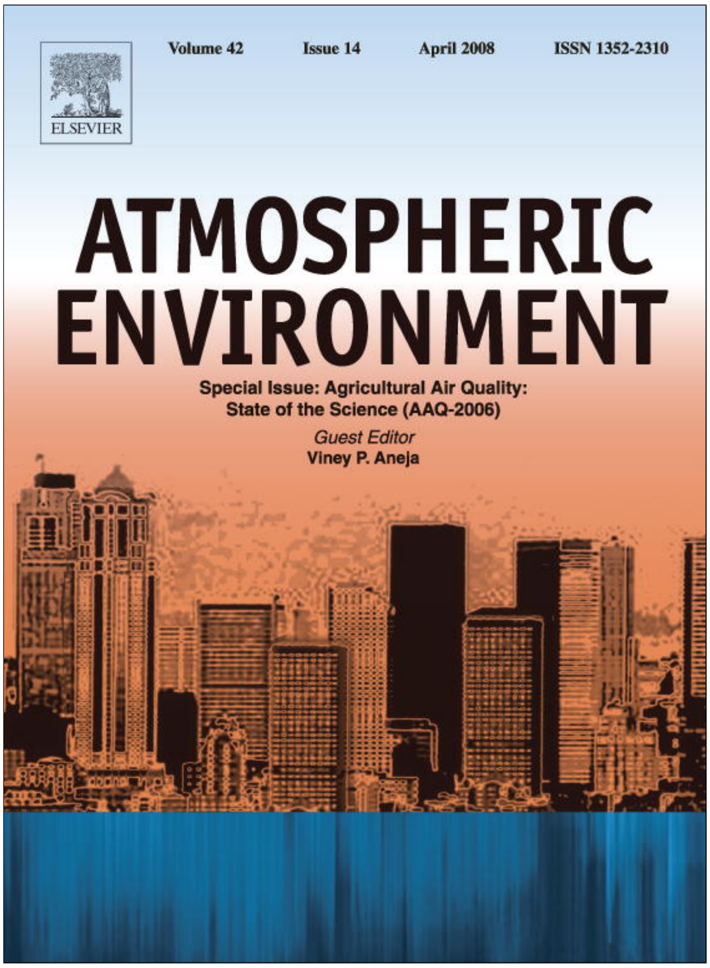
Volume 42
Issue 14
April 2008
ISSN 1352-2310
ELSEVIER
ATMOSPHERIC ENVIRONMENT
Special Issue: Agricultural Air Quality: State of the Science (AAQ-2006)
Guest Editor
Viney P. Aneja

Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Atmospheric Environment 42 (2008) 3238–3252
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

Trends in agricultural ammonia emissions and ammonium concentrations in precipitation over the Southeast and Midwest United States

Konarik Stephen, Viney P. Aneja*

Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695-8208, USA

Received 19 September 2006; received in revised form 25 May 2007; accepted 26 May 2007

Abstract

Emissions from agricultural activities, both crop and animal, are known to contain gaseous ammonia (NH_3) which through chemical reaction in rainwater changes into ammonium ion (NH_4^+). Using wet deposition data of ammonium from several National Atmospheric Deposition Program/National Trends Network (NADP/NTN) and ambient levels of ammonium from Clean Air Status Trends Network (CAST Net) sites as well as calculated NH_3 emissions from North Carolina, and the Southeast and Midwest regions of the United States, trends in ammonium concentrations in precipitation were analyzed for the period of 1983–2004. The beginning of 1997 coincides with the implementation of a swine population moratorium in the state of North Carolina. Results from the analysis in North Carolina indicate a lessening in the rate of increases in NH_4^+ concentration in precipitation since the moratorium went into effect. Sampson County, NC, saw stable NH_4^+ concentrations from 1983 to 1989, an average rise of 9.5% from 1989 to 1996, and an average increase of only 4% from 1997 to 2004. In addition, HYSPLIT back-trajectory model was used to determine that when ambient air in downwind sites arrived from the high NH_3 emissions source region, ammonium concentrations in precipitation were enhanced. For the Southeast United States domain, analysis shows that NH_4^+ concentrations generally increased with increasing NH_3 emissions from within the same region. Similar analysis has been performed over the Midwest United States and compared to the results from the Southeast United States. Emissions from the Midwest are attributed to larger animals, including hogs and cattle, whereas the Southeast has a higher percentage of emissions coming from smaller livestock, such as chickens. In addition, the states of the Midwest United States have a much more uniform spatial distribution of emissions.

Keywords: Ammonia emissions; North Carolina hog moratorium; Ammonium wet deposition

1. Introduction

Agricultural-related ammonia (NH_3) emissions from crops and animals provide a means for the formation of ammonium ion (NH_4^+) in the atmosphere, through the reactions with acidic compounds and water (Pio et al., 1992). These two compounds, $NH_3 + NH_4^+ = NH_x$, are beneficial to plant growth and act as nutrients at low concentrations, but at larger concentrations can cause acidification problems, eutrophication of water, decline in forest growth, and an increase in the formation of $PM_{2.5}$ (Nelson, 2000). Because of this, there is need to study

*Corresponding author. Tel.: +1 919 515 7808.
E-mail address: viney_aneja@ncsu.edu (V.P. Aneja).

1352-2310/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2007.05.062

the effects of the ammonia emissions from agricultural sources, including their concentration, distribution, and transport, so that a better understanding of effective means to control or reduce excess amounts of ammonia and ammonium deposition (Aneja et al., 2006).

Globally, domestic animals are the largest source of atmospheric ammonia [32×10^{12} g NH_3-N (ammonia-nitrogen) yr^{-1}], comprising approximately 40% of both the natural and anthropogenic emissions combined. Synthetic fertilizers and agricultural crops together contribute an additional 9×10^{12} g NH_3-N yr^{-1} (12% of total emissions). Manufacturing accounts for 2.2×10^{12} g NH_3–N yr^{-1} (3% of total emissions (Aneja et al., 2001).

Ammonia (NH_3) released from near-surface sources (e.g. animal waste treatment lagoons, confinement houses, agricultural crops) into the atmosphere has a relatively short lifetime of ~1–5 days (Aneja et al., 2001) and may deposit near the source through dry or wet deposition. However, ammonia can also participate in atmospheric chemical reactions (e.g. gas-to-particle conversion) once airborne, forming ammonium (NH_4^+) salts, which tend to have longer atmospheric residence lifetimes (~1–15 days) owing to a decrease in dry deposition velocity (Aneja et al., 2001) and therefore may be transported and deposited further downwind from the source.

At the Earth's surface, NH_x ($=NH_3+NH_4^+$) has a range of well-understood beneficial and detrimental consequences for humans and the environment. For example, nitrogen fertilizers have had a beneficial effect on agriculture globally by increasing crop yields. However, the high loading of reactive nitrogen has led to deleterious effects on the environment, such as acidification of soils, forest decline, decreased visibility from increased aerosol production, and elevated nitrogen (both ammonia and oxides of nitrogen (NO_x)) concentrations in ground and surface waters, possibly leading to enhanced eutrophication in downwind ecosystems (Asman, 1994; Aneja et al., 1998, 2001; Krupa, 2003; Baek and Aneja, 2004). Thus, there is a need to study the ammonium deposition changes, spatial distribution, and transport of the ammonia emissions from agricultural sources in order to gain a better understanding of effective means to control or reduce excess amounts of ammonia and ammonium deposition.

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) was developed in 1978 in an effort to collect data on the chemistry and amount of precipitation for monitoring spatial and temporal long-term trends and is a cooperative effort between many different groups, including the State Agricultural Experiment Stations, US Geological Survey, and the US Department of Agriculture (NADP/NTN, 2004). In addition to other chemistry data, the NADP/NTN monitors NH_4^+ concentration associated with precipitation, currently operating over 250 sites nationwide.

Agriculture, forest, and range production practices are increasingly subject to US state and federal regulations. Intended to protect air and water resources, numerous governmental regulations (local, regional, and national) have been set in order to curb the negative effects of excess NH_x levels (Aneja et al., 2006). Despite these efforts, the emission of NH_3-N to the atmosphere remains largely unregulated. To facilitate the development of appropriate policies and regulations it is imperative that spatial distribution data on agricultural emissions of ammonia associated with specific geographic areas are accurate. Combining data from several different sources, this study attempts to provide generalizations in the trends of ammonia emissions, ammonia concentrations in the atmosphere, and ammonium concentrations in wet deposition. Comparisons were made between NH_x characteristics in the Midwest United States and the Southeast United States. In addition, North Carolina was used as a case study to gauge the corollary effects of the 1997 swine production moratorium on ammonia emissions. This study attempts to show the effects of ammonia emission reductions as a result of hog population control, on localized deposition of ammonium in precipitation, since hog waste is a significant source of ammonia emissions (Baek and Aneja, 2004).

