Status Report on Emissions and Deposition of Atmospheric Nitrogen Compounds from Animal Production in North Carolina

NCDENR
North Carolina Department of Environment and Natural Resources
Division of Air Quality

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North Carolina Department of Environment and Natural Resources

Wayne McDevitt, Secretary

Division of Air Quality

Alan W. Klimek, P.E., Director

Bill Cure	Planning Section
Sheila Holman	Planning Section
Ron McCulloch	Ambient Monitoring Section
George C. Murray, Jr.	Chief, Ambient Monitoring Section
Brock Nicholson	Chief, Planning Section
Jim Southerland	Planning Section
Robert Wooten	Planning Section

Table of Contents

List of Abbreviations

AAL	Acceptable Ambient Level
ADS	Annular Denuder System
ARS	Agricultural Research Service
AVHRR	Advanced Very High Resolution Radiometer
CAFO	confined animal feeding operation
CASTNet	Clean Air Status and Trends Network
CAT	Computed Tomography
Cl^-	chloride
DAQ	Division of Air Quality
DON	Dissolved Organic Nitrogen
EC	European Community
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared
g	gram
GIS	Geographic Information System
ha	hectare
HCl	hydrogen chloride
HNO_3	nitric acid
HONO	nitrous acid
IMS	Institute of Marine Sciences
kg	kilogram
LCC	Lenoir Community College
MARS	Model for an Aerosol Reacting System
MCNC	Microcomputer Center of North Carolina
N	nitrogen
N_2	molecular nitrogen
N_2O	nitrous oxide
NADP	National Atmospheric Deposition Program
NADP/NTN	National Atmospheric Deposition Program/National Trends Network
NC DENR	North Carolina Department of Environment and Natural Resources
NC	North Carolina
NCARS	North Carolina Agricultural Research Service
NCDA	North Carolina Department of Agriculture
NCSC	North Carolina Supercomputing Center
NCSU	North Carolina State University
NCSU-CALS	North Carolina State University-College of Agricultural and Life Sciences
NCSU-MEAS	North Carolina State University-Marine, Earth and Atmospheric Sciences
NH_3	ammonia
NH_4^+	ammonium
NH_4^+	ammonium
NH_X	($NH_3 + NH_4^+$)
NO	nitric oxide

NO_2	nitrogen dioxide
NO_3^-	nitrate
NOAA	National Oceanic and Atmospheric Administration
NO_X	$(NO + NO_2)$
NO_Y	reactive oxides of nitrogen
NSW	Nutrient Sensitive Waters
NWS	National Weather Service
OP-FTIR	Open-path Fourier Transform Infrared
RADM	Regional Acid Deposition Model
RADM	Regional Acid Deposition Model
RPM	Regional Particulate Model
SO_2	sulfur dioxide
$SO_4^=$	sulfate
TKN	Total Kjeldahl Nitrogen
U.S. EPA	United States Environmental Protection Agency
UNC	University of North Carolina
UNC-CH	University of North Carolina, Chapel Hill
UNC-IMS	University of North Carolina-Institute of Marine Sciences
USDA	United States Department of Agriculture
VA	Virginia
WRRI	Water Resources Research Institute
WWW	World Wide Web

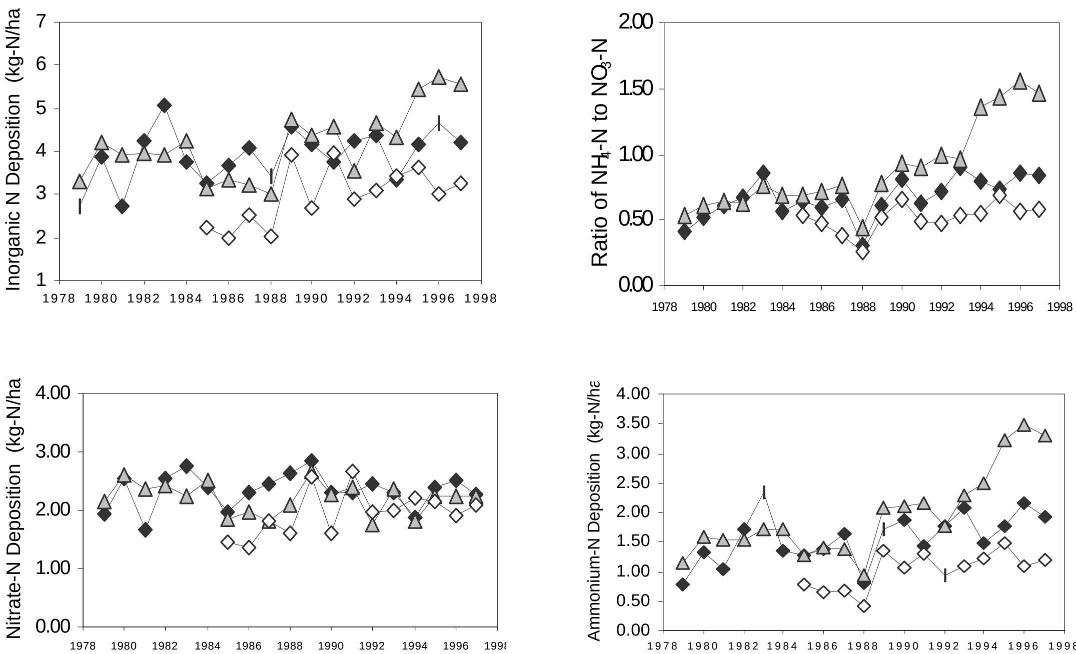
Introduction and Executive Summary

I. Introduction

The atmosphere has long been recognized as a source of nutrients that can stimulate plant growth. Only recently has it been realized, however, that atmospheric inputs are a substantial portion of the new nutrients entering some aquatic systems. For example, EPA's Second Great Waters Report to Congress reports that more than 40% of the nitrogen (N) entering the Albemarle-Pamlico Sounds is estimated to come from the atmosphere. Comparisons between current and historical levels of N input are difficult but if atmospheric inputs are on the rise, then atmospheric deposition could be a major factor contributing to the over-enrichment, or eutrophication, of coastal waters and estuaries.

While nearly four-fifths of the atmosphere is composed of N gas, it is in a diatomic form (N_2) that is almost chemically inert. It is the reactive oxidized and reduced forms, while present only in trace amounts that are the focus of atmospheric deposition studies. Oxidized-N results primarily from combustion processes and typically more than 90% is man-made. Lightning and biological processes involved in the N cycle contribute in a minor way. Oxidized-N is of major concern because of its role in enhancing the formation of ozone in the lower atmosphere (troposphere) and as one of several factors contributing to acidity in rainfall. Reduced-N is present in the atmosphere mainly as ammonia gas and aerosol forms derived from ammonia. Ammonia emissions are largely associated with agricultural activities though some industrial processes such as fertilizer manufacture can also result in significant ammonia emissions. As a regional-scale example, in an emissions inventory prepared by the European Environment Agency, covering 28 European countries, over 92% of the more than 5.6 million metric tons of ammonia emitted was agricultural in origin. Of this 92%, about 80% was associated with the decomposition of livestock manure and the rest with the volatilization of fertilizer-N. Unlike oxidized forms, however, reduced-N plays only a very minor role in ozone formation. Very recent research has focused on another class of atmospheric N compounds, organic N. The significance of organic N and its contribution to atmospheric N budgets for North Carolina is not understood at present. See Paerl, 1995, for a discussion of this emerging area of research. In this report, the term "inorganic-N" is used to denote the sum of oxidized-N and reduced-N.

