in the weekly and monthly analyses of NH_4^+ concentrations associated with aerosols and precipitation. To assess the influence of NH_3 emissions on wet and dry NH_4^+ concentrations, the remaining NADP and CASTNet sites located in the southeast United States which were active during 1997 were added to the analysis. Table 2 lists the CASTNet and NADP sites used in the analysis of NH_3 emissions and NH_4^+ concentrations in this study.

2.2. Data Analysis

[11] In this study, regression analysis, specifically the method of ordinary least squares, was used to identify relationships between dependent and independent variables. This method assumes that the regression errors have constant variance, are uncorrelated with each other in time, and have a normal distribution. Analyses were performed using SAS statistical analysis software.

2.3. Estimating Annual NH_3 Emissions

[12] The first goal of this study is to resolve the spatial variability of NH_3 emissions from agricultural sources in the southeast United States. To develop this regional emissions inventory, emission estimates from all major agricultural sources in the southeast United States were calculated using data from 1997. The sources considered in this inventory include dairy and beef cattle, poultry, swine, horses, and sheep, as well as fertilizer application. County totals are obtained for each source, and NH_3 emission estimates are performed at the county level. For the purpose of this study, NH_3 emissions are assumed to be uniform across the county. This provides a general spatial distribution of estimated NH_3 emissions across the eight-state region. County-level NH_3 emission estimates for each source type are based on the following equation:

$$
\begin{aligned}
&Emission\ rate\left(kg\ NH_3\ yr^{-1}\right)\\
&\quad = Activity\ Data(animal\ population)\\
&\quad \times Emission\ Factor\left(kg\ NH_3\ animal^{-1}\ yr^{-1}\right)
\end{aligned}
$$

The activity data is simply the number of animals present in each county, and is obtained from the 1997 U.S. Census of Agriculture [*USDA*, 1999]. The emission factors are based on experimental measurements of average emissions per animal (kg NH_3 animal^{-1} yr^{-1}) and mass balance calculations. Most of the experimental emission factors are obtained from Europe, where animal practices may vary significantly from the United States. Furthermore, the NH_3 emissions are sensitive to changes in animal diet, atmo-

Table 2. CASTNet and NADP Sites Used in the NH_3 Emissions Analysis

	State	County	Identifier	Lat./Long. (°)	Elevation (m)
CASTNet	AL	Dekalb	SND	34.29/85.97	352
	FL	Liberty	SUM	30.11/84.99	14
	GA	Pike	GAS	33.18/84.40	270
	KY	Morgan	CKT	37.92/83.07	455
	KY	Washington	MCK	37.70/85.05	353
	MS	Yalobusha	CVL	34.00/89.80	134
	NC	Montgomery	CND	35.26/79.84	198
	NC	Macon	COW	35.06/83.43	686
	NC	Avery	PNF	36.10/82.04	1219
	NC	Carteret	BFT	34.88/76.62	2
	TN	Claiborne	SPD	36.47/83.83	361
	TN	Dekalb	ESP	36.04/85.73	302
NADP	AL	Dallas	AL10	32.46/87.24	58
	AL	Dekalb	AL99	34.29/85.97	349
	FL	Bradford	FL03	29.97/82.20	44
	FL	Citrus	FL05	28.75/82.55	3
	FL	Dade	FL11	25.39/80.68	2
	FL	Gadsen	FL14	30.55/84.60	60
	FL	Sarasota	FL41	27.38/82.28	25
	FL	Brevard	FL99	28.54/80.64	2
	GA	Charlton	GA09	30.74/82.13	47
	GA	Evans	GA20	32.14/81.97	62
	GA	Pike	GA41	33.18/84.41	270
	GA	Tift	GA99	31.52/83.55	107
	KY	Washington	KY03	37.70/85.05	293
	KY	Letcher	KY22	37.08/82.99	335
	KY	Rowan	KY35	38.12/83.55	204
	MS	Hinds	MS10	32.31/90.32	86
	MS	Newton	MS19	32.33/89.17	115
	MS	Yalobusha	MS30	34.00/89.90	134
	NC	Bertie	NC03	36.13/77.17	22
	NC	Macon	NC25	35.06/83.43	686
	NC	Rowan	NC34	35.70/80.62	219
	NC	Sampson	NC35	35.03/78.28	41
	NC	Scotland	NC36	34.97/79.53	132
	NC	Wake	NC41	35.73/78.68	120
	NC	Yancey	NC45	35.74/82.29	1987
	SC	Clarendon	SC06	33.54/80.44	24
	TN	Anderson	TN00	35.96/84.29	341
	TN	Sevier	TN11	35.66/83.59	640
	TN	Haywood	TN14	35.47/89.16	107

Table 3. Published Emission Factors for Livestock (kg NH_3 animal^{-1} yr^{-1})

Source	ECETOC (1994)[a]	EMEP (1996)[b]	*Misselbrook et al.* [2000]	*Bouwman et al.* [1997]	Buijsman (1987)[a]	*Asman* [1992]	UNECE [c]
Dairy Cow	39.5	29.1	26.52	24.8	–	39.7	28.5
Beef Cow	27.8	14.6	6.8	9.5	13.7	23.1	14.3
Pigs	4.25	–	–	4.9	2.8	5.34	–
Sow	–	16.6	5.2	–	–	–	16.43
Finishing pig	–	6.46	4.8	–	–	–	6.39
Poultry	0.19	–	–	0.24	0.26	.24	.37
Laying hen	–	0.38	.45	–	–	–	–
Broiler	–	0.27	.23	–	–	–	.28
Sheep	1.8	1.46	.73	0.77	3.16	1.7	1.34
Horses	11.9	–	–	9.2	9.35	12.1	8.0

[a] Data from *Sutton et al.* [1994].