Also, in order to effectively implement proper regulations, it is necessary to quantitatively determine the effectiveness of monitoring programs such as NADP/NTN and theorize ways to improve there usefulness and/or alter them for use in agricultural air quality.

2. Methods

2.1. Data selection

For the purpose of comparison between the Midwest and Southeast United States, 16 states (eight from each region) were chosen as part of the study. The states of Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, and Tennessee were defined as states in the Southeast United States. The Midwest United States was defined as the states of Illinois, Indiana, Iowa, Michigan, Minnesota, Missouri, Ohio, and Wisconsin.

In order to estimate ammonia emissions, the 2002 Census of Agriculture data was used. County level data of the population of cattle (both beef and dairy), horses, hogs (both sows and fattening pigs), sheep, broilers, chickens (including laying hens, young pullets, and more mature pullets), and turkeys were obtained. In addition, the acres of fertilized land and the type of fertilizer applied were also obtained.

For ammonium concentrations in the atmosphere associated with aerosols, data from 22 sites of the Clear Air Status and Trends Monitoring Network (CAST Net) was obtained. CAST Net is a network of rural sites that collect site-specific measurements of total deposition and is the source for dry acidic deposition (US EPA, 2003). The sites measure weekly average ambient atmospheric concentrations of particulate NH_4^+, as collected on a Teflon filter. The sites chosen have continuous data measurements from 1989 to 2004, so data were readily available for a long-term study such as this.

Next, data on NH_4^+ concentrations associated with precipitation were obtained from the NADP/NTN. From the data set of over 200 sites, 59 were chosen (30 from the Midwest United States and 29 from the Southeast United States). These sites have collected data weekly since 1978 (NADP/NTN, 2005).

The hybrid single-particle LaGrangian integrated trajectory (HYSPLIT) model was used to determine whether or not atmospheric transport was playing a role during periods of high NH_4^+ concentrations over sites in North Carolina. This information was used in the determination of the effectiveness of the North Carolina Swine Moratorium. HYSPLIT is a joint effort between NOAA and Australia's Bureau of Meteorology (NOAA, 2005). It is able to compute air parcel simulations and dispersion and deposition simulations. For this study, HYSPLIT was used to perform a ''backwards'' dispersion model run for specified time periods at each site. The model assumed puff dispersion, where the puff expands and splits into several new puffs, each containing a portion of the pollutant mass (NOAA, 2005). The dispersion shows the source region where the pollutant concentrations are coming from, and is therefore beneficial in determining if the swine facilities played a role in the ammonium concentration for that time period. For each model run, a 48 h ''backwards'' dispersion of deposition was performed from a source height of 100 m.

The Carnegie Mellon University (CMU) Ammonia Emissions Model Version 3 (Davidson, 2004) was used to compare calculated emission rates with model estimates. The CMU model is a graphically interfaced software application with modifiable input files of emissions factors and activity levels designed to perform sensitivity analyses and inventory updates. In addition to livestock and fertilizer emissions, the CMU model provides emissions estimates for non-livestock animals (i.e. cats, dogs, and wild animals), soils, and mobile and industrial sources.

Additionally, 2002 Ammonium Ion Concentration in Precipitation and Wet Deposition maps produced by NADP/NTN (2005) were used to compare and contrast both consistencies and inconsistencies between the calculated and modeled ammonia emission rates and its estimated wet deposition.

2.2. Data analysis

The first goal of the study was to develop a spatial representation for agricultural ammonia emissions over both the Southeast United States and Midwest United States. To develop the emissions inventory, the data from the 2002 Census of Agriculture from the United States Department of Agriculture (USDA) was used. Since the data were county level, emissions were assumed to be constant throughout each individual county. To calculate the emissions total for each county, the animal population inventory numbers were multiple by an animal-specific emissions factor, in kilograms of ammonia per animal per year. These emissions factors have been obtained through experimentation and mass balance calculations, generally done in Europe, so there could be some error, since animal practices vary greatly between the two continents. In addition, the animal's specific diet can highly alter the NH_3 emissions. Other factors, such as temperature, humidity, and waste handling, add to the uncertainties in the estimated emission factors. The final emission factors chosen to be used in the study were the same as those in the Aneja et al. (2003) study in which similar analysis was performed on 1997 Census of Agriculture data. The emission factors used are shown in Tables 1 and 2. The total emissions per county were used to develop a spatial distribution across the two regions as well as to compare and contrast various characteristics of the distribution. Emissions and flux (i.e. normalized for area) were calculated and the data were further combined to provide statewide total emissions and flux estimates. Results are presented in Table 3.

Table 1
Emission factors used

Source	Emissions factor ($kg\,NH_3\,animal^{-1}\,yr^{-1}$)
Beef cattle	10.2
Dairy cattle	28.04
Horses	8
Hogs and pigs	
Sows	16.43
Fattening pigs	6.39
Sheep	1.34
Broilers	0.28
Chicken	
Laying hens	0.37
Pullets 13–20 weeks old	0.269
Pullets <13 weeks old	0.17
Turkeys	0.858

Source: Aneja et al. (2003).

Table 2
Emission factors used (fertilizer)

Crop	N fertilizer rate ($kg\,N\,ha^{-1}$)
Alfalfa	0
Barley	75
Corn	125
Cotton	100
Bean	0
Idle cropland	0
Hay	25
Oats	75
Pasture	0
Peanut	0
Potatoes	250
Rice	140
Sorghum	75
Soybean	0
Spring wheat	50
Sugarbeets	150
Sugarcane	200
Sunflower	100
Tobacco	100
Vegetables	100
Winter wheat	75

Source: NASS (2006).

Table 3
Annual ammonia emissions flux from livestock and fertilizer sources, 2002

State	Ammonia emissions ($\times 10^6$ kg)	Ammonia flux ($kg\,km^{-2}\,yr^{-1}$)
Southeast		
Alabama	61.371	1209.268
Florida	28.324	524.544
Georgia	80.263	1385.793
Kentucky	45.683	1149.790
Mississippi	59.669	1271.881
North Carolina	142.234	2919.565
South Carolina	35.768	1187.882
Tennessee	70.109	1700.891
Total	523.421	1417.105
Midwest		
Illinois	95.073	1710.149
Indiana	77.231	2153.062
Iowa	153.915	2754.631
Michigan	39.738	699.502
Minnesota	142.194	1785.981
Missouri	102.959	1494.371
Ohio	75.805	1851.045
Wisconsin	70.544	1298.818
Total	757.458	1691.024

CAST Net and NADP data were then used to develop statistical analyses of several locations to determine the correlations between NH_3 emission, NH_4^+ concentrations in ambient air, and NH_4^+ concentrations in precipitation. In addition, sites in North Carolina were analyzed both before and after the installation of the hog moratorium to determine its effectiveness.

3. Results

3.1. Spatial distribution of NH_3 emissions

A map of the annual county-scale agricultural ammonia flux was developed. Fig. 1 depicts calculated and modeled livestock fluxes as well as overall agricultural flux (total of livestock and fertilizer) per county and the modeled total ammonia flux (agriculture plus all other sources combined). Emissions levels in these counties exceeded 10,000 $kg\,km^{-2}\,yr^{-1}$. Various counties along a belt stretching from North-Central Alabama across