Atmospheric deposition of N has been recorded in eastern North Carolina in weekly samples collected and analyzed as part of the network maintained by the National Atmospheric Deposition Program (NADP) since the late 1970's. These rainfall samples are used to approximate wet deposition, as opposed to dry deposition, which denotes the direct transfer of gaseous and particulate species to the Earth's surface. In the NADP database, concentrations of oxidized-N have usually exceeded those of reduced-N (see figures). Regulatory efforts aimed at controlling tropospheric ozone formation and decreasing the acidity of rainfall have been successful, in at least maintaining concentrations of oxidized-N, despite substantial increases in population, industrial and motor vehicle activity. Reduced-N levels, however, have been increasing during the same time period.



Wet deposition data from NADP stations in eastern North Carolina and South Carolina depicting annual depositions of inorganic-N (nitrate-N plus ammonium-N), oxidized-N (as nitrate-N), the ratio of reduced-N (measured as ammonium-N) to oxidized-N and reduced-N (as ammonium). Filled diamonds represent data from station NC03 near Lewiston in Bertie County, NC; shaded triangles the data from station NC35 at the Clinton Crops Research Station in Sampson County, NC and open diamonds the data from station SC06 at the Santee National Wildlife Refuge in Clarendon County, SC. Data collection began at the two NC sites in late 1978 and in mid July, 1984 at SC06. These data can be found at the NADP website, http://nadp.sws.uiuc.edu.

This report details the efforts by the North Carolina Division of Air Quality (DAQ), in conjunction with university, federal and other state scientists, to study the emissions, deposition and fate of N in eastern North Carolina. The impetus for this work has been the rapid expansion of confined animal operations in this part of the state and concern over the potential effects of increased ammonia emissions. Efforts generally have fallen into four categories: ambient monitoring, source strength measurements, deposition studies and modeling, all areas that support the overall goal of developing and evaluating regional- and local-scale models of ammonia emissions and deposition.

The conception, development and evaluation of regional scale models of atmospheric N cycling depends upon the availability of a historical database that includes measurements of both oxidized and reduced forms of N in the atmosphere. The NADP data set permits reasonable estimates of wet deposition and gaseous oxidized-N has been monitored statewide over the years as part of regulatory efforts to control ground-level ozone formation. The situation for ammonia gas, however, is far less satisfactory. Gaseous ammonia readily dry-deposits to vegetative surfaces, especially large, forest canopies. However, it also associates rapidly with sulfates in the atmospheric to form fine aerosol particles and these particles deposit much more slowly to surfaces than ammonia gas. Instead, they are primarily removed in rainfall. This difference in the mechanism and rates of removal from the atmosphere will alter deposition patterns. In the gaseous form, ammonia-N will tend to deposit near the source while as an aerosol, ammonia-N will be transported over much greater distances.

Monitoring of atmospheric concentrations of ammonia and ammonium began in 1997 at several locations in eastern North Carolina. Measurements were started in the fall of that year at Lenoir Community College (LCC) and on the grounds of a cooperating hog-producing operation (referred to as the "eastern farm site"). Sites have since been established at North Carolina State University's (NCSU) Clinton Crops Research Station near Clinton in Sampson County and at the Institute of Marine Sciences in Morehead City. These data will be valuable for evaluating the results of efforts to model the fate of ammonia/ammonium on a regional scale. Unfortunately, monitoring of ammonia/ammonium is more time-consuming than with most other atmospheric constituents; several hours are required to collect a useable sample, and then sample tubes must be taken to a laboratory for analysis. A major outcome of the efforts so far has been the realization of just how variable these measurements are over relatively short distances. At LCC, average values were approximately 5 gm $^{-3}$ with about 80% in the gas form. On the eastern farm, average values were average values were 10 gm $^{-3}$ with approximately 90% as gas.

Source strength measurements provide a basis for formulating emission factors for the different processes at a facility. They are necessary for estimating inputs into models and for judging the efficacy of changes in management practices aimed at controlling emissions. Measurements of ammonia emissions coordinated by the DAQ have so far been confined to one working swine operation in eastern North Carolina, the "eastern farm site". A cooperating USDA researcher has shared data from one other North Carolina swine operation as well as from one in Georgia. North Carolina hog producers typically house animals in large barns, use anaerobic lagoons to treat and store waste and then spray the waste effluent onto growing crops as fertilizer. Current management practices require land-application at agronomic rates for N. Major objectives at the eastern farm site have been to quantify ammonia emissions from housing units, lagoons and spray fields and to compare these with published emission factors. Since a limited amount of published data from the USDA suggest that lagoons are the major ammonia source at a swine production facility, measurements have so far been concentrated on characterizing ammonia emissions from waste lagoons. These exhibit variability, dependent upon measurement methodology (Table 6). They also reflect the problem of trying to estimate annual emissions from data taken over short time periods from sources with emissions dependent upon local meteorological conditions. The limited number of measurements of emissions from barns, however, suggests that these are also a strong source. It must be emphasized that these are observations from a single farm and a single lagoon.

While source strength measurements provide a direct means of obtaining emission factors, they must be consistent with estimates of imports and exports that make up the N-budget in the model of a large-scale animal operation. In such a model, imports might include the N in feed and in any animal biomass brought onto the farm. Exports would take into account, for example, the N content of animals taken to market, the N recovered in crop biomass fertilized with lagoon effluent and losses as ammonia volatilized from manure anywhere on the farm. N-budgets will be especially useful to the future development of interfaces with water quality models. Some of the exports from the model farm will be imports to the model watershed. Characterization of the complex of processes involving N that are associated with land-application of animal wastes will be particularly important because they occur across this interface. These will include ammonia loss during spraying and volatilization from the soil surface before infiltration, nitrification, denitrification, crop uptake of nitrate and ammonium, and nitrous oxide loss during denitrification. Work sponsored by the DAQ has so far provided some measure of the nitrification and denitrification potential of the soils at the eastern farm site. Research scheduled for the summer of 1999 will supply estimates of ammonia losses during and after spray application of wastes to crop canopies.

Accurately assessing the importance of the dry deposition of ammonia in eastern North Carolina has so far proven the most problematical aspect of the DAQ's efforts to develop and evaluate regional and local scale models of ammonia emissions and deposition. [Dry deposition refers to the direct transfer of gases and particles to the surface of the Earth.] Discerning trends in the wet deposition of N (i.e., via rainfall) has been greatly aided by the availability of the NADP database, which includes more than 20 years of measurements at some sites (see above figure). Unfortunately, no such regional database exists for the study of dry N deposition which, for a "sticky" molecule like ammonia, will vary substantially with the distance from the source and the roughness of the surrounding land cover. More ammonia-N would be expected to dry-deposit to a large forest canopy than to a pasture. As a surrogate for dry deposition, throughfall estimates have been used extensively in European studies. These are derived from comparisons between nutrient concentrations in rainfall samples collected in the open with those from samples washed off forest canopies. Throughfall estimates must be treated as only an approximation of dry deposition, however, and interpreted with caution. Canopy uptake and leaching of ions from the canopy foliage will introduce uncertainties in the interpretation of the data. Analysis of samples collected from five different locations in the eastern part of the state between August 6, 1997, and April 16, 1998, does indicate that dry deposition of N as ammonia/ammonium at the eastern farm site, 10.2 kg-N/ha, was nearly twice that from wet deposition. Deposition of inorganic N (i.e., wet plus dry deposition and including both oxidized and reduced forms of N) during this 9 month period totaled 14.5 kg-N/ha. Within 3 km of animal production facilities, inorganic N deposition ranged between 7.2 and 13.1 kg-N/ha. At sites further than 5 km, depositions were between 3.8 and 5.2 kg-N/ha. The significance of these levels, in terms of the ability of forests and other land cover types to absorb and retain N, is not known. These data do, however, emphasize the highly variable nature of dry deposition and the complex spatial patterns to be expected in an area like eastern North Carolina that is dotted with strong sources.

Modeling of N cycling provides a powerful tool for assessing the effects on deposition of emissions of both oxidized and reduced forms of N. Regional-scale models, such as the EPA's RADM (Regional Acid Deposition Model), however, have been developed more with a focus on the behavior of oxidized forms of N and their role in acid rain and ozone formation. The atmospheric chemistry and deposition characteristics of ammonia were not of major concern.