[b] Data from *Misselbrook et al.* [2000].

[c] Data from *Van Der Hoek* [1998].

spheric temperature and humidity, waste-handling practices, and many other parameters [*Asman*, 1992]. Because of the many uncertainties, it may be difficult to obtain an accurate NH_3 emission estimate. Table 3 is a summary of documented emission factors that were considered in developing the emission inventory for this study. The large variation in estimates illustrates the difficulty in developing precise estimates.

[13] Emission factors were selected for each livestock group including beef and dairy cattle, hogs and pigs, chickens, broilers, turkeys, horses, and sheep. An earlier study and literature review by *Battye et al.* [1994] refined European emission factors based on United States agricultural practices. Their results have been used as a guide to obtain the emission factors employed in this study. The U.S. Census of Agriculture has provided estimates for both beef and dairy cattle; therefore, a unique emission factor was determined for each. *Battye et al.* [1994] recommend 15.19 kg NH_3 animal^{-1} yr^{-1} for beef cattle or "young cattle for fattening." This estimate includes total emissions resulting from animal housing, grazing, manure storage, and land spreading. The recommendation by *Battye et al.* [1994] is based on research and literature reviewed by *Asman* [1992]. Considering these estimates to be somewhat out of date, an average of more recent estimates by *Bouwman et al.* [1997], *Misselbrook et al.* [2000], and *Van Der Hoek* [1998] is used here resulting in an emission factor of 10.2 kg NH_3 animal^{-1} yr^{-1}. A similar approach is used for dairy cattle, taking the average of emission factors given by *Misselbrook et al.* [2000] and *Van Der Hoek* [1998] to obtain 28.04 kg NH_3 animal^{-1} yr^{-1}.

[14] Hogs and pigs are not divided into weight or class categories in the 1997 Census of Agriculture; however, *Van Der Hoek* [1998] suggests that 3 classes can be determined based on the total population of hogs. One can assume that approximately 50% are fattening hogs, 10% are sows, and the remaining 40% are young sows and piglets. Two unique emission factors, 6.39 and 16.43 kg NH_3 animal^{-1} yr^{-1}, are derived for fattening hogs and sows respectively. The factor 16.43 for sows includes a correction for young sows and piglets that account for 40% of the population. Therefore, to estimate total NH_3 emissions from a general hog population, 50% of the population was multiplied by 6.39 and 10% of the population by 16.43. This equates to an average emission factor of 4.84 kg NH_3 per hog, which has proved to be a satisfactory estimate based on recent studies at a commercial hog farm by *McCulloch* [1999]. His study estimated total NH_3 emissions from hog facilities to be in the range 3.4–6.9 kg NH_3 animal^{-1} yr^{-1} [*McCulloch*, 1999]. *Battye et al.* [1994] proposed emission factors for sheep, broilers, and laying hens older than 20 weeks based on the study of *Asman* [1992]. These estimates have been refined based on new experimental data, and the updated values are employed in this study [*Van Der Hoek*, 1998].

[15] For the remaining animal groups (pullets 13–20 weeks, pullets less than 30 weeks, and turkeys) and fertilizer application, the emission factors proposed by *Battye et al.* [1994] are used. Table 4 lists the estimated emission factors for various nitrogen fertilizers, based on total U.S. consumption in 1993. A summary of emission factors and corresponding 1997 emissions estimates for all domestic livestock and fertilizer application in the southeast are given in Table 5. Based on the emission factors and agricultural census data, both the relative

Table 4. Emission Factors, U.S. Consumption (1993), and Nitrogen Content of Selected Fertilizers [*Battye et al.*, 1994]

Fertilizer	U.S. Consumption (mg[a]) (1993)	Nitrogen Content (%)	Emission Factor (kg NH_3/mg N)
N-P-K	8,191,414	11.2	48
Nitrogen Solutions	7,162,419	33.9	30
Ammonium Phosphates	5,813,042	15.5	48
Anhydrous NH_3	3,593,380	82.0	12
Urea	3,247,631	45.9	182
Ammonium Nitrate	1,582,039	33.9	25
Other Straight Nitrogen	944,803	20.0	30
Ammonium Sulfate	718,400	21.0	97
Aqua NH_3	271,288	20.4	12
Ammonium Thiosulfate	156,047	12.0	30

[a] 1 Mg = 10^3 kg.

Table 5. Emission Factors and Total Emission Estimates for the Southeast United States

Source	Emission Factor ($kg\ NH_3\ animal^{-1}$)	Total Emissions in Southeast (kt)
Beef Cattle	10.2	150.1
Dairy Cattle	28.04	20.5
Horses	8	3.6
Hogs and Pigs	–	62.8
Sows	16.43	–
Fattening Pigs	6.39	–
Sheep	1.34	0.1
Broilers	0.28	174.4
Chickens	–	32.7
Laying Hens	0.37	–
Pullets 13–20	0.269	–
Pullets <13	0.17	–
Turkeys	0.858	21.8
Fertilizer	listed in Table 2	62.9

contribution from each source category (Figure 1) and the spatial distribution of NH_3 emissions were determined (Figure 2).