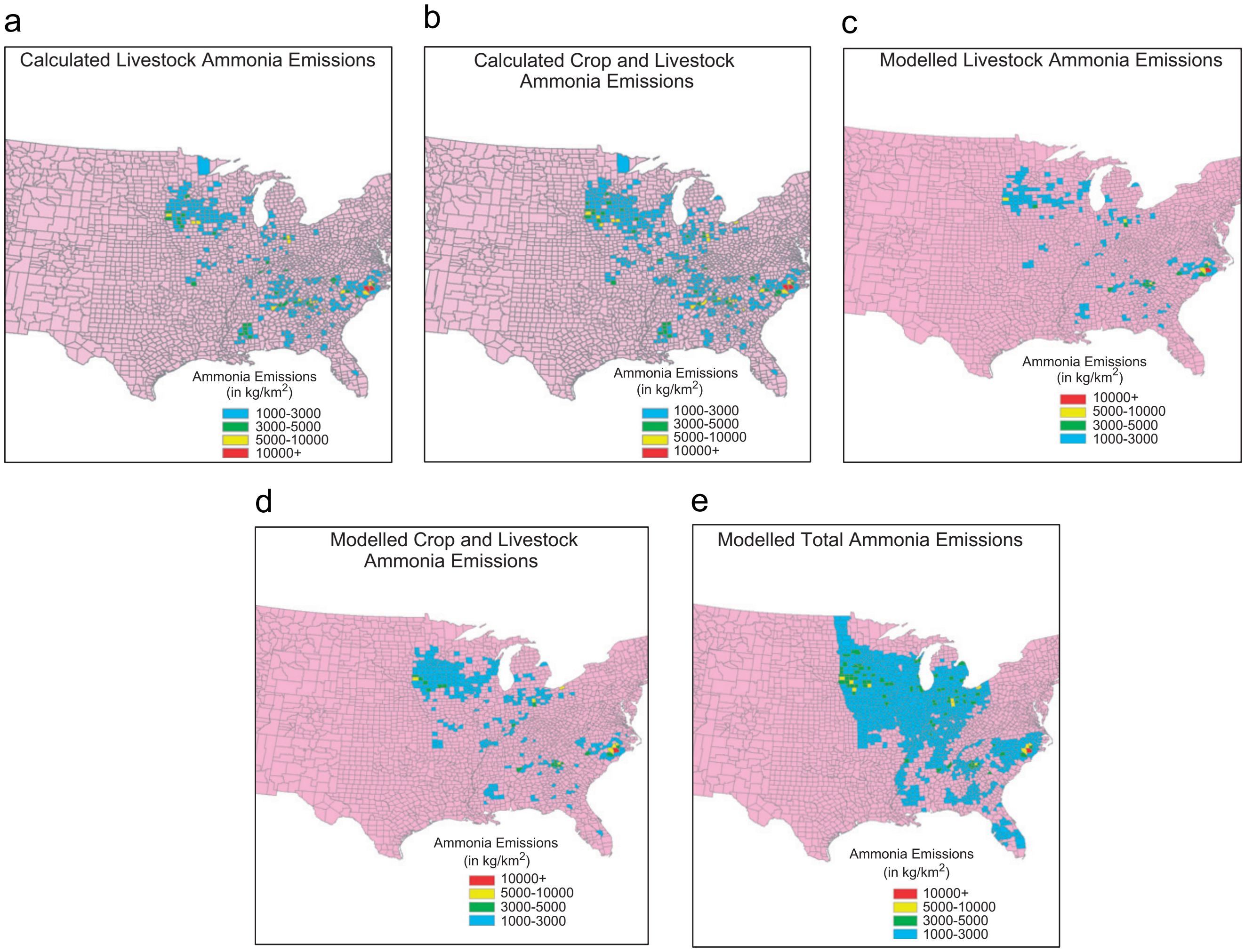

Fig. 1. Spatial distribution of NH_3 flux (kg km^{-2} yr^{-1}).

Table 4
Ten counties with highest annual agricultural emissions

Southeast	NH_3 (kg km^{-2} yr^{-1})	Midwest	NH_3 (kg km^{-2} yr^{-1})
Duplin County, NC	24209.41	Mercer County, OH	12943.77
Sampson County, NC	19569.96	Hardin County, IA	10689.74
Franklin County, GA	14858.32	Hamilton County, IA	10592.47
Greene County, NC	13687.89	Sioux County, IA	9511.132
Wayne County, NC	12711.48	Darke County, OH	8606.599
Madison County, GA	10662.38	Buena Vista County, IA	7701.534
Kullman County, AL	10227.02	Martin County, MN	6918.426
Habershan County, GA	10132.06	Washington County, IA	6852.765
Banks County, GA	9813.943	Carroll County, IA	6797.724
Union County, NC	9776.172	Dubois County, IN	6268.582

Northern Georgia and South Carolina and to Southeastern South Carolina had emissions levels well in excess of 5000 kg km^{-2} yr^{-1}. Maximum values over the Midwest were significantly lower, with highest values over several counties in Western Ohio and central and Western Iowa. Table 4 lists the top 10 county in terms of annual agricultural emissions for both the Southeast United States and Midwest United States. Again, one can note the excessive values over southeastern North Carolina caused by the hog population; and over portions of Northern Alabama and Georgia, caused mainly due to the explosive growth of the broiler industry in those regions. The top 10 counties in the Midwest are characterized by significant beef cow populations across Northwest Iowa, large poultry farms in Ohio, and hogs across Iowa and Indiana. Overall, when making the addition of North Dakota, South Dakota, and Nebraska to complete the entire agricultural region of the middle part of the United States, the Midwest had average ammonia emissions of 1691 kg km^{-2} yr^{-1} while the Southeast had emission levels of 1417 kg km^{-2} yr^{-1}.

Perhaps the most obvious distinction between the two regions in terms of agricultural ammonia emissions is the source of the emissions. Great variation in terms of the major type of livestock produced exists between the two regions. Fig. 2a and b shows the average NH_3 emissions deriving

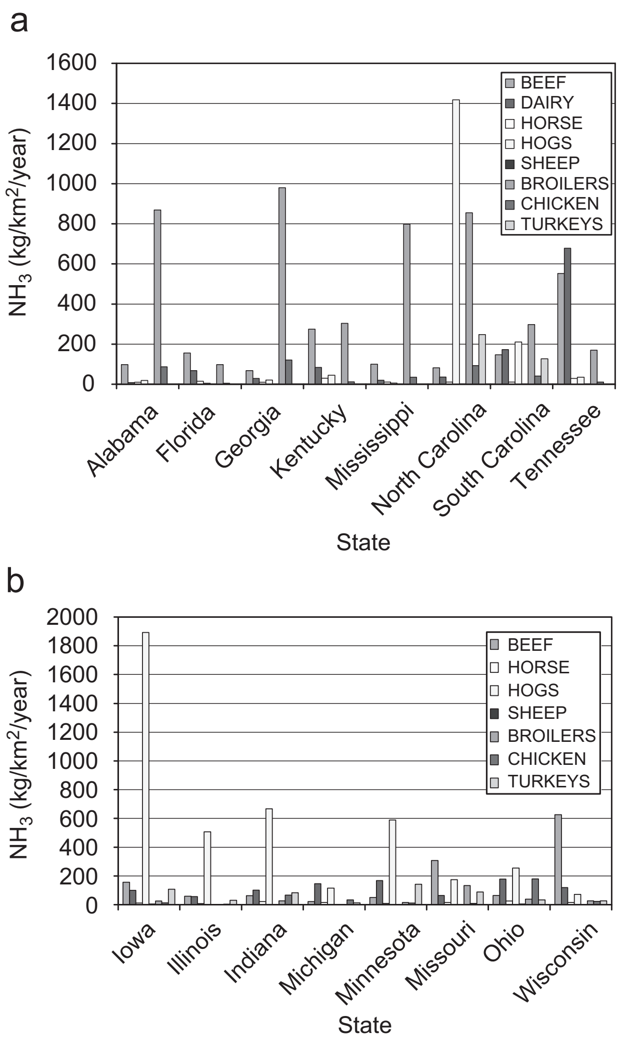

Fig. 2. Total ammonia emissions from specific agricultural sources, by state.

from specific agricultural sources in the Southeast and Midwest, respectively.

The figures indicate that high ammonia emissions totals over the Southeast United States in general come from broilers, but with the distinct exceptions of North Carolina in terms of hog emission as well as the dairy and beef cow industries in Tennessee. In contrast, the Midwest United States has its high ammonia emissions totals deriving mainly from the hog industry, especially over Indiana, Iowa, and Minnesota. Cows, in particular beef, play a major role in agricultural ammonia emissions over Wisconsin and Missouri.

In terms of the regions as a whole, the Midwest had roughly 40% of its total agricultural emissions stemming from hogs, with 8% and 12% coming from beef and dairy cows, respectively. Fertilizer accounted for 14% of the emissions, whereas turkeys, chickens, and broilers combined to contribute 15%. In the Southeast, an overwhelming 43% of agricultural emissions of NH_3 came from broilers, with 11% deriving from fertilizer, and 16% stemming from the hog industry. Beef and dairy cows made up 12% and 9%, respectively, and chickens and turkeys contributed 4% each. A previous study from 5 years early over the same Southeast region reported 33% broiler contribution, 28% beef cattle, 12% hog and 12% fertilizer (Aneja et al., 2003). This indicates that the broiler industry is rapidly growing, while the beef industry is declining over the region as indicated by the Census of Agriculture Data (USDA, 2005). The details of the relative contribution of each specific source to the total emissions for the region are shown in Fig. 3.