Work is now underway to upgrade the treatment of ammonia chemistry in the RADM and to develop linkages to the Regional Particulate Model (RPM). This revised model, termed the Extended-RADM, will insure better model representation of the processes related to aerosol formation. The degree of aerosol formation will likely shift the transport distance of the atmospheric mix of ammonia gas and ammonium aerosols due to differences in deposition characteristics. These interactions with sulfates, and to a lesser extent, nitrates, highlight the need not only to develop emissions inventories for ammonia, but also for sulfates and nitrates. Strong seasonal variations in ammonia gas and aerosol levels are expected since both emissions and reaction rates will depend on temperature.

A. Conclusions to Date from DAQ's Research Efforts

1. Ammonia emissions from a hog waste lagoon are substantial and are higher in the summer than in the winter. However, variation exists between estimates made by different measurement techniques.
2. Preliminary measurements to determine the relative strength of ammonia emissions from animal barns, waste lagoons and spray fields suggest that emissions from the barns are similar to those from the lagoon (measurements of spray field emissions are scheduled for the summer of 1999).
3. Data collected so far are inadequate for approximating emission factors to compare with published values (most of which are based upon European studies).
4. Based upon studies of the NADP database, wet deposition of reduced-N (as the ammonium ion) is increasing in eastern North Carolina.

B. Recommendations

1. Measurements of ammonia emissions should be extended to other hog farms to begin developing an understanding of the variability in emissions estimates that result from different management practices and from similar practices at different locations. Studies should also be planned to evaluate ammonia emissions at large poultry operations.
2. Expand research efforts on the dry deposition of ammonia to different ecosystem types in North Carolina, especially forests.
3. Expand the monitoring of ambient ammonia gas and aerosol concentrations in eastern North Carolina.
4. Begin research on the likely response of different ecosystem types to continued N loading at current rates. Quantification of the ability of these systems to absorb and retain N will be critical to relating atmospheric deposition to water quality.

1 Background

1.1 Project History

1.1.1 Growth of Swine Production and Associated Concerns

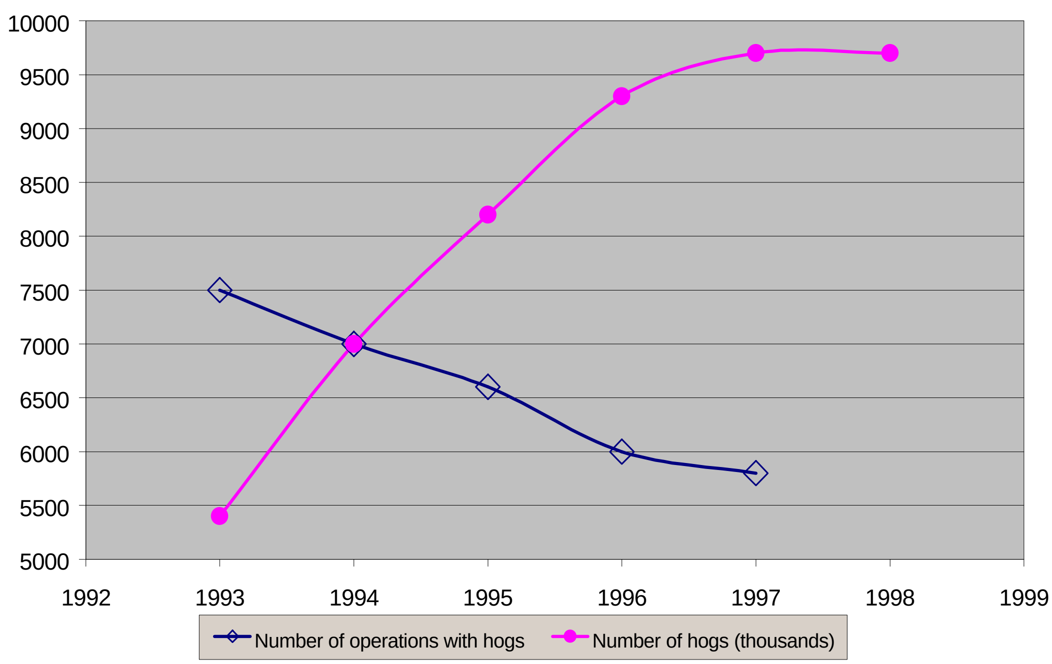
Various animals, including swine, cattle and poultry, are included in the general concern for ammonia emissions. Swine production has the largest ammonia emissions among animal types in North Carolina, has been involved in the most recent controversies, and seems to be the most logical sector to evaluate for atmospheric emission problems as a first step. Similar evaluations may be warranted for other types of animal production as the work on swine production reaches maturity.

Swine have been raised in North Carolina since colonial times. The traditional method of raising these animals has been free range, in fenced fields or small outdoor pens. In each case, waste disposal is dependent on the degree to which the swine are allowed to roam. In the 1980's, the predominant method of raising swine changed considerably. By the late 1980's, there were approximately 2 million pigs in North Carolina housed in covered, ventilated barns with concrete floors. Waste removal in the confined operations is generally via waste wash down/removal systems, draining into anaerobic lagoons. By 1997, when a moratorium on swine production expansion was enacted by the North Carolina Legislature, there were approximately 10 million swine in the state, with the vast majority of production using confined operations. Within the constraints of the moratorium on new construction and its implementation, there were approximately about 10 million swine in the state at the beginning of 1999. The human population of the state is approximately seven million. This includes all swine (breeding operations through the finishing operations), counting all animals on the hoof at any point in time, as distinguished from an annual production figure. There are also about 60 million turkeys and 620 million broilers (chickens) produced in North Carolina each year. Overall, North Carolina ranks number two among states in swine production, number one in turkeys and is a major producer of broilers.

Coincident with the growth of swine numbers in the state, there has been a decline in the total number of farms raising swine (Figure 1) (NCDA, 1999). The decrease in the total number of farms raising swine is the result of the closure and consolidation of small family farms and a move toward the industry preference of large farms that house more than 2,000 head. Given the increased scale, consolidation of production systems into large-scale operations has become economically more favorable than a larger number of smaller operations.

The confined method of feeding and waste removal currently being used by the swine industry creates substantial quantities of anaerobic waste. Chemical reactions within the waste result in substantial concentrations of ammonium in the waste effluent, which is a source of ammonia emissions to the atmosphere. These wastes also contribute to other issues outside the scope of this report, such as odor, accumulation of metals in sludge, and concerns about elevated concentrations of nitrates in ground water. In contrast, beneficial effects of atmospheric ammonia have also been identified. Some fraction of the total requirement of nitrogen and other nutrients may potentially be provided by atmospheric deposition (Erisman et al, 1998).

Figure 1: Hog Population and Number of Farms



Depending upon the size and age of a pig, it may generate from two to four times the weight of waste as a human. This presents operators of waste disposal systems at confined animal feeding operations (CAFO's) with a number of operational challenges. In addition, the types of swine production farms prevalent in North Carolina have four main potential sources for ammonia emissions:

- Animal housing units;
- Waste storage and treatment lagoons;
- Spraying waste on crops;
- Revolatilization from soils after spraying.

All of these sources are expected to exhibit a high degree of variability, especially with seasonal changes.

Two major issues stimulated interest within DAQ to evaluate these issues. First, estimates of nitrogen emissions in the state, based on factors published by the U.S. Environmental Protection Agency (Battye, et al., 1994) indicated large amounts of nitrogen being released to the atmosphere from several sources. Second, recent studies have suggested that there may be significant atmospheric deposition of nitrogen compounds in the Neuse River basin and estuary (Paerl, 1995). The National Atmospheric Deposition Program (NADP) has been measuring wet (precipitation) deposition of several nutrients, including nitrate and ammonium, at several sites throughout the country, including North Carolina for over 20 years.