2.4. Influence of NH_3 Emissions on Atmospheric NH_4^+ Concentrations

[16] Exploratory regression analysis is used to determine relationships between county-scale NH_3 emissions and within-county observed annual average concentrations of NH_4^+ associated with aerosols and annual volume-weighted average concentration of NH_4^+ in precipitation (Table 2). This analysis is performed for the year 1997 to correspond with the NH_3 emission inventory described above.

2.5. Weekly NH_4^+ Concentration Analysis

[17] A statistical analysis is performed to investigate and model trends in NH_4^+ concentration associated with aerosols and precipitation based on correlation with meteorological parameters such as surface temperature, relative humidity, wind speed, and wind direction. Measurements of NH_4^+ concentration in aerosols from 10 CASTNet sites across the southeast United States and NH_4^+ concentration in precipitation from 10 neighboring NADP sites were analyzed for the period January 1990 to December 1998. Due to the proximity of each CASTNet and NADP site (Table 1), the same meteorological data were used for both analyses.

[18] To investigate the relationship between ambient and wet NH_4^+ concentration and meteorology, a multiple linear regression model of the following type was employed at all sites [*Walker et al.*, 2000a; *Holland et al.*, 1999; *Buishand et al.*, 1988; *Dana and Easter*, 1987]:

$$\log(C_t) = a_0 + [a\cos(2\pi t/52) + b\sin(2\pi t/52)] + ct + d_n x_n + e_i \tag{1}$$

where $\log(C_t)$ refers to the natural log-transformed weekly concentration of ambient NH_4^+ ($\mu g\ m^{-3}$) or wet NH_4^+ in precipitation ($mg\ L^{-1}$) at time t weeks from 1 January 1990. Raw data were transformed to help achieve the condition of normality in regression residuals. The second term in model (1) contains sine and cosine functions, which are commonly used to model seasonal cycles in data [*Lynch et al.*, 1995; *Holland et al.*, 1999]. In model (1), the amplitude (A) of the cycle is determined as:

$$A = \sqrt{a^2 + b^2} \tag{2}$$

and the phase angle (ϕ) is determined as:

$$\begin{aligned} \hat{\phi} &= \arctan(b/a) && \text{if } a \geq 0 \\ \hat{\phi} &= \arctan(b/a) + \pi && \text{if } a < 0. \end{aligned} \tag{3}$$

The regression routine calculates p-values for coefficients a and b under the null hypothesis that no cycle is present at frequency $2\pi t/52$ (a = 0 and b = 0). If the p-value for either of the regression coefficients is less than the specified alpha level, the null hypothesis may be rejected. Meteorological parameters (temperature, precipitation amount, relative humidity, wind speed, and wind direction) included in the model are represented by $x_n = x_1, x_2, x_3, x_4$, and x_5. Finally, a_o represents the intercept of the regression line, while the residual (e_i) represents the error in the point prediction of $\log(C_t)$. Only parameters with regression coefficient p-values < 0.1 were considered statistically significant.

2.6. Monthly Mean NH_4^+ Concentration Analysis

[19] Monthly averaged concentrations of NH_4^+ associated with aerosols and monthly volume-weighted average concentrations of NH_4^+ associated with precipitation were also investigated at each CASTNet and NADP site for the period January 1990 to December 1998 (Table 1). For this exercise, two models were applied to all sites in an attempt to better understand the interactions between overall trend, seasonality, and temperature dependence [*Holland et al.*, 1999]. Other meteorological parameters were excluded from this model because monthly averages would perform poorly as predictive parameters. The selected models are:

$$\log(C_t) = a_0 + a\cos(2\pi t/12) + b\sin(2\pi t/12) + ct + e_i \tag{4}$$

$$\log(\mathrm{C_t}) = a_0 + bT_t + ct + e_i \tag{5}$$

Model (4) accounts for seasonal variability of C_t at each site, while model (5) accounts for the dependence of C_t on air temperature. Parameters in model (5) are defined as in model (1). In model (5), T represents monthly average temperature while the remaining terms are defined as in model (1). The use of both temperature and seasonality in

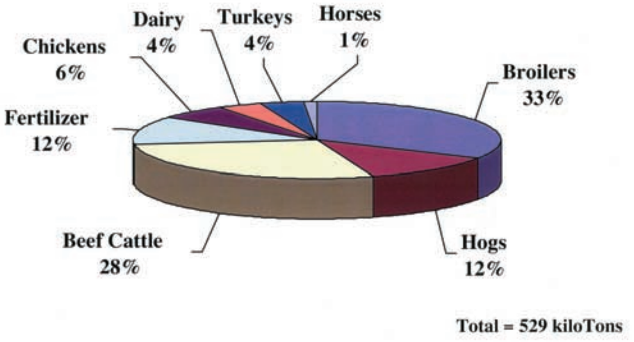


Figure 1. Relative contribution of NH_3 emissions in the southeast United States Source: Nelson, 2000.