In comparing spatial distributions of agricultural ammonia emissions between the two regions, the Southeast has a much greater deviation in emissions locally. One of several explanations of this is that the Southeast United States is characterized by a more complex terrain, with mountains, swamps, and forests all separating localized areas of intensive agriculture. In addition, the denser population of the Southeast again provides a more localized nature to agricultural areas. The Midwest, in contrast, is characterized by flat or gently rolling open plains, and with a much less dense population, there is a great uniformity to the intensity of agriculture in the region, allowing for more extensive, yet relatively moderate levels of agricultural ammonia emissions. Another possible explanation is the aforementioned fact that livestock in the Midwest is characterized by larger animals

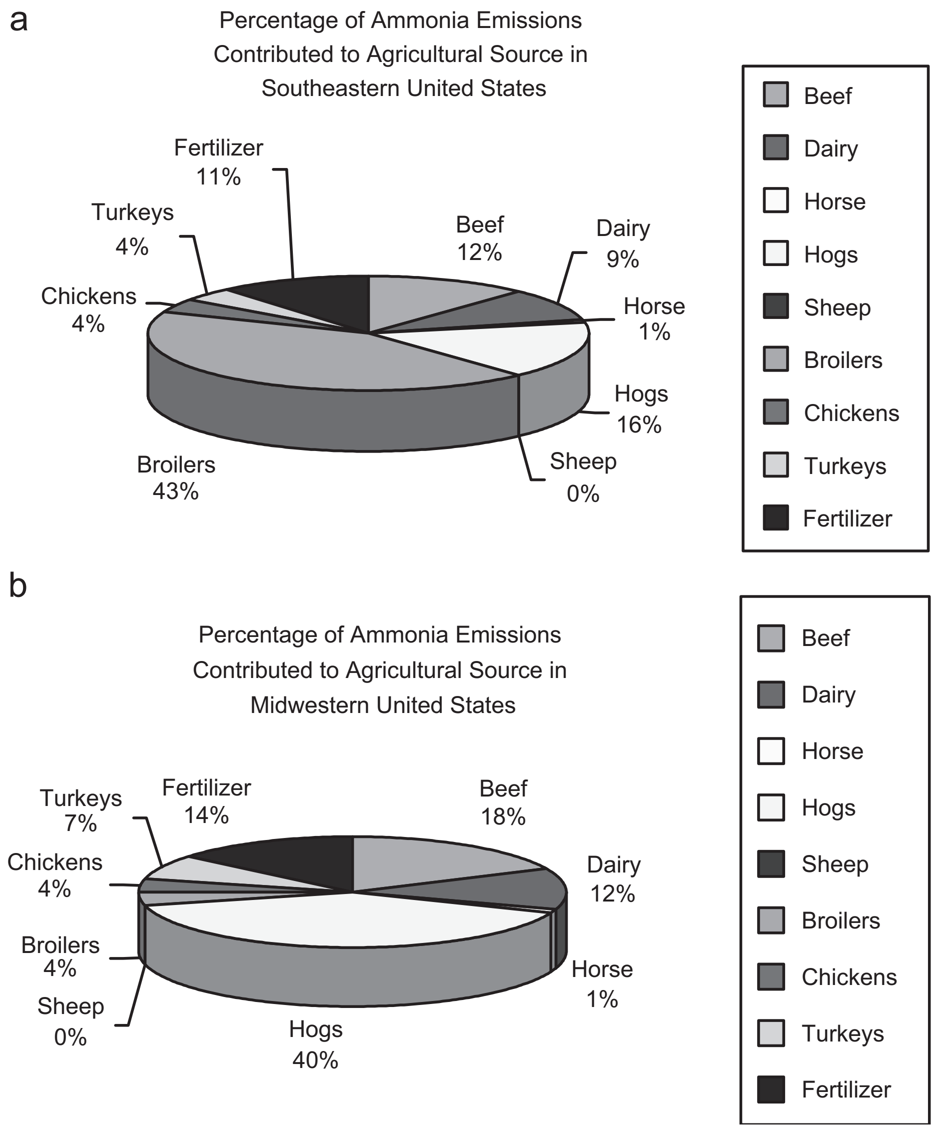

Fig. 3. Emissions from specific agricultural sources, by region.

(which make up about 64% of the emissions, as opposed to 37% in the Southeast), which cannot be as densely populated as the smaller animals of the Southeast. Fig. 4 shows the average standard deviation between emission totals in counties of the states included in the study. It is clear that the variation in emissions is much greater in the Southeast than in the Midwest. The highest variation occurs in the states with the highest overall emissions totals as well as those with the highest percentages of small animal inventories.

3.2. NH_4^+ concentration analysis

In order to analyze the relationship between NH_3 emissions at the county level and NH_4^+ concentrations in both precipitation and ambient air, comparisons were made between the average levels of NH_4^+ concentrations from the NADP and CAST Net sites and the total agricultural ammonia emissions calculated from the annual emissions totals. The correlation between the NH_4^+ concentrations and the emissions data gave an R^2 value of 0.475 for both regions combined, with 0.384 being the R^2 value for the Southeast and 0.531 for the Midwest. Hence, there is significant relationship between a county's ammonia emissions and the concentration of NH_4^+ in the atmosphere and in precipitation. The Southeast's correlation was lower due to the same reasons as stated above, i.e., higher variability in NH_3 emissions. Specifically, the more varied terrain and higher variations between neighboring counties would allow for a county with low emissions next to a high emissions county to possess high NH_4^+ values due to

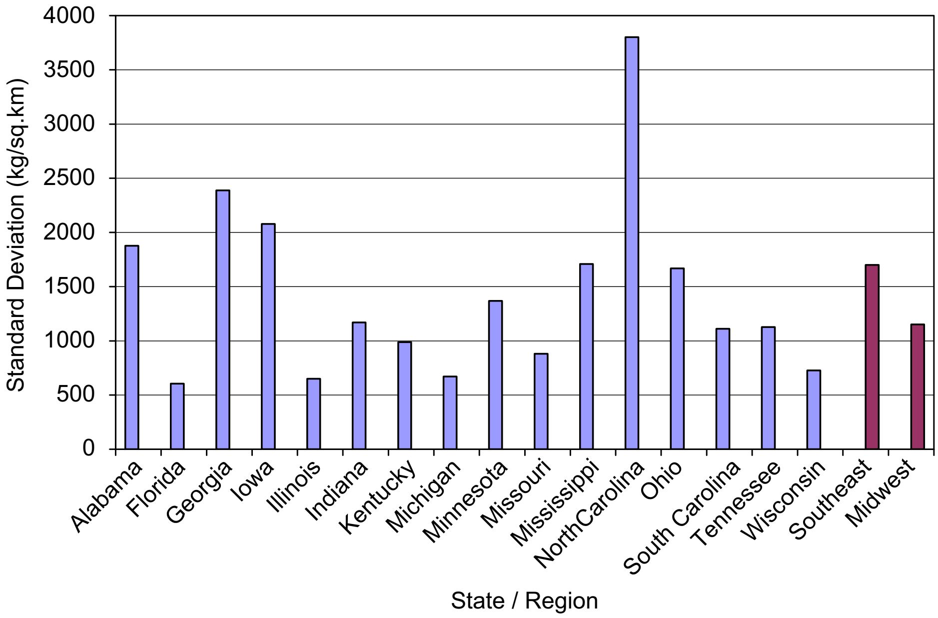

Fig. 4. Standard deviation of ammonia emissions between counties in specific states.