In 1996, the Division of Air Quality began a program to evaluate emissions and deposition of atmospheric ammonia. The primary purpose was to take the first steps toward evaluating the fate of ammonia from animal operations, beginning with swine. Several efforts were mounted and are discussed in this report. Although specific funding was directed at this effort by the Legislature through the UNC Board of Governors, and ultimately the NC Agricultural Research Service, significant additional efforts were mounted by the Division to answer broader questions than those raised by the Legislature. The primary purpose of the special funding from the Legislature was to conduct modeling. However, much additional information and input data were needed before modeling could be undertaken with meaningful results. Such questions as emission rate refinement and validation, deposition and removal mechanisms and their efficiencies, ambient levels of ammonia, and other similar questions were included in the work initiated and still ongoing in DAQ.

1.1.2 Blue Ribbon Panel (Swine Odor Task Force)

In 1994, the North Carolina Legislature first began to recognize the potential impact of animal operations on the environment as related to odor. They appointed a Blue Ribbon Panel of distinguished scholars, civic leaders and representatives of a wide sector of the economy and interests in North Carolina to conduct a study or review of the seriousness of the problem in the state. Their report, released in March 1995, presented several important conclusions. This effort, although focused on odors, was important, in that it began to draw scientific attention and funding to the impact of these operations on the environment and efforts to manage them in a manner that would enhance their economic and aesthetic viability.

1.1.3 Legislative Appropriations to Board of Governors/DAQ

In early 1996, DAQ prepared an expansion budget request for the study of the emissions of nitrogen compounds (mostly ammonia and ammonium) into the air from animal farming operations. The amount originally requested was $900,000, but instead $450,000 was appropriated and assigned to the UNC Board of Governors for research efforts. Dr. Johnny Wynne, the Director of the North Carolina Agricultural Research Service, administered these funds at North Carolina State University. Dr. Wynne and the DAQ cooperated in the determination of how to accomplish the most important work using the legislative funds. The primary focus of the funding was for modeling of the emissions, fate, and deposition of nitrogen compounds.

Ammonia and ammonium compounds are reactive and undergo chemical and physical changes in the atmosphere. In order to properly model the emissions, better information was needed on how much was emitted from various sources. Though estimates were available from EPA, most of the measurement work had been performed in Europe. Also USDA was performing some emissions measurements in Georgia. Emissions data were needed to verify that available data were representative of North Carolina. In addition to the legislative funding, DAQ used fuel tax reserves funding to support several emissions measurement projects and the operation of several ambient monitoring sites. DAQ also sought help from EPA researchers, who were able to provide additional support needed to improve the appropriate regional scale model. EPA committed to spend up to $500,000 in support of the modeling efforts. The legislative funding, the EPA modeling support funding and the other funds expended by DAQ have allowed measurements to be made that will improve the accuracy of the modeling that is underway.

1.1.4 Early Estimates of Nitrogen Loading and USEPA Report to Congress

The atmosphere as a source of N readily useable by plants was recognized in Germany in the 1820's. However, an appreciation of the magnitude of atmospheric deposition relative to the total N loading of aquatic systems has only recently developed, as has the contribution of anthropogenic activities. In the *2^nd^ Report to Congress on Deposition of Air Pollutants to the Great Waters,* EPA presents estimates of atmospheric N loading for some selected coastal waters (Table IV-11). These range from only a few percent for Narragansett Bay (RI), Guadeloupe Bay (TX) and the Potomac River basin (VA) to 27% for the entire Chesapeake Bay, 38% for the New York Bight, 44% for the Albemarle-Pamlico Sounds, 26% for Sarasota Bay (FL), and 28% for Tampa Bay (FL). The highest proportion was for the coastal waters off Morehead City, fed by the Newport River, where the range was given as between 36% and 80%, dependent upon flow conditions.

Estimates cited in the above report to Congress for the Albemarle-Pamlico sound and the

Newport River were developed by Hans Paerl of the UNC Institute for Marine Sciences at Morehead City. These calculations were made by using deposition estimates from regional-scale models, in conjunction with areas of water bodies, to first approximate the direct fall contribution to loading. Various methods were then developed to estimate the portion of the loading from sources within the watershed. In the case of the Newport River, the situation was simplified by the fact that a single river drained a small watershed and that flow of nutrients had been well characterized. The size of the river's discharge plume into the coastal zone was problematic in this case and satellite imagery (AVHRR) was used to define the sizes of low and high flow plumes based upon measured temperature differences. For the sounds, contributions from watersheds were based upon the use of export coefficients. The coefficients reflect the ratio nutrients depositing from the atmosphere that are retained by the terrestrial ecosystem and thus unavailable for export; they usually are high: 80% or more. Most are assumed constant and do not reflect any tendency of a system to saturate over time as loads accumulate.

1.2 Actions Taken by DAQ

The Division of Air Quality (then Air Quality Section) began an assessment based on concerns voiced in the literature, complaints from the public and general sensitivities to ongoing developments and issues in other media. These preliminary efforts grew quickly, within the bounds of limited resources, and the Division initiated several efforts prior to the special appropriations to the Board of Governors by the Legislature. Summaries of several of these efforts are provided below.

1.2.1 Pre-Appropriation Steps/Plans

The Division of Air Quality was approached by Dr. Viney Aneja through the Water Resources Research Institute to fund a project to characterize animal and poultry emissions in North Carolina in late 1995. This proposal lead to a quick survey of available information concerning ammonia emissions from animal production and other sources. The Division found that the EPA had previously produced a summary report of ammonia emission factors (Battye, 1994). These emission factors are largely based on

European studies. A few simple calculations suggested that a large amount of ammonia was being released into North Carolina's atmosphere from animal operations. Given the problems with excess nutrients in the Neuse and the Tar-Pamlico, the need was apparent to investigate the possibility that ammonia released from animal production and other sources into the air could find its way to these sensitive waters.

Methods for making field measurements of ammonia emissions were discussed at a meeting held in December 1995. Dr. Lowry Harper (USDA-ARS) was present, as was Dr. Viney Aneja (NCSU-MEAS). EPA experts who were involved with the emission factor report were present to discuss the suitability of these emission factors for NC production methods and conditions.

The Division of Air Quality decided that there was no one perfect measurement technique for ammonia emissions, and that the available emission factors gave no estimate of confidence levels or seasonal variability. It is possible, fortunately, to place an upper bound on ammonia emissions from manure based on chemical analysis of the manure. The EPA representatives felt that the available emission factors could benefit from verification and improvement. The emission factors based on European measurements needed verification against North Carolina animal husbandry practices before any future emission regulations could be contemplated. Further, careful measurements of emissions from facilities using today's waste management practices would provide a baseline to evaluate alternative technologies.

With available funds, the Division of Air Quality contracted with the Water Resources Research Institute (WRRI), an agency of North Carolina State University, for Dr. Viney Aneja to measure ammonia emissions from a swine waste lagoon with the dynamic chamber technique. DAQ also contracted with the US Dept. of Agriculture, Agricultural Research Service, for Dr. Lowry Harper to simultaneously make ammonia emissions measurements with the micrometerological technique. This technique has the advantage of providing an estimate for the entire area of the lagoon. However, the equipment for this method is expensive and there are constraints on where it can be appropriately deployed. For example, the lagoon should be four or more acres in size with no trees or tall structures near the shore that will disturb the wind flow. The chamber technique is less expensive and can be employed on small lagoons without regard to surrounding structures. The arguments against it are that it samples a very small portion of the lagoon surface and the ammonia release rate inside the chamber may not match that outside the chamber. It was DAQ's hope that both methods would give essentially the same results or that a reasonable way would be found to evaluate measurements for the greatest possible accuracy. DAQ would then have a means to accurately and less expensively measure ammonia emissions from any size lagoon. It was thought that DAQ eventually would want to make measurements at a number of animal production facilities (swine, cattle, and poultry , with several replications of each) to have statistically supportable results.