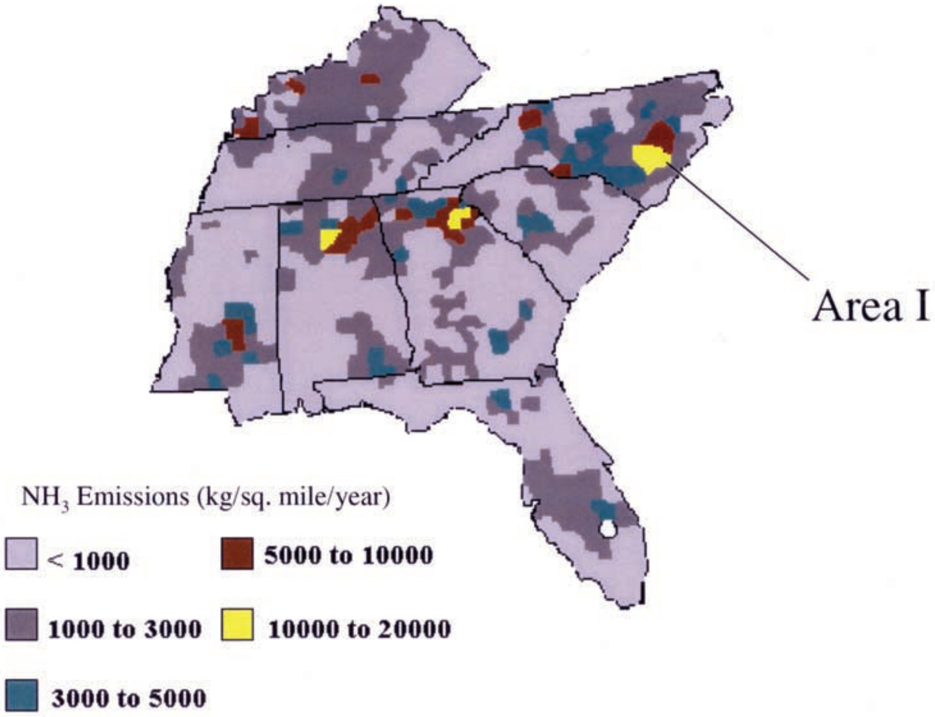


Figure 2. Spatial distribution of NH_3 emissions.

the same model can actually degrade the quality of the model because the two parameters are so highly correlated. Where a trend in NH_4^+ concentration was detected at a particular site, regression models were employed to test for trends in temperature and precipitation volume. This was necessary to determine if the trend in NH_4^+ concentration may have been caused by temporal changes in precipitation volume or temperature.

3. Results

3.1. Spatial Distribution of NH_4^+ Concentrations

[20] Linear regression analysis was performed to investigate the relationship between annual county-scale agricultural NH_3 emission density (Figure 2) and observed annual average NH_4^+ concentrations in aerosols and precipitation within that county during 1997. To improve the normality of regression residuals, NH_4^+ concentrations in aerosols and precipitation, along with emissions, were first natural log-transformed. Regression analyses were performed on transformed variables. Results show that natural log-transformed annual NH_4^+ concentrations associated with aerosols increase with natural log-transformed county annual NH_3 emission density ($R^2 = 0.86$, $p < 0.0001$, N = 12) (Figure 3a). The untransformed data show a clear logarithmic increase in NH_4^+ concentrations in aerosols with increasing emissions. This relationship suggests that local NH_3 emissions strongly influence ambient NH_4^+ concentrations, but that there exists a level above which NH_3 emission is no longer the primary source of variability in ambient NH_4^+ concentration. This can be explained by the fact that NH_4^+ aerosol formation is limited by the availability of acid gases in the presence of excess NH_3. Thus, counties with high NH_3 emission densities likely represent areas within which NH_4^+ aerosol formation is no longer NH_3 limited. A similar regression analysis shows that natural log-transformed annual volume-weighted average NH_4^+ concentration in precipitation shows only a very weak positive correlation with natural log-transformed annual NH_3 emission densities within the corresponding county ($R^2 = 0.12$, p = 0.04, N = 28) (Figure 3b). Perhaps the primary reason for this much weaker relationship is that the incorporation of NH_4^+ into rainfall takes place on a spatial scale greater than the area of individual counties. In most cases, the majority of NH_4^+ observed in rainfall at a particular location originates from relatively distant sources, and the local signal may result from the relatively inefficient process of below-cloud scavenging of NH_3 and NH_4^+ [*Shimshock and De Pena*, 1989]. In general, agricultural NH_3 sources are shown to influence local concentrations of NH_4^+ in aerosols and precipitation both in the United States and Europe [*Marquardt et al.*, 1996; *Erisman et al.*, 1998; *Asman et al.*, 1998; *Aneja et al.*, 2000; *Walker et al.*, 2000a; *Sutton et al.*, 2001a, 2001b].

3.2. Analysis of Weekly NH_4^+ Concentration Associated With Aerosols

[21] Table 6 summarizes the results from model (1) applied to the weekly ambient concentration data at each CASTNet site (Table 1). The R^2 values range from 0.18 at SUM (Liberty County, Florida) to 0.73 at PNF (Avery County, North Carolina). The poor performance of the model at site SUM may be attributed to its location, a Florida site with very little seasonal variability and strong coastal influence.

[22] Precipitation amount was the most significant parameter at 7 out of 10 sites, having a negative regression coefficient ranging from −0.0045 to −0.005. This inverse relationship has also been reported in other studies [*Prado-*