its proximity to the high NH_3 emissions nearby. With the more uniform emissions in the Midwest, there is less of a difference between neighboring counties, and thus less of a difference in concentrations of NH_4^+ if NH_3 comes from sources from a neighboring county instead of from within. Fig. 5 shows several examples from the Southeast United States. The figure indicates 4-week averaged ammonium ion concentrations in ambient air (from the CAST Net site) and precipitation (from the NADP site) as well as the long-term trend from 1989 to 2004. These examples show counties that contained both CAST Net and NADP sites. Fig. 5a shows Pike County, GA. Pike County is located in West-central Georgia, just to the south–southwest of metropolitan Atlanta. It is to the south and east of the highest agricultural ammonia emissions counties in the United States, while 2005 kg km^{-2} yr^{-1} of ammonia was calculated to be emitted from agricultural sources within the county annually, mostly from the broiler population. For this study, Pike County was considered a moderate-emissions county. The terrain of the county is generally rolling farmland. Average daily concentrations of ammonium in precipitation have slowly risen from about 0.30 mg L^{-1} over the past 5 years or so to 0.35 mg L^{-1}, whereas ammonium ion concentrations in ambient air have decreased from a mean of 1.6 μg m^{-3} during the same time frame to 1.3 μg m^{-3}. Fig. 5b shows DeKalb County, AL, which in the northeastern tip of Alabama, in the heart of the extreme broiler ammonia emissions region, with DeKalb itself having agricultural ammonia emissions of about 8102 kg km^{-2} yr^{-1}. The county is also characterized by rolling farmland. Ammonium ion concentrations over the county in ambient air remained generally constant at 2.5 μg m^{-3}, whereas the average concentration in precipitation rose from 0.3 mg L^{-1}. Fig. 5c shows Anderson County, TN, located on the western side of the Knoxville area, and is characterized by mixed agricultural use to the north of the large high-emissions areas in Georgia and Alabama. This county, considered low agricultural-related ammonia emissions, again, has rolling farmland, with an annual emissions total of 239 kg km^{-2} yr^{-1}. Both concentrations of ammonium ion in ambient air and in precipitation dropped, from 2 μg m^{-3} and 0.33 mg L^{-1} to 1.5 μg m^{-3} and 0.28 mg L^{-1}, respectively.

Fig. 6 shows the data from three sites in the Midwest United States. Fig. 6a shows data from Butler County, OH, considered a moderate agricultural ammonia emissions county for the midwest with 406 kg km^{-2} yr^{-1} emissions. Butler County is located in Southwestern Ohio, on the northwest side of Cincinnati. There are counties to the north that have significantly higher levels of hogs, which is also the key constituent of agricultural activities in this county, characterized by rolling farmland. Ammonium ion concentrations in ambient air have been dropping, from 2 μg m^{-3}, as have concentrations in precipitation, dropping from 0.4 mg L^{-1}. Fig. 6b shows Champaign County, IL, located in

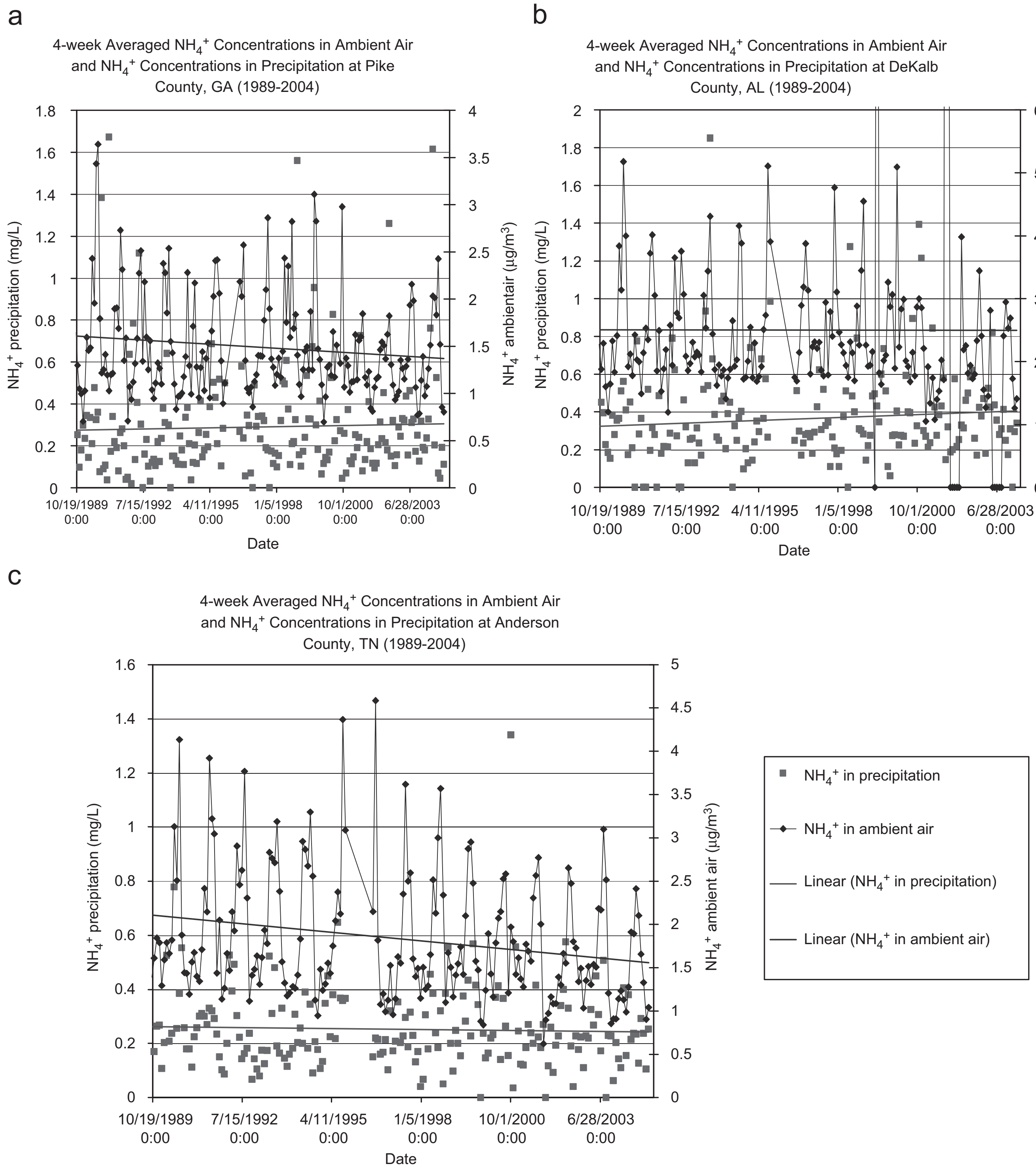

Fig. 5. Ammonium ion concentrations from three Southeast sites.

East-central Illinois, in a relatively low emissions area far to the east and southeast of the major hog and cow agricultural centers of the Midwest. The site is characterized by flat farmland, and county-level agricultural ammonia emissions are at a mere $155\,kg\,km^{-2}\,yr^{-1}$. Surprisingly, NH_4^+ concentrations in precipitation are rising from 0.5 to $0.55\,mg\,L^{-1}$, whereas ambient air concentrations of NH_4^+ have been dropping. Finally, Fig. 6c shows Knox County, IN, which is considered the high emissions example for the midwest. Knox County is located in southwestern Indiana, and is part of a cluster of counties whose rolling farmland is dotted with hog facilities. The annual agricultural-related