In the winter and spring of 1996, DAQ developed a list of additional projects to improve understanding of ammonia emissions, ambient concentrations, transport, and fate. Additional funding was sought from the Legislature. In the summer of 1996, the Legislature appropriated funds for study of ammonia emissions but placed the research responsibility on the N C Agricultural Research Service (NCARS) under the leadership of Dr. Johnny Wynne. Our list of proposed projects was then provided to Dr.Wynne to suggest how the money could best be spent. These proposals were largely adopted. The cooperation and information flow between NCARS and DAQ has been very good and continues.

1.2.2 Development of Action Plan

The Division of Air Quality first became actively involved in an objective examination of potential environmental problems associated with intensive livestock production in the fall of 1995. This interest was stimulated by studies suggesting that there may be significant air deposition of nitrogen compounds in the Neuse River basin and estuary.

DAQ undertook initial discussions internally and with the Division of Water Quality, the U.S. Department of Agriculture, North Carolina Agricultural Extension Service, North Carolina State University, the University of North Carolina, and the U.S. Environmental Protection Agency. These discussions resulted in preliminary strategies regarding how the perceived problems and related theories could be better measured, analyzed, modeled, and confirmed or dismissed. During this approximate time period, the Blue Ribbon Commission on Animal Waste was conducting its investigations and developing its recommendations, which are detailed in the February 1996 "Draft Interim Plan: Neuse River Nutrient Sensitive Waters (NSW) Management Strategy." Steps envisioned at that time, as necessary to further define the complex atmospheric deposition phenomena, were also outlined in that plan. DAQ held planning and implementation coordination meetings, resulting in refinements to the plans, with flexibility built-in to allow continued changes as more was understood about the issue.

In March 1997, the Division of Air Quality held a technical workshop at the McKimmon Center at North Carolina State University to launch efforts to address the issues of nitrogen emissions and deposition from all known sources in North Carolina with short and long term objectives. DAQ has continued to develop strategies to study these issues in order to better understand the present situation as it relates to all known sources of nitrogen loading into the state's nutrient sensitive ecosystems. These sources include emissions from automobiles, non-road vehicles, large combustion sources, municipal water treatment plants, animal waste disposal, and fertilizer applications. Estimates of emissions from many of these source types have already been provided in past studies.

The basic mission of this project has been to characterize and quantify emissions and deposition of nitrogen compounds from animal production facilities relative to other sources, in order to be able to assess the effects of various management practices and applied technologies on the current situation as a whole, and to answer the following questions:

- Is there an air quality problem?
- If so, what are the magnitude and scope of the problem?
- What are the air quality impacts of current practices and proposed solutions?
- What is the best approach to quantify and satisfactorily document these facts?

Initial field study efforts were planned in areas affecting the Neuse River focusing on hog production. The area of interest was later broadened to the eastern part of the state where swine production is most concentrated. Similar studies may be planned later to characterize emissions from other animal production operations (e.g. turkeys and chickens), depending upon the results of these initial studies.

1.2.3 International Review Meeting

After the North Carolina Legislature appropriated funds for studies of impacts upon the Neuse watershed due to ammonia emissions from animal operations, an international meeting was held at the McKimmon Center at North Carolina State University to assemble a credible body of knowledge and experiences on the topic. This was initiated so that the information could be shared, exchanged, debated and evaluated for the common good. It also served as a venue for the unveiling of DAQ's study plans and a forum debating what improvements might be made in that plan. The sponsors of the workshop were the Division of Air Quality of the North Carolina Department of Environment and Natural Resources, the Water Resources Research Institute of the University of North Carolina, and North Carolina State University. This workshop took place March 10-12, 1997, and was attended by approximately 200 individuals representing general public, academia, the media, advocacy groups and government. Attendees included at least one representative from the European knowledge base as studies on this topic have been underway in the Netherlands, Scandinavia, the United Kingdom, and elsewhere in Europe for a number of years. At this meeting, general background information was shared, as well as comment periods and general workshop sessions. During these sessions, the plans of study developed by the Division of Air Quality, in cooperation with representatives of the funded entity, the NC University System Board of Governors (coordinated by Dr. Johnny Wynne of NCSU), were discussed and revised.

A summary of the program and findings discussed at the meeting, along with written submittals by the presenters are included in "Proceedings of the Workshop on Atmospheric Nitrogen Compounds, Transport, Transformation, Deposition & Assessment", which was compiled by NCSU and DAQ. A second similar workshop is scheduled for June 7-9, 1999. This workshop will provide a forum to: discuss results of studies completed by the North Carolina investigators; share information with others from the scientific community; receive feedback on advances in the state of knowledge; and evaluate future steps to further investigate and mitigate problems.

1.2.4 Effects of Excess Nitrogen: The Scientific Literature

The scientific literature on the effects of excessive nitrogen (N) on terrestrial and aquatic ecosystems is voluminous. Some general aspects will be discussed, especially with respect to atmospheric deposition and ammonia/ammonium effects, but a detailed review is not attempted here.

Much of the concern over atmospheric deposition of N compounds has focused on the effects of nutrient over-enrichment, or eutrophication, in aquatic systems. Added nitrogen, regardless of the source, stimulates algae growth in the nitrogen-limited estuaries and shallow coastal waters of North Carolina. The subsequent death and decomposition of these organisms depletes dissolved oxygen in the water, a major factor in fish kills. Though it has long been known that the atmosphere is a source of N, only recently have researchers realized that the amounts deposited were significant enough to cause problems (Fisher and Oppenheimer, 1991, Paerl and Fogel, 1994, Paerl, 1995). Estimates of the proportion of the total N that enters these coastal waters from the atmosphere vary substantially, but for the Albemarle-Pamlico Estuary they range between 38% and 44% (Paerl and Fogel, 1994; 2nd EPA Report to Congress).

High N-loading also can have detrimental effects in terrestrial ecosystems, effects that can result in the greater export of N to surface and groundwater. Aber et al. (1989, 1998) hypothesized that high N inputs lead to “nitrogen saturation.” Saturation reduces the ability to assimilate and retain further N additions in an ecosystem. The result is increased nitrate formation and its subsequent loss to surface and groundwater. The level of N input required to saturate an ecosystem will depend to a very great extent on the makeup of the community and will include many non-biotic factors related to the properties of the soil and climate.

European research has lead to the critical load approach to understanding N-dynamics in ecosystems (see Erisman, et al., 1996 and references cited therein). Critical loads reflect the level of N input likely to impair and/or alter ecosystem structure and function. Most work with this concept has focused on tree species in forest ecosystems. The critical load can be defined at the ecosystem level or for system components. For tree species of forest systems in the Netherlands, for example, critical loads for N are in the range of 10 to 50 kg-N ha^{-1} yr^{-1} when stress tolerance and nutrient uptake are criteria. For species diversity in the understory, however, 10 to 20 kg- N ha^{-1} yr^{-1} is considered the critical load. Critical loads have been estimated for aquatic ecosystems as well. In the lowlands of Western Europe, many rain-fed soft water lakes and ponds are found on sandy soils with little buffering capacity. These nutrient-poor systems are characterized by the presence of rare and endangered plant species (Roelofs, 1983; Arts, et al., 1990). Since the 1950s, this vegetation type has disappeared from many of these sites and has been replaced by acid- and nitrogen-loving species. Studies have indicated that critical loads in these more sensitive systems should be on the order of 5 to 10 kg- N ha^{-1} yr^{-1} (Bobbink and Roelofs, 1995). In the Netherlands, average N deposition is 39 kg-N/ha/yr.

High N loads also cause problems for individual plants. Nitrogen addition tends to increase shoot growth over root growth, rendering plants become more susceptible to wind-throw and sensitive to water stress. Also, N additions at inappropriate times during the season cause problems for species that go through a dormant cycle during the cold months. Nitrogen added late in the season can stimulate growth at a time when the plant would normally be progressing into a dormant state. Failure to adequately harden-off for winter will make the plant more likely to suffer frost damage.