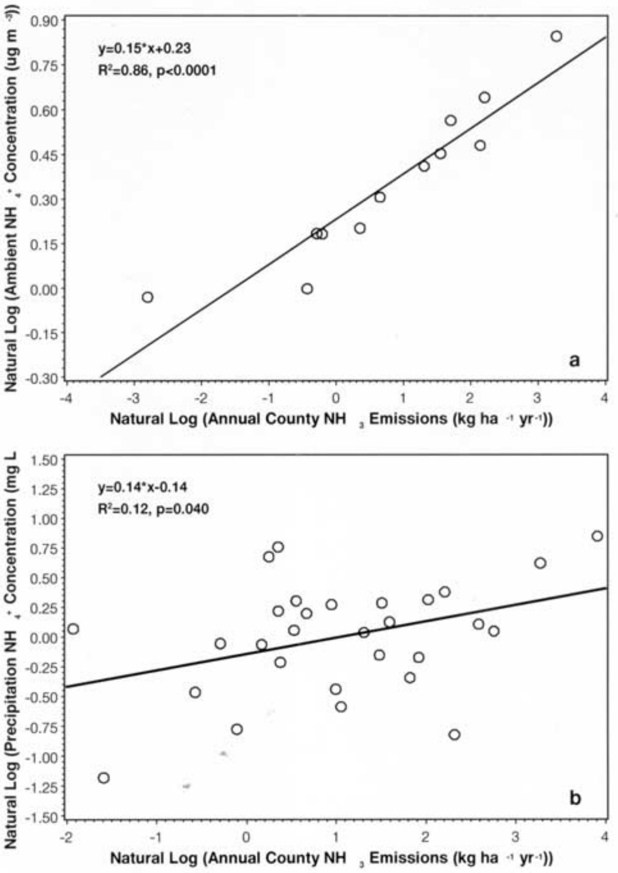


Figure 3. Natural log-transformed annual average ambient NH_4^+ concentrations (μg m^{-3}) versus natural log-transformed annual county NH_3 emission density (kg NH_3 ha^{-1} yr^{-1}) (a) and natural log-transformed annual volume-weighted average NH_4^+ concentration in precipitation (mg L^{-1}) versus natural log-transformed annual county NH_3 emission density (kg NH_3 ha^{-1} yr^{-1}) (b).

Fiedler, 1990; *Walker et al.*, 2000a]. Relative humidity is found to be a significant ($p < 0.05$) parameter at 6 sites. The positive regression coefficient (0.001–0.005) suggests that higher relative humidity leads to increased concentrations of NH_4^+ associated with aerosols. Therefore, increased water vapor in the atmosphere near sources of NH_3, lead to higher concentrations of NH_4^+ [*Andersen et al.*, 1999; *Asman*, 1994; *Warneck*, 1988; *McMurry et al.*, 1983]. Moreover, at high relative humidity (>62%) ammonium nitrate is less likely to dissociate into HNO_3 and NH_3 [*Stelson and Seinfeld*, 1982]. Wind speed is a significant parameter in the model at 6 sites and is negatively correlated to NH_4^+ concentrations. Low wind speeds often coincide with stable conditions and limited dispersion whereas lower concentrations are often characterized by higher wind speeds and increased mixing throughout the boundary layer [*Arya*, 1999]. Temperature is also a significant model predictor at half of the sites. Finally, wind direction is significant at 6 CASTNet sites. From the regression coefficients, however, it is difficult to interpret the effect wind direction has at any particular site and is better illustrated by showing NH_4^+ concentration associated with aerosols relative to wind direction for CASTNet site CND located in Montgomery County, North Carolina (Figure 4) [*Yamamoto et al.*, 1995]. From this plot, it is clear that higher concentrations of NH_4^+ associated with aerosols occur when the wind is from the E and SE. Indeed, Area I, previously defined as an area of elevated NH_3 emissions, is located to the E/SE of site CND (see Figure 2).

[23] The model with the best fit (R^2 = 0.73) was for CASTNet site PNF located in Avery County, North Carolina. A plot of measured and predicted concentrations at site PNF, for the period January 1990 to December 1998, shows that the model follows the general seasonal trends of the ambient NH_4^+ concentration but fails to predict the peaks (Figure 5). Temperature was found to be the most statistically significant parameter in this model ($p < 0.05$), and an analysis of temperature and NH_4^+ over the 9-year period

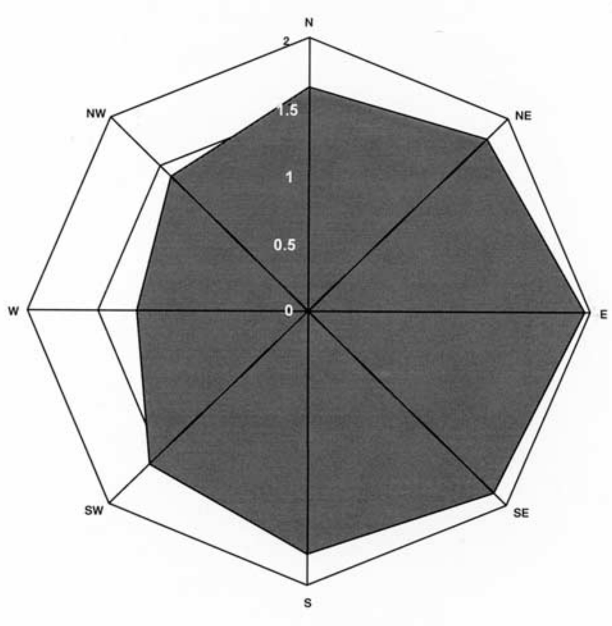
Table 6. Results of Regression Model (1) for CASTNet Weekly NH_4^+ Ambient Concentrations at Each Site

CASTNet Site	N[a]	Parameters[b,c]	MSE	R^2
CKT	224	T, WS, P	0.0115	0.68
CND	369	P, WS, WD, RH	0.0146	0.58
COW	449	P, T, WD	0.0218	0.65
CVL	380	P, RH, WD, WS	0.0250	0.43
GAS	398	P, T	0.0176	0.51
MCK	368	P, RH, T	0.0183	0.54
PNF	413	P, T, RH	0.0204	0.73
SND	262	WD, WS, RH, P	0.0232	0.41
SPD	394	P, WD, WS	0.0155	0.63
SUM	426	RH, WS, WD	0.0347	0.18

[a] Number of observations.