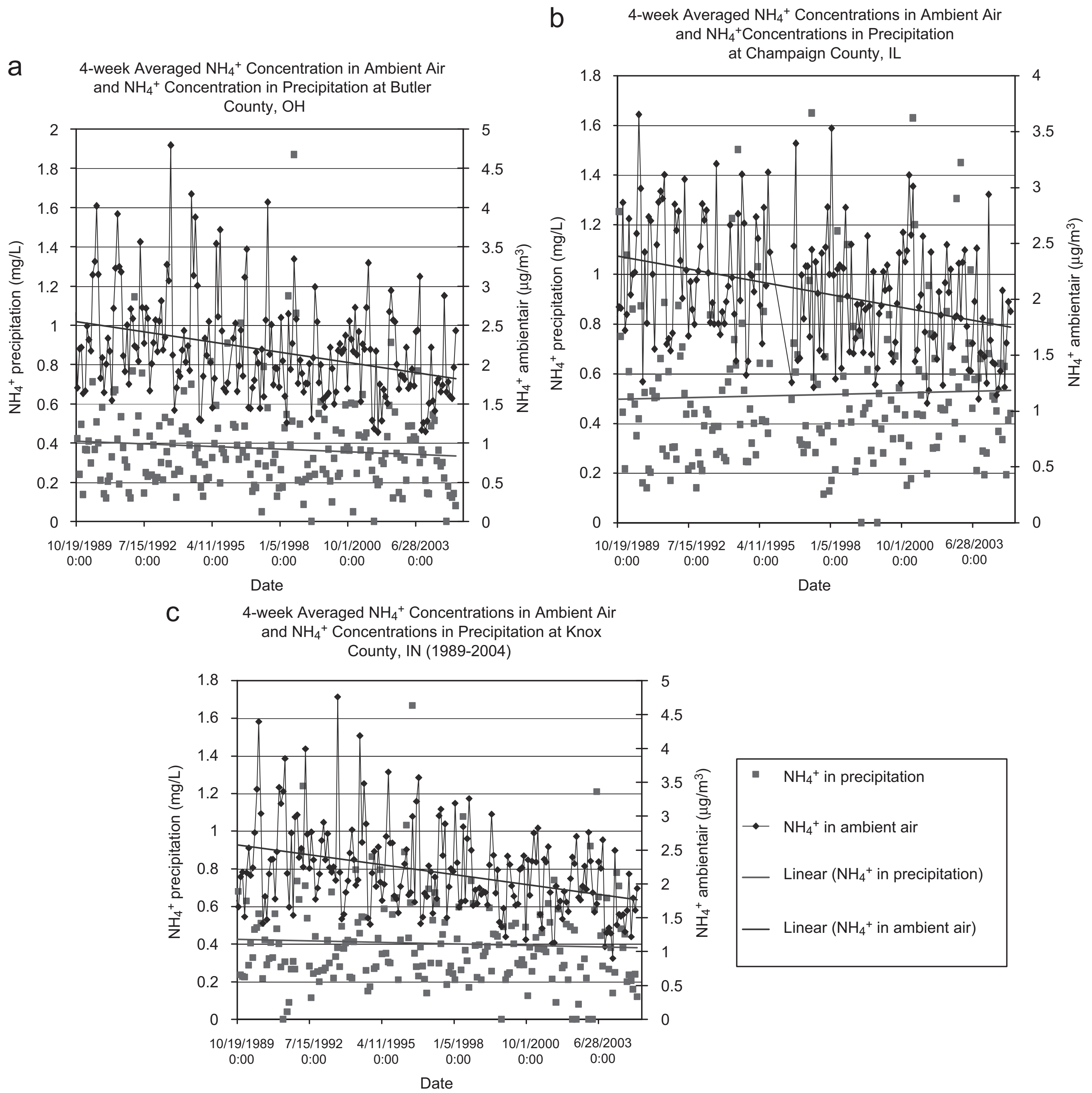

Fig. 6. Ammonium ion concentrations from three Midwest sites.

ammonia emission from the county is estimated at $1436\,kg\,km^{-2}\,yr^{-1}$. The levels of ammonium ion concentration in ambient air has been dropping from a mean of about $2\,\mu g\,m^{-3}$, whereas the mean in precipitation has slightly dropped from around 0.42 to $0.38\,mg\,L^{-1}$.

In comparing the trends between the sites detailed in Figs. 5 and 6, as well as others used in the studies, it is evident that agricultural emissions are higher in certain counties over the Southeast, but are overall higher in the Midwest. Also, concentrations of NH_4^+ in precipitation are higher in the Midwest. Ambient air concentrations of ammonia in the Midwest seem to be much more dependent on local emissions, with high-level emission areas having higher NH_4^+ concentrations in ambient air. An explanation for the enhanced NH_4^+ in precipitation over the Midwest may have to do with the fact that most moisture from the Midwest arrives from the South, which could mean a significant amount of agriculturally emitted ammonia from the Southern United States is being transported to the Midwest, where it is being released through precipitation.

Fig. 7 shows NADP maps for the annual 2002 ammonium ion concentration and ammonium ion wet deposition (NADP/NTN, 2004). Comparing these maps to both the calculated and modeled ammonia emissions, there is a significant inconsistency between the emissions and deposition. The Midwest and Southeast United States have similar calculated and modeled emissions; however, the Midwest has much higher ammonium deposition

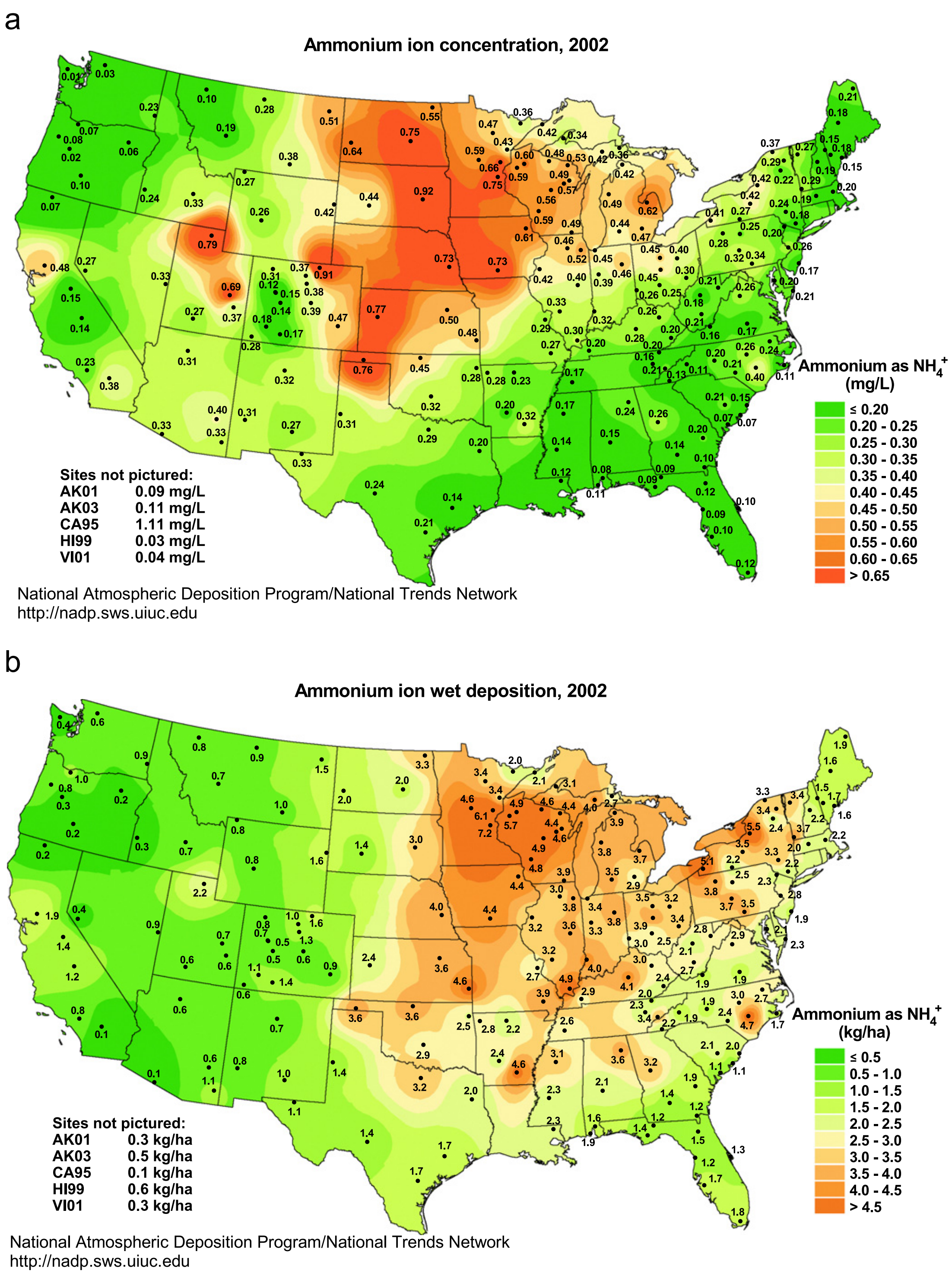

Fig. 7. NADP maps for 2002 ammonium ion concentration (a) and ammonium ion wet deposition (b) (obtained from NADP/NTN, 2005).

values (deposition is normalized for precipitation amount). The ammonium deposition values indicate that on average, the Midwest United States has double the amount of deposition, 4.0–2.0 kg ha^{-1}, whereas Table 3 indicates that the emissions levels in the Midwest are only about 20% higher. This discrepancy appears particularly distinct in Iowa and Minnesota, where emissions values average around 2000 kg km^{-2} yr^{-1} but ammonium ion concentrations averages exceed 0.6 mg L^{-1} with deposition values of 4.0 kg ha^{-1}. In contract, North Carolina with emissions values of 2700 kg km^{-2} yr^{-1} has ammonium ion concentrations of approximately 0.3 mg L^{-1} and deposition values of 2.5 kg ha^{-1}.