2 Development and Implementation of Assessment Plans

2.1 Components of Plan and Summary of Activities Involved

2.1.1 Ambient Measurements (outside air concentrations)

The DAQ plan included ambient measurements upwind and downwind of animal production operations. Local site-specific meteorological data also were collected to support the analysis and interpretation of the resulting data. Equipment was purchased and/or modified by DAQ in preparation for this work and was installed when a suitable and accepting site was located.

2.1.2 Source Strength Measurements (emissions to outside air)

Three methods were originally identified in the DAQ plan for estimating ammonia emission flux from a waste lagoon:

- A dynamic flow-through chamber method employed by Dr. Viney Aneja of the NCSU Department of Marine, Earth, and Atmospheric Sciences;
- A Micrometeorological gradient method employed by Dr. Lowry Harper of USDA-Agricultural Research Service;

- A multiple open path Fourier transform infrared (FTIR) method employed by Dr. Lori Todd of UNC, Chapel Hill.

The three methods were chosen to measure waste lagoon ammonia emission fluxes, and intensive field studies were planned so that the methods could be evaluated concurrently. The U.S. EPA, Office of Research and Development joined the project, using another open path FTIR method. This effort concentrated on measuring ammonia emissions from the barns.

2.1.3 Nitrogen Emissions Inventory for North Carolina (estimates of total emissions)

Nitrogen oxide emissions are routinely inventoried every year for large industrial sources in North Carolina. Due to the requirements of ozone modeling, area and mobile source emission inventories for nitrogen oxides were prepared for the State for 1990. A calculation of ammonia emissions was made for 1995 (at the time, this was the latest year that statistics were available for all the ammonia sources) using the emission factors published by the EPA. Table 1 shows the general picture of nitrogen emissions in the form of nitrogen oxides (NO_x) and ammonia (NH_3):

Table 1: Nitrogen emissions inventory for North Carolina

Source	*Nitrogen Species Emitted*	*Estimated Tons of Nitrogen Emitted per Year*[1]	*% of Total N*[2]
Highway Mobile (1990)	NO_x	78,509	23.31
Point Sources (1994)	NO_x	77,798	23.10
Area & Non-Road Mobile (1990)	NO_x	24,452	7.26
Biogenic NO_x	NO_x	9,926	2.95
Swine (1995)	NH_3	68,540	20.35
Cattle (1995)	NH_3	24,952	7.41
Broilers (1995)	NH_3	13,669	4.06
Turkeys (1995)	NH_3	16,486	4.89
Fertilizer Application (1995)	NH_3	8,270	2.46
"Other" Chickens (1995)	NH_3	6,476	1.92
Industrial NH_3 Point Sources (1995)	NH_3	1,665	0.49
Human (1995)[3]	NH_3	1,629	0.48
Publicly Owned Treatment Works (1995)[4]	NH_3	4,440	1.32
Total		336,812	100

1: NO_x emissions are reported as if all emissions were NO_2 although most emissions occur as NO, and convert to NO_2 in the atmosphere (NO_x in the atmosphere is about 95% NO_2). Calculation of nitrogen emitted per year from NO_x sources is from multiplying tons of NO_x per year by (14/46). Calculation of nitrogen emitted per year from ammonia sources is from multiplying tons of ammonia per year by 14/17.
2: About 56.6% of nitrogen is from NO_x and about 43.4% is from NH_3.
3,4: Emission factors are based on limited data and are not believed as accurate as for other sources.

2.1.4 Assessments of Deposition

Initially, three projects were planned to assess deposition of atmospheric nitrogen compounds:

- A study of rain throughfall measurements in tree canopies compared to open areas, to assess the magnitude of local dry deposition;
- A statistical analysis of National Atmospheric Deposition Program (NADP) precipitation chemistry data, to assess the magnitude and range of potential impacts of intensive animal production on wet deposition of nitrogen compounds;
- A spatially refined analysis of NADP data, to develop estimates of wet deposition of ammonium and nitrate from the atmosphere for North Carolina and specifically, coastal plain river basins.

Following detailed analysis of emission fluxes, new efforts to accurately determine dry deposition fluxes of ammonia over various surfaces are underway, and are expected to last into 2001.

2.1.5 Modeling Emissions and Fate of Ammonia

Understanding the amounts and patterns of atmospheric nitrogen deposition in eastern North Carolina is essential for assessing potential impacts on terrestrial and aquatic ecosystems. Computer models that reflect the current scientific understanding of the behavior of nitrogen compounds in the atmosphere are required tools for this work. Models presently in use, however, have been developed primarily to simulate ozone formation in the lower atmosphere. For these applications, the behavior of nitrogen oxides is the main focus, not ammonia volatilized from animal manure. To begin enhancing the existing models to better accommodate the characteristics of ammonia:

- Computer code in the EPA’s Regional Acid Deposition Model (RADM) must be re-evaluated and re-written where necessary to reflect current knowledge of ammonia chemistry and deposition characteristics;
- Emission inventories, the inputs to models, must be evaluated and improved where necessary;

- The best land-use data available, a major determinant in deposition, must be obtained for future modeling;
- Significant gaps in knowledge relating to ammonia emissions and deposition must be identified and means found to develop research approaches to get the required information.

2.2 Implementation

2.2.1 Working with Board of Governors/NCSU Agriculture Research

Dr. Johnny Wynne, Director of the NCSU Agriculture Research Service was assigned to administer the funding provided by the Legislature. Since the DAQ already had been determining what research was needed to better understand and quantify the emissions and deposition of nitrogen compounds, Dr. Wynne suggested that DAQ work with NCSU in selecting needed projects and awarding the contracts. In this manner, the work supported by the legislative funding could be enhanced by the work supported by DAQ funding and the EPA.

2.2.2 Efforts to Find a Study Farm

The DAQ made many contacts to major farm corporations to seek permission to make air quality measurements on a hog farm. The efforts to find a farm involved direct contacts with the corporations, the North Carolina Pork Producers Association (now the North Carolina Pork Council), USDA, NCSU researchers who already had permission to conduct other research at corporate farms, including Dr. Mike Williams at NCSU, and others. One corporation promptly refused to cooperate, while most corporations took time to consider DAQ’s request and then declined. The corporations expressed concern about security of the farms and the prevention of the spread of disease to the herds on the farms. This process began in March 1996 and continued until February 1997, when a major corporation finally agreed to allow the measurements at one of their farms. The corporation wished to remain anonymous. An agreement was signed that allowed three years of measurements. The farm became known as the Eastern Farm and is located in

Sampson County. Measurements can continue until May 2000 under the existing agreement.

2.2.3 Evaluating and Refining Projects to Accomplish Goals

A number of DAQ staff from the Planning and Monitoring Sections began meeting nearly weekly. This group later became known as the Science Team. Knowledgeable researchers were invited to meet frequently with the Science Team to discuss the State's objectives and how to achieve them. Many meetings were held with NCSU, UNC, USDA, EPA researchers, and a few private contractors. Literature was reviewed. Projects were discussed, selected and refined that would help reach the goal of determining the source and fate of the nitrogen compounds in eastern North Carolina. In March 1997, the Workshop previously described was held in which each project was further described and further refined to accomplish the objectives.

3 Progress to Date

3.1 Ambient Assessment Studies

3.1.1 Local Ambient Measurements

DAQ has measured the following parameters at Eastern Farm.