[b] Statistically significant parameters ($p < 0.05$).

[c] T = temperature, WS = wind speed, P = precipitation amount, WD = wind direction, RH = relative humidity.



Gridlines show NH_4^+ concentration at 0.5 μg m^{-3} intervals

Figure 4. Ambient NH_4^+ concentration versus wind direction at CASTNet site CND located in Montgomery County, North Carolina.

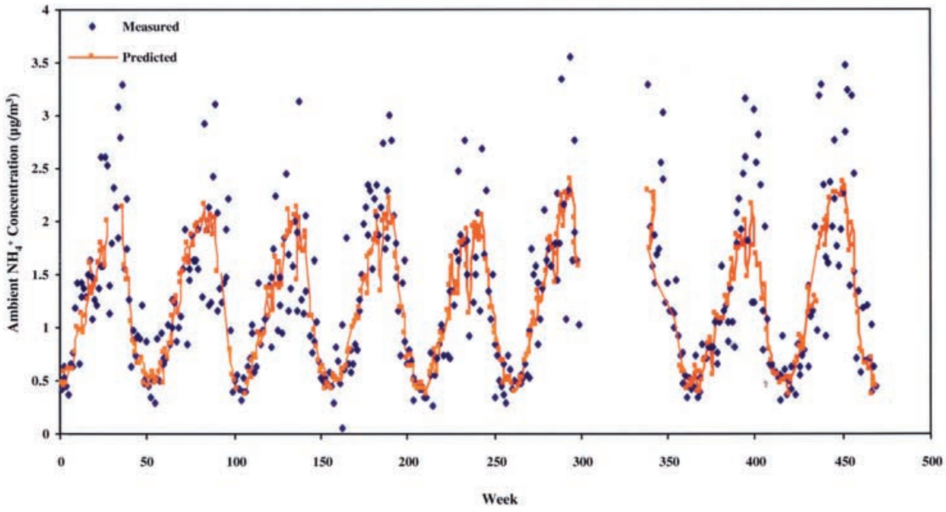


Figure 5. Measured versus predicted (model (1)) weekly NH_4^+ concentration in air at CASTNet site PNF located in Avery County, North Carolina. Week 0 corresponds to the first week in January 1990.

revealed that the concentration of NH_4^+ peaks during the summer when temperatures are warm. This relationship is to be expected based on the fact that atmospheric NH_4^+ is primarily a product of NH_3 reacting with acids formed in the atmosphere, such as H_2SO_4, HNO_3, and HCl and the formation of these acids depends on the availability of hydroxyl radical (OH) and O_3 in the atmosphere, which peak during the summer months [*Seinfeld*, 1986]. Furthermore, biogenic NH_3 emissions from soils and animal waste storage and treatment lagoons [*Aneja et al.*, 2000] are in part driven by temperature, where a 10°C increase in temperature approximately doubles the rate of ammonification [*Addiscott*, 1983].

3.3. Analysis of Monthly Mean NH_4^+ Concentration Associated With Aerosols

[24] Monthly mean concentrations of NH_4^+ associated with aerosols were modeled to test for the general trend and seasonal trends over the period 1990–1998. Models (4) and (5) were applied to each selected CASTNet site and the highest R^2 value [$R^2 = 0.86$, model (4)] was again found at site PNF. The results for all CASTNet sites (Table 1) selected are summarized in Table 7.

[25] The models of monthly NH_4^+ concentrations perform much better than those of weekly concentrations with R^2 values ranging from 0.14 to 0.86 for seasonality model (4) and 0.07–0.81 for temperature model (5). If we remove the Florida site SUM, the average R^2 for models (4) and (5) are 0.69 and 0.63, respectively. This means that 69% of the variability in NH_4^+ concentration in aerosols is explained by seasonality factors in model (4), while 63% of the variability is explained by temperature dependence in model (5). These results suggest that most of the variation in NH_4^+ concentrations in aerosols can be explained by temperature or seasonal effects. In general, Table 7 shows that R^2 values are consistently higher for the seasonality model (4), which is to be expected based on the strong interaction between temperature and seasonality inherent in this model. However, to account fully for spatial variations in ambient NH_4^+ concentrations and deposition, one must also consider such variables as ambient concentrations of NH_4^+ precursors, surface roughness, and vegetation properties, which have large spatial and temporal variability [*Asman*, 1994].

[26] Statistically significant trends were evident at 2 of the CASTNet sites over the period 1990–1998. A positive trend was present at site SUM in Sumatra County, Florida ($p = 0.05$). However, this site performed poorly in the above analyses, so this result may be inaccurate. A negative trend was observed at site SPD, located in Claiborne County, Tennessee. Mean concentrations of NH_4^+ associated with aerosols fell from approximately 2.14 in 1990 to 1.88 in 1998 ($p = 0.06$). Trends in mean surface temperature were investigated at site SPD (Claiborne County, Tennessee). However, no statistically significant trend was present over the period 1990–1998 suggesting that temperature is likely not responsible for the decreasing trend in NH_4^+ concentration at these sites.