3.3. Effects of North Carolina's hog moratorium on ammonia emissions

In early 1997, a moratorium was put into effect by the North Carolina General Assembly, to cap the number and size of hog-confinement facilities in the state to that existing at the time of enactment. The NC General Assembly was reacting to the hog operations' detrimental effect on the environment, in terms of water pollution, odor, disease, and air pollution. The moratorium banned the creation of any new confinement facilities in the state, effectively eliminating the growth of the swine population in the state. One of the key air pollution problems associated with the hog facilities are the ammonia emissions. The facilities, particularly in the south-eastern part of North Carolina (Fig. 1), have been allegedly responsible for enhanced ammonium ion concentrations throughout eastern parts of the state. Given the effect the moratorium has had on stopping the rapid growth of the industry in North Carolina, it is of interest to examine whether there has been a reduction, or at least halting of the increase, in ammonium ion concentrations in the area relative to the years before the moratorium was in place. This study looked at pre-1997 trends in ammonium ion concentrations and compared them to post-moratorium trends.

Table 5 shows the percentages of total annual NH_3 emissions from agricultural sources that derive each specific source, using the emissions calculations from 2002 Agricultural Census data. If compared with data from Fig. 3, it is clear that emissions from hogs play much more of a major role in North Carolina than in the rest of the Southeast, making up near a half of all agricultural-related ammonia emissions in the state.

In order to take a look at how this ammonia emissions source region affects other areas of the state's ammonium ion concentration, analysis was performed using weekly NADP data coupled with HYSPLIT back-trajectory runs. A comparison was made between the 90th percentile and the 10th percentile (chosen as representatives of high concentration days or low concentration days, respectively) for concentrations of ammonium ions in precipitation at each of two NADP sites. HYSPLIT model back-trajectories were performed to determine if those percentile distributions of ammonium concentrations corresponded with air masses transiting the source region. A statistical F-test analysis was done, assuming a large sample size, for NADP sites NC41 (Wake in eastern central North Carolina) and NC34 (Rowan in Western central North Carolina) using Microsoft Excel (Table 6). The analysis identified the number of days with air at the site derived from the source region with NH_4^+ in precipitation in the 90th or 10th percentile, i.e. each date which had ammonium concentrations that were higher than 90% of other dates or $<$90% of dates, respectively. The source region was defined as the area 50 km in radius from a center point of 35.1N, 77.9W, and is representative of the area with the highest concentration of hog facilities. HYSPLIT was used for each of the dates that fell within the 90th or 10th percentile to determine the

Table 5
Percentages of agricultural ammonia emissions deriving from specific sources in North Carolina

Beef	3
Dairy	1
Horse	0
Hogs	47
Sheep	0
Broilers	28
Chicken	3
Turkeys	7
Fertilizer	10

Table 6
Results of binomial proportion test for difference in source region air on high and low NH_4^+ concentration days

	90th percentile concentration days	10th percentile concentration days	p-Value
Rowan	17	10	0.1747
Wake	22	12	0.0241

original of the source air on these dates. Any day on which over 50% of the air at the site that had passed over the source region within the 48 h leading up to the sample time and a concentration of NH_4^+ in the minimum/peak category was considered a 'yes' day. The sample was considered a 'no' day if it did not meet the preceding criteria. The test indicated a statistically greater number of days in the 90th percentile for air transiting the source region for Wake County (p-values <0.05). The site in Rowan County, further to the west, did not show a statistical relationship between ammonia in precipitation and air transiting the source region. Theses results indicate that NH_4^+ concentrations over eastern North Carolina, at least 80 miles from the source region, are significantly dependent on the emissions from hog facilities.

The concentrations of ammonium ions in precipitation were analyzed from seven NADP sites in North Carolina from 1989 to 1996 and again from 1997 to 2004 (Fig. 7). Four of the sites are considered low agricultural emissions locations. NC25 is located in Macon County, in the far western part of the state. Although highly vegetated and mountainous, it is located close to the extreme agricultural ammonia emissions area of Northern Georgia. Its annual estimate of agricultural-related ammonia emissions is 59.0 kg km^{-2}. Also in the west, but north of NC25 in a higher terrain, is NC45, in Yancey County (elevation 1987 m). NC45 has an annual estimated ammonia emissions rate of 113 kg km^{-2}. Further to the east, sandwiched between the Greensboro–Winston–Salem and Charlotte metropolitan areas lies Rowan County (NC34), consisting of blossoming suburbs growing between agricultural regions. This area still has relatively low areas of emissions, with 398 kg km^{-2} of ammonia emissions related to agricultural activities annually. The final low-emissions site was Wake County, where the capital of Raleigh is located. NC41, in Wake County, is <80 miles to the north–northwest of the extremely high swine population region, but despite this, the county's estimated annual emissions of agricultural-related ammonia is 31 kg km^{-2}. The three high emissions sites, NC03, NC35, and NC36, are located in the eastern half of the state. NC36 is located in

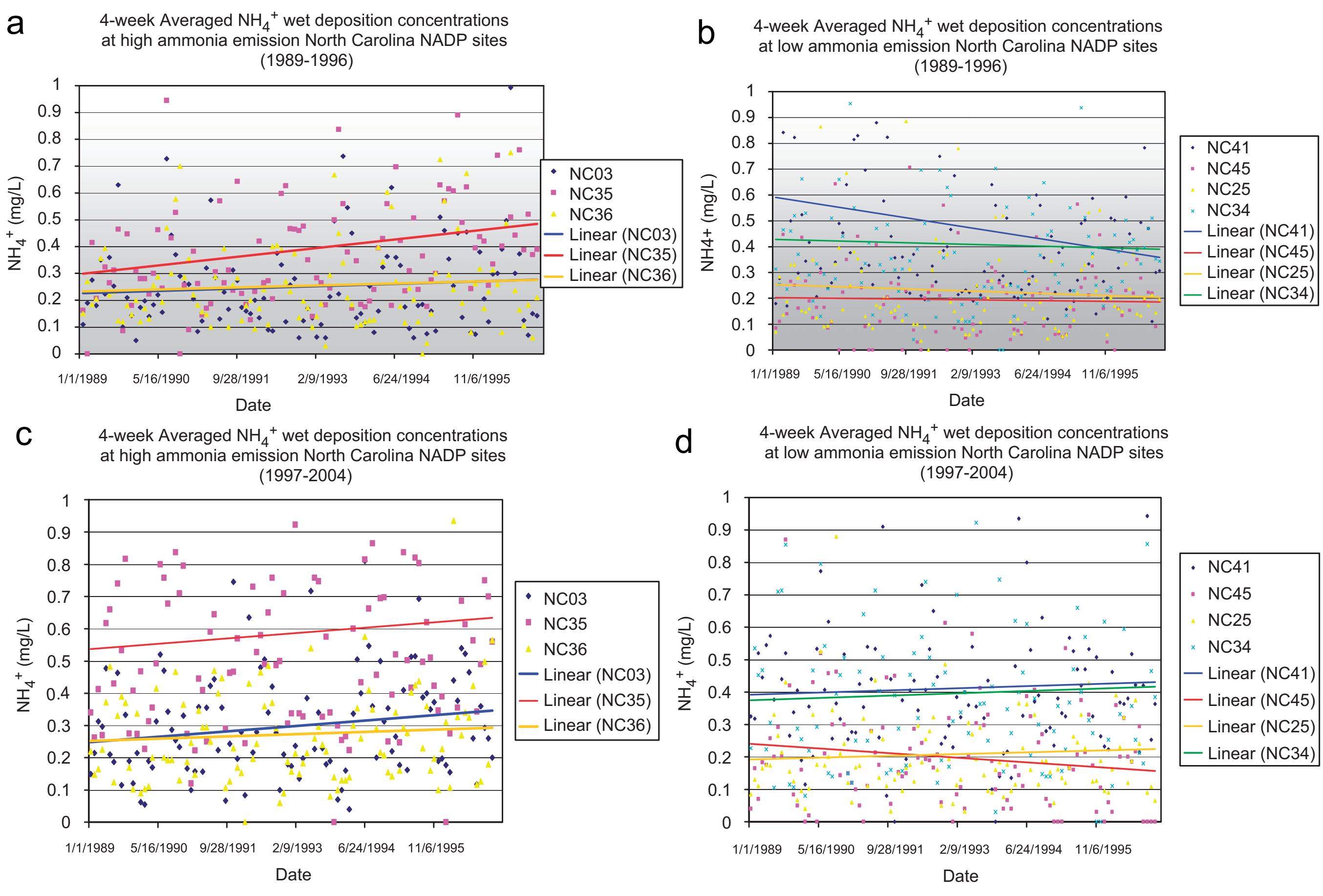

Fig. 8. NH_4^+ wet deposition concentrations and trends over North Carolina, from 1989 to 2004.