- Gaseous species: nitric acid (HNO_3), nitrous acid (HONO), hydrogen chloride (HCl), sulfur dioxide (SO_2), and ammonia (NH_3) using Annular Denuder System (ADS) Acid gases and ammonia react to form ammonium aerosols. Nitrogen oxides are emitted by vehicles, combustion sources and industrial processes, and react in the atmosphere to form nitric acid, one of the acid gases measured.
- Aerosol species: chloride (Cl^-), nitrate (NO_3^-), sulfate ($SO_4^=$), ammonium (NH_4^+) using the Annular Denuder System (ADS)
- Aerosols measured at Eastern Farm consist primarily of ammonium sulfate, with a small contribution from ammonium nitrate and ammonium chloride.
- Meteorological measurements are also made at Eastern Farm for modeling and data analysis efforts.

Table 2 summarizes gas and aerosol concentrations measured at Eastern Farm from September 1997 through December 1997. DAQ is continuing to collect and process additional sample data. Typical rural air concentrations are in the low parts per billion range for hydrogen chloride (Okita et al., 1974); <0.1-1.5 g/m^3 for nitrous acid (Platt and Perner, 1980); 1-2 g/m^3 for nitric acid (Cadle et al., 1982); 1-50 g/m^3 for sulfur dioxide and fine particle sulfate (Mueller et al., 1980); and 2.5 g/m^3 and 3.5 g/m^3 for ammonia and fine particle ammonium, respectively (Warneck, 1988).

Table 2: *Summary statistics of gas and fine aerosol species concentrations ($\mu g/m^3$) at Eastern Farm [ppb concentrations of gases given in brackets]*

	HCl	HONO	HNO_3	SO_2	NH_3	Cl^-	NO_3^-	$SO_4^=$	NH_4^+
Mean	0.743	0.255	0.154	2.986	10.48	0.321	0.548	3.247	1.102
	[0.50]	[0.13]	[0.06]	[1.14]	[15.1]				
Median	0.637	0.226	0.154	1.644	4.722	0.238	0.379	2.458	0.857
	[0.43]	[0.12]	[0.06]	[0.63]	[6.8]				
Std. dev.	0.413	0.142	0.008	3.902	14.75	0.327	0.516	4.609	1.464
	[0.28]	[0.07]	[0.003]	[1.49]	[21.2]				
Min	0.321	0.142	0.145	0.199	0.337	0.139	0.147	0.331	0.036
	[0.22]	[0.07]	[0.06]	[0.08]	[0.48]				
Max	3.513	1.176	0.164	41.76	106.2	2.556	3.472	48.47	14.58
	[2.36]	[0.61]	[0.06]	[15.9]	[153]				
Typical	~1	0.1-1.5	1-2	1-50	2.5	--	--	1-50	3.5
	[~0.7]	[0.05-0.8]	[0.4-0.8]	[0.4-19]	[3.6]				

- Continuous ammonia measurements have been made at Eastern Farm, starting May 1998. This effort was delayed by equipment problems. The first continuous ammonia monitoring system was purchased in August 1996. Since an existing nitrogen oxide analyzer was available that the manufacturer assured DAQ could be modified to measure ammonia, DAQ purchased the modification needed to convert and measure ammonia. The modified system was not useful for low concentration measurements. The converters were suitable for higher concentration measurements and were used by one researcher in emission measurements, but could not be used for ambient concentration measurements. Two new ammonia analyzers were purchased and were received and made operational in May 1998. These analyzers were very sensitive and would properly measure low concentrations of ammonia in the atmosphere. The analyzers were installed at two sites at the Eastern Farm. The North Farm site was located near the northeast corner of the waste lagoon, and the South Farm site was located near the entrance at the southern end of the farm. Concentrations measured at both sites exceeded the concentration range of the analyzers and the analyzers were reset and recalibrated to the next higher range. Concentrations at the most distant site were within the new range of the analyzer, but concentrations at the closest site to the lagoon were still above the measurement range of the analyzer. The closest site to the lagoon had to be reset and recalibrated to a higher range. New, higher concentration calibration gas was required to make this change. The new calibration gas was received and the monitor in the site closest to the lagoon was calibrated in the new higher range in early September 1998. Both analyzers at the Eastern Farm sites are expected to operate for at least one year to provide concentration measurements for all seasons of the year. Table 3 summarizes data collected by the continuous analyzers from mid-May 1998 through December 1998.

Table 3: Summary data for continuous ammonia measurements (ppb)

	North Farm	*South Farm*	*Both sites*
Max	1193	500*	1193
Min	<1	<1	<1
Mean	105	23	63
Median	35	14	18

*Max value of 500 includes momentary readings above the instrument's measurement range

3.1.2 Regional Ambient Measurements

Lenoir Community College (LCC) in Kinston was chosen as a site generally representative of the region. An annular denuder system, like those installed at Eastern Farm, was deployed to measure gas and aerosol concentrations. Table 4 summarizes gas and aerosol concentrations measured at Lenoir Community College from September 1997 through December 1997.

Table 4: Summary statistics of gas and fine aerosol species concentrations ($\mu g/m^3$) at LCC

[ppb concentrations of gases given in brackets]

	HCl	HONO	HNO_3	SO_2	NH_3	Cl^-	NO_3^-	$SO_4^=$	NH_4^+
Mean	1.09	0.23	0.35	3.99	3.95	0.23	0.46	4.25	1.09
	[0.73]	[0.12]	[0.14]	[1.52]	[5.68]				
Median	0.92	0.18	0.25	1.55	3.04	0.23	0.32	3.22	0.89
	[0.62]	[0.09]	[0.1]	[0.59]	[4.37]				
Std. dev.	0.51	0.11	0.28	8.36	3.10	0.07	0.36	3.72	0.93
	[0.34]	[0.06]	[0.11]	[3.19]	[4.46]				
Min	0.47	0.14	0.17	0.22	0.66	0.14	0.17	0.15	0.03
	[0.32]	[0.07]	[0.07]	[0.08]	[0.95]				
Max	3.44	0.51	0.99	63.24	15.35	0.41	1.28	23.89	6.07
	[2.31]	[0.27]	[0.38]	[24.2]	[22.1]				

3.1.3 Plans for an Expanded Sampling / Measurement Network

Ammonia nitrogen exists in two forms in the atmosphere: gaseous ammonia (NH_3) and in particulate form as ammonium (NH_4^+) aerosols. The distribution between the two forms dictates the fate and transport of the ammonia nitrogen as it moves away from a given source. Annular denuder system (ADS) technology allows scientists to determine the concentrations of both forms in the atmosphere at the same time. Plans are underway to expand the current network of ADS sampling. This expanded network will provide speciated gas and aerosol data needed for modeling efforts being conducted by U.S. EPA and NOAA.

Since the project's inception, staff from DAQ, NCSU and USDA-ARS have collaborated on measurements using annular denuder systems (ADS). This combination of resources is the most effective way to address the issue of making sustained ADS measurements necessary for the success of this project. Currently, DAQ and NCSU have ADS samplers deployed at a commercial hog farm in Sampson County, the NC Agricultural Research Service Clinton Horticultural Research Station, and Lenoir Community College in Kinston. Preliminary feedback from modeling efforts by U.S. EPA and NOAA suggest that the monitoring effort should be expanded and moved further away from the high density of animal production facilities in Sampson and Duplin counties. Based on this need, Hans Paerl of the UNC Institute of Marine Sciences (IMS) at Morehead City joined this project in October 1998. Plans involving UNC-IMS involve two more samplers: one at Open Grounds Farm in Carteret County and one at Morehead City. This expanded network will provide a regional estimate of speciated gas and aerosol data. These observations will help to close the gap between modeling and field research by helping to calibrate and evaluate model projections.

3.2 Source Strength Measurements and System Characterization

3.2.1 Development of a GIS-Based Nitrogen Budget for the State of North Carolina and Associated Coastal Plain River Basins (W. Robarge, NCSU-Soil Science)

Sources of nutrients (specifically nitrogen) within the state's river basins are many and varied and include agricultural, industrial, urban, and natural sources. Long range transport of atmospheric nitrogen (N) species (acidic wet and dry deposition) is another source of N input into the state's river basins. Efforts to reduce N inputs into the state's river ecosystems must, therefore, take into account the N balance of the entire ecosystem and not just selected components. The overall objective of this project is to develop a nitrogen budget for the state of North Carolina and for the major river basins located primarily within the Coastal Plain. This document is an interim assessment of the current state of the project, and a first evaluation of the data sets available from academic, state and federal agencies that are being used to construct the budgets.