3.4. Analysis of Weekly NH_4^+ Concentration Associated With Precipitation

[27] Model (1) was run for all NADP sites (Table 1) to select the best parameter fit. The results from this analysis were low with R^2 ranging from 0.13 to 0.31. Due to the

Table 7. Results of Regression Models for CASTNet Monthly Mean NH_4^+ Concentration Associated With Aerosols

CASTNet Site	Temperature R^2[a]	Seasonal R^2[b]	Trend p-value[b]
CKT	0.73	0.69	0.86
CND	0.62	0.67	0.74
COW	0.81	0.83	0.47
CVL	0.35	0.45	0.57
GAS	0.66	0.67	0.89
MCK	0.61	0.73	0.09 (–)[c]
PNF	0.81	0.86	0.76
SND	0.38	0.54	0.22
SPD	0.69	0.77	0.06 (–)
SUM	0.07	0.14	0.05 (+)[d]

[a] Model (5).
[b] Model (4).
[c] Indicates negative trend.
[d] Indicates positive trend.

Table 8. Results of Regression Models for NADP Monthly Mean NH_4^+ Concentration in Precipitation[a]

NADP Site	Temperature R^2[b]	Seasonal R^2[c]	Trend p-value[c]
KY35	0.34	0.56	0.004 (+)[d]
NC34	0.15	0.36	0.12
NC25	0.30	0.54	0.52
MS30	0.12	0.30	0.07 (+)
GA41	0.11	0.25	0.56
KY03	0.32	0.62	0.97
NC45	0.35	0.48	0.78
AL99	0.45	0.49	0.26
TN00	0.30	0.50	0.48
FL14	0.06	0.31	0.23
NC35	0.46	0.50	<0.0001 (+)

[a] KY = Kentucky, NC = North Carolina, MS = Mississippi, GA = Georgia, AL = Alabama, TN = Tennessee, FL = Florida.

[b] Model (5).

[c] Model (4).

[d] Indicates positive trend.

poor performance of this model, no conclusions could be made regarding the relationship between weekly NH_4^+ concentration in precipitation and local meteorological parameters. However, an investigation of monthly mean volume-weighted NH_4^+ concentration in precipitation proved to be more insightful.

3.5. Analysis of Monthly Mean NH_4^+ Concentration Associated With Precipitation

[28] Models (4) and (5) were applied to all NADP sites (Table 1) using monthly mean volume-weighted NH_4^+ concentration in precipitation. The results for each NADP site are summarized in Table 8. The seasonality dependence in model (4) resulted in R^2 values ranging from 0.25 to 0.62, while the temperature dependence in model (5) had an R^2 range of 0.06–0.46. In general, models performed better when applied to monthly rather than weekly values. Volume-weighted averaging of weekly values to generate monthly averages tends to smooth the noise present in weekly values, resulting in higher R^2 values associated with monthly models. The site FL14, located in Gadsden County, Florida, had the worst overall performance. This site is located near CASTNet site SUM, which also performed poorly in the NH_4^+ associated with aerosols analysis. The exact reason for the poor performance of these sites is not known, although their proximity to the coast and possible

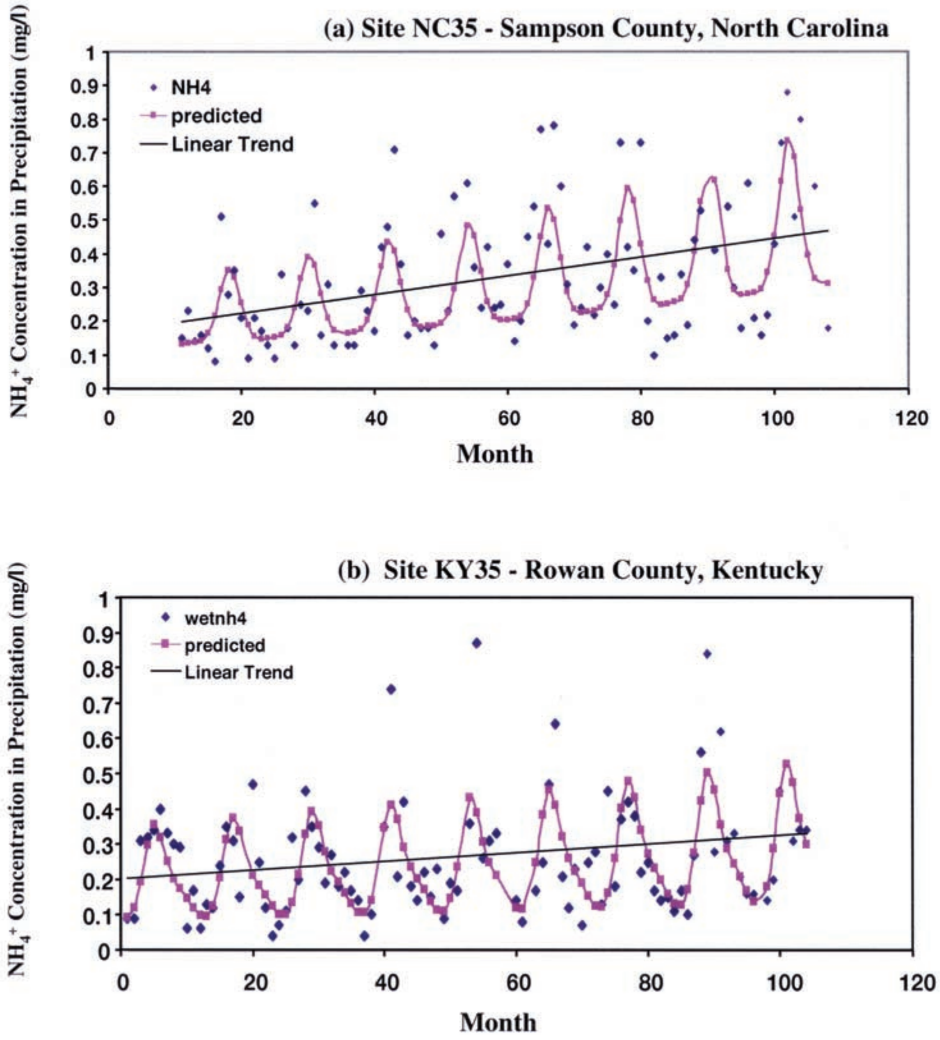


Figure 6. Trends at NADP sites NC35, Sampson County, North Carolina and KY35, Rowan County, Kentucky over the period 1990–1998 where month 0 corresponds to January 1990.