Scotland County, in the south-central part of the state, west of the highest ammonia-emitting county, but itself emitting 1408 kg km^{-2} of ammonia annually. NC03, in Bertie County, in the low-lying northeastern section of the state, has emission estimates of 2502 kg km^{-2} annually, and with mean wind (southwesterly) transporting air directly from the source. Finally, Sampson County, in the heart of the hog production region in North Carolina in the southeastern part of the state, has an annual emissions rate of agricultural-related ammonia of 19,560 kg NH_3 km^{-2} annually, making it the highest emitter in the state.

Fig. 8 shows the weekly ammonium ion concentrations (a 4-week rolling average) in wet deposition at each of the seven sites. As expected, Sampson County (NC35) has higher wet deposition values over both periods than the other high-emission sites. However, Wake County (NC41) and Rowan County (NC34) have generally high average wet deposition values than the other two high emission sites. For Wake County, this feature can easily be explained by its proximity to high emissions areas, but for NC34, the reason for the high levels is more uncertain. As for the trends, the hog moratorium has clearly cut down on the rate of increase of NH_4^+ concentrations in precipitation over Sampson County (NC35), whose rate of increase over the 8-year period before the moratorium was 9% yr^{-1}, and since the moratorium is 4% yr^{-1}. The other sites show much less of an effect. Bertie County (NC03) and Scotland County (NC36) have steady but slow increase in NH_4^+ concentration in precipitation from 1989 to 2004. For the lower emission sites, Wake County (NC41) saw a significant decrease in concentrations before the moratorium took into effect, with steady levels since then. The urbanization of Wake County over the last 15 years may be a reason for the interesting trends, and this could also explain the enhanced levels after the moratorium over suburban Wake County (NC41). The other two low-emission sites, Macon County (NC25) and Rowan County (NC34), have been generally stable. It is worth noting that NC45 has had a slight increasing trend before the moratorium, with a slight decreasing trend afterwards, whereas NC35 has had the opposite trends.

4. Conclusions

Calculating ammonia emissions totals using animal inventories and emission factors can provide a useful means of depicting the spatial scale, distribution, and characteristics of agricultural-related ammonia emissions at the county level. Improvements are needed in the accuracy of the emission factors on animals in the United States as well as diet specific emission factors, which will greatly enhance the accuracy of these estimates. The estimates provide a means of correlating ammonia emissions to ammonium ion concentrations, both in ambient air and in precipitation. A reasonable positive correlation seems to exist, but future work is needed to add in other factors which may affect the transport, deposition, and chemical transformation of both ammonia and ammonium ion, particularly with regards to meteorological parameters and non-agricultural-related emissions. The atmospheric chemical composition is being altered in the agricultural environments, owing in large part, to intensively managed crop and animal agriculture. The National Atmospheric Deposition Program network of measurements has served the nation well largely for monitoring the changes associated with energy and urban issues. However, a new paradigm needs to be evolved for agricultural needs and how it impacts air quality.

The effects of the hog moratorium in North Carolina, which undoubtedly curbed the increasing rates of agricultural ammonia emissions in addition to its intended effect of stopping the growth of the hog industry, are not seen clearly in merely analyzing the trends of ammonium ion concentrations in precipitation over the last 7 years, with the exception of areas immediately in the vicinity of the high hog facility density. There are a number of reasons that could be postulated as to why the level of NH_4^+ has not leveled off in the last 7 years since the installation of the moratorium, but as with the NH_3 emissions, meteorological parameters, industrial activity, and other emission rates (such as SO_2 and NO_x) would need to be taken into account before a more clear understanding of the effect of the moratorium on ammonia emissions is obtained.

Acknowledgments

This research was supported by a grant (Number 2003-05360) from the United States Department of Agriculture's National Research Initiative. We wish to thank members of the Air Quality Research Group, North Carolina State University, for their assistance during the course of this study.

References

Aneja, V.P., Murray, G.C., Southerland, J., 1998. Atmospheric nitrogen compounds: emissions, transport, transformation, deposition and assessment. Environmental manager, 22–25.

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

Aneja, V.P., Nelson, D.R., Roelle, P.A., Walker, J.T., Battye, W., 2003. Agricultural ammonia emissions and ammonium concentrations associated with aerosols and precipitation in the southeast United States. Journal of Geophysical Research 108 (D4), 4152.

Aneja, V.P., Schlesinger, W.H., Niyogi, D., Jennings, G., Gilliam, W., Knighton, R.E., Duke, C.S., Blunden, J., Krishnan, S., 2006. Emerging national research needs for agricultural air quality. EOS 87 (3), 25–29.

Asman, W.A., 1994. Emission and deposition of ammonia and ammonium. Nova Acta Leopold 70, 263–297.

Baek, B.H., Aneja, V.P., 2004. Measurement and analysis of the relationship between ammonia, acid gas, and fine particulates in eastern North Carolina. Journal of Air Waste Management Association 54 (5), 623–633.

Davidson, C., 2004. Carnegie Mellon University Ammonia Model, CMU Ammonia Emission Inventory for the Continental United States. Available at ⟨http://www.cmu.edu/ammonia/⟩.

Krupa, S.V., 2003. Effects of atmospheric ammonia (NH_3) on terrestrial vegetation: review. Environmental Pollution 124, 179–221.

National Atmospheric Deposition Program (NRSP-3)/National Trends Network (NADP/NTN), 2005. NADP/NTN Coordination Office, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL. Available at ⟨nadp.sws.uiuc.edu/⟩.

National Oceanic and Atmospheric Administration (NOAA), 2005. Air Resources Laboratory READY. HYSPLIT Model. Available at ⟨http://www.arl.noaa.gov/ready/hysplit4.html⟩.

Nelson, D.R., 2000. Analysis of ammonia emissions from agriculture and ammonium concentrations in the southeastern United States. M.S. Thesis, Department of Marine, Earth and Atmospheric Science, North Carolina State University, Raleigh, NC.

Pio, C.A., Nunes, T.V., Leal, R.M., 1992. Kinetic and thermodynamic behavior of volatile ammonium compounds in industrial and marine atmospheres. Atmospheric Environment 26 (3), 505–512.

USDA (United States Department of Agriculture), 2005. 2002 Census of Agriculture Volume 1: Part 1. Nat. Agric. Stat. Serv., Washington, DC Chapter 2.

U.S. Environmental Protection Agency (EPA), 2003. Clean Air Status and Trends Network (CAST Net) Deposition Summary Report 1996–2003. Available at ⟨www.epa.gov/castnet/⟩.

Further reading

Chemical Speciation of PM2.5 in Urban and Rural Areas, 2003. National Air Quality and Emissions Trends Report.

Clean Air Status and Trends Network (CAST Net), 2003. Annual Report. Available at ⟨www.epa.gov/acidrain/castnet/annual03/annual03.html⟩.

Elminir, H.K., 2005. Dependence of urban pollutants on meteorology. Science of the Total Environment.

Hoppin, J.A., Umbach, D.M., London, S.J., Alavanja, M.C., Sandler, D.P., 2003. Animal production and wheeze in the Agricultural Health Study: interactions with atrophy, asthma, and smoking. Occupational and Environmental Medicine 60 (8), e3.

Lo, A.K., Zhang, L., Sievering, H., 1999. The effect of humidity and state of water surfaces on deposition of aerosol particles onto a water surface. Atmospheric Environment 33 (28), 4727–4737.

Rhome, J.R., Niyogi, D.S., Raman, S., 2001. Assessing seasonal transport and deposition of agricultural emissions in eastern North Carolina, USA. Pure and Applied Geophysics 160, 117–141.

Walker, J.T., Aneja, V.P., Dickey, D.A., 2000a. Atmospheric transport and wet deposition of ammonium in North Carolina. Atmospheric Environment 34 (20), 3407–3418.

Walker, J.T., Nelson, D., Aneja, V.P., 2000b. Trends in ammonium concentrations in precipitation and atmospheric ammonia emissions at a Coastal Plain site in North Carolina, USA. Environmental Science and Technology 34, 3527–3534.