overriding influences of sea and land breezes are considered to be contributing factors [*Arya*, 1999]. Two of the NADP sites showed a statistically significant positive ($p < 0.05$) trend for the period 1990–1998; KY35, located in Rowan County, Kentucky, and NC35, located in Sampson County, North Carolina. The linear trends for these two sites are shown in Figure 6.

[29] At the Sampson County, North Carolina site (NC35), located in Area I (see Figure 2), monthly mean volume-weighted NH_4^+ concentration in precipitation rose from approximately 0.2 mg L^{-1} in 1990 to 0.48 mg L^{-1} ($p < 0.0001$) in 1998. The dramatic increase in NH_4^+ wet deposition is also documented by *Aneja et al* [1998] and *Walker et al.* [2000a, 2000b]. Their findings reveal that no significant increasing trends in temperature or precipitation are present for the period 1990–1996; therefore, meteorology is likely not responsible for the increasing trend in NH_4^+. *Walker et al.* [2000b] go on to relate the increasing trend in NH_4^+ in precipitation to an increase in local NH_3 emissions caused by swine facilities. In fact, the hog population in North Carolina rose from approximately 2 million to 10 million hogs between 1990 and 1998, with 50% of the statewide population, and hence the emissions, located in the concentrated area surrounding Sampson County. The natural summertime peaks of NH_4^+ concentration in this area are further enhanced by the presence of waste from hogs.

[30] At site KY35, the average NH_4^+ concentration in precipitation rose from approximately 0.2 mg L^{-1} in 1990 to 0.35 mg L^{-1} ($p = 0.004$) in 1998. Analyses of precipitation and temperature revealed no statistically significant trend in either variable over the 8-year span; therefore, temperature and precipitation amount do not appear to be responsible for the increasing trend in NH_4^+ concentration in precipitation found at NADP site KY35. The reason behind the increasing NH_4^+ trend at KY35 is less obvious than at NC35, because Rowan County, Kentucky, has an average NH_3 flux of only 131 kg NH_3 km^{-2} yr^{-1}. Based on CASTNet meteorological data, the prevailing wind at site KY35 is from the SW; however, concentrations of NH_4^+ in aerosols, and presumably NH_4^+ in precipitation, are slightly higher when the wind is out of the N. The trend observed at this site likely results from increasing upwind NH_3 source strengths over the period.

4. Conclusions

[31] This study provides insight into the coupling between NH_3 emissions and NH_4^+ concentrations associated with both aerosols and precipitation and how environmental parameters affect these relationships. Regression modeling shows that counties with relatively higher agricultural NH_3 emissions exhibit higher annual average concentrations of NH_4^+ associated with aerosols though the influence on NH_4^+ concentration in precipitation is much less clear. Analysis of NH_4^+ concentration in aerosols at the various CASTNet sites revealed that temperature, precipitation amount, and relative humidity are the most statistically significant ($p < 0.05$) parameters in predicting the weekly concentrations of NH_4^+. Wind speed and direction were also statistically significant ($p < 0.05$) at several CASTNet sites, but the results were less consistent. Investigation into NH_4^+ concentration in precipitation yielded temperature as a statistically significant ($p < 0.05$) parameter. Trends over the period 1990–1998 revealed a slight decrease in ambient NH_4^+ concentration at CASTNet site SPD, Claiborne County, Tennessee (2.14–1.88 μg m^{-3}, $p = 0.06$), while positive trends in NH_4^+ concentration in precipitation were evident at NADP sites NC35, Sampson County, NC (0.2–0.48 mg L^{-1}, $p < 0.0001$) and KY35, Rowan County, Kentucky (0.2–0.35 mg L^{-1}, $p = 0.004$)) over the period 1990–1998. Analyses of NH_4^+ emissions and deposition in the United States are complicated by a lack of data on ambient levels of NH_3 gas and the complex interrelations among NH_3 gas, HNO_3 gas, and SO_4^{2-} and NO_3^- particulate components.

[32] Results from this study provide additional evidence that agricultural NH_3 source strengths are seasonally dependent. Modeling exercises which use annual emissions estimates derived from factors such as those presented in this study should attempt to account for this effect. Furthermore, seasonality in NH_3 emissions may translate to seasonality in ammonium nitrate and ammonium sulfate aerosol concentrations in some areas. This relationship, however, is confounded by seasonality in nitric and sulfuric acid concentrations. Further research (both measurement and modeling) is warranted to investigate such dynamic NH_3/aerosol relationships and the influence of NH_3 on total $PM_{2.5}$. The general form of the parametric models presented here may be useful in examining the temporal variability in NH_3, SO_4^{2-}, NO_3^-, HNO_3, and sulfuric acid to better characterize the seasonal nature of NH_3/NH_4 partitioning.

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