Like the financial budget employed in most households, a N budget is an accounting of the inputs and outputs of N for a given system, where a system is defined as a set of objects (or components) united by some form of interaction or interdependence. This definition places no restrictions on the scale of the system to be studied. Expressed mathematically, the N budget for a system can be written as:

$$I_{(t)} = U_{system(t)} + L_{(t)}$$

where $I_{(t)}$ is the input and $L_{(t)}$ is the output of N for a given time period (t), and $U_{system(t)}$ is the change in the N content of the system for this same time interval. It is possible for individual systems to be part of larger systems. Under these circumstances, the larger system is said to be composed of subsystems. In this project, the various subsystems identified for construction of the N budgets are: atmosphere (wet and dry deposition); point sources (industrial, internal combustion engines, municipalities); forests; agriculture (row crop and animal production); septic systems; groundwater; and river and streams.

Estimates of wet deposition of N across the state and within individual river basins can be obtained from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). A detailed analysis of this database for two years (1989 and 1994) was performed as part of another study (see abstract entitled "Estimation of Atmospheric Deposition of Ammonium and Nitrate in North Carolina and Coastal Plain River Basins", E. Cowling, C. Furiness, L. Smith and M. Henderson). The results of this analysis are being incorporated into this project. For example, in 1994, approximately 9,790 tons of N was deposited via wet deposition to the total cultivated land area in the state. Currently lacking in support of this project, however, is an accurate assessment of the dry deposition of N across the state. Some information concerning dry deposition can be obtained from the National Dry Deposition Network, but this database is very limited and is still open to question concerning the accuracy of the methodology being used. Estimates of dry deposition will be obtained from a modified version of the U.S. EPA Regional Acid Deposition Model (RADM), but these data are currently not available. Since dry deposition is dependent in part on canopy structure, land cover data have been obtained from the Center for Geographic Information and Analysis, Office of State Planning, for the purpose of determining the distribution of land cover type across the state and within its major river basins. This information will be used to assess the accuracy of dry deposition estimates generated using the modified RADM model.

Various databases are being used to estimate N emissions from point sources within the state. As an example, estimated atmospheric emissions of nitrogen for 1996 are shown in Table 5. Also shown for comparison purposes are estimated emissions of ammonia-N from animal production systems within the state. The data demonstrate that in North Carolina a substantial amount of N is emitted into the atmosphere: approximately 325,000 tons of N per year. However, this estimate is based on a number of assumptions as essentially none of the databases used in generating the data in Table 1 are designed specifically for the purposes of constructing a N budget. These values represent extrapolations based on best-available data, and/or on reported emission factors. The applicability of emission factors selected by the U.S. EPA for animal production systems has been questioned for animal production systems in North Carolina (Aneja et al., 1997).

Measurements of ammonia emissions from a swine lagoon in Sampson County, when extrapolated to the state's current swine population (approximately 10 million), suggest total yearly emissions of ammonia from swine effluent lagoons between 9,000 tons N per year and 63,000 tons N per year. The total swine ammonia emissions suggested by the EPA's recommended factor (Battye et al., 1994) is approximately 77,700 tons N per year from all phases of swine production.

Table 5: Estimated emissions of nitrogen as oxides, ammonia, and percent total nitrogen across the physiographic regions of North Carolina. Year = 1996.

Type and source of emissions	*Mountain Districts*	*Piedmont Districts*	*Coastal Districts*	*State total*	*Fraction of total fixed N*
	----(Tons of nitrogen emitted per year x 1000)----				(%)
<u>Oxides of nitrogen from:</u>					
Motor vehicles	9.4	35.7	17.4	62.5	19.2
Industrial sources	6.8	71.4	13.5	91.8	28.2
Area sources	4.4	19.7	14.4	38.6	11.9
Total NO_x	20.6	126.8	45.3	192.9	59.3
<u>Ammonia from:</u>					
Swine	0.2	3.5	74.0	77.7	23.9
Cattle	7.0	13.5	4.2	24.7	7.6
Poultry	2.6	10.7	16.6	29.9	9.2
Total NH_3	9.8	27.7	94.8	132.3	40.7
Total N	30.4	154.5	140.0	325.2	100.0

Total forested area in the state is estimated to be 19,996,477 acres (8,092,463 ha), which means that on average, 60% of the state's land area is covered by trees. In certain river basins, the forested area is over 80% of the land area. In this study, forested area has been divided into standing forest and clear-cut areas. In 1995, approximately 2% (352,000 acres) of the forested area was designated as clear-cut (NCCGIA, 1998). Nitrogen input into the remaining standing forest is estimated to be 339,600 tons of N from mineralization, wet deposition, fertilization and retranslocation. Nitrogen input into clear-cut areas is estimated to be 20,000 tons of N from mineralization and wet deposition (NCCGIA, 1998; NADP, 1996). Mineralization of N from the forest floor is considered to be an input in this study as it represents release of N into the N cycle of a forest ecosystem. This N can either be incorporated into the forest stand itself (conserved) or lost via leaching or surface runoff. The above estimate does not account for dry deposition of N to the forest canopy. The combined estimate of 359,600 tons of N entering the N cycle within the state's forested area is comparable to the estimate of atmospheric N emissions listed in Table 5.

Total cultivated area in the state is estimated to be 4,845,235 acres (1,960,840 ha), excluding certain crops for which there is a lack of adequate information. The percent of land area designated as cultivated varies from 2% to 34.5 % for all of the state's river basins. For the Coastal Plain river basins, the area designated as cultivated varies from 12% to 26%. Commercial N fertilizer input to cultivated area is estimated to be 146,240 tons of N. Biological N fixation associated with production of soybean and peanut crops contributes another 66,190 tons of N. Mineralization is calculated to be 133,240 tons of N. Taken together, these three sources (commercial fertilizer, biological N fixation, and soil organic matter mineralization) amount to 345,670 tons of N introduced yearly into the N cycle of the state's cultivated acreage. This number is probably substantially underestimated due to uncertainties in the reported acreage for many crops and in the actual N application rates being used by farmers. Also, accurate estimates of N inputs from land disposal of animal wastes currently are not available and are being generated as part of this project.

Databases to allow calculation of N inputs into septic systems, groundwater, and rivers and streams are still being developed. Once completed, an estimate of N input into the state and the major Coastal Plain river basins will be possible. Attention will then be directed to quantification of the internal N cycles within each of the identified subsystems, and generation of suitable estimates of N outputs from each subsystem. This later step will be done in close cooperation with modeling efforts by the Division of Air Quality and the Division of Water Quality, NC DENR, the U.S. EPA and NOAA, and other academic and private institutions. The primary vehicle that will be used in developing the N budgets will be a Geographical Information System (GIS). Visual display of the information concerning the identified subsystems and projected N budgets provides an effective means of presentation of potential problems or concepts related to N management on a regional scale. Availability of this information via an electronic format on the World Wide Web (WWW) is also being planned for to make the data readily available to all interested parties.

3.2.2 Climatology of Synoptic-Scale Weather Systems for Eastern North Carolina (Desimone, et al., 1998), NCSU

Local and long-range transported nitrogen compounds are considered part of the cause of increased algae growth in the Neuse River Basin. Synoptic-scale meteorological conditions are important in understanding the factors that lead to the atmospheric transformation, transport and deposition of these compounds. Therefore, a climatology of synoptic-scale meteorological conditions typical to eastern North Carolina was performed. Over 3650 Daily Weather Maps from 1986 to 1995 were analyzed for this study.

An approaching cold front is the most predominant synoptic-scale weather system typical to eastern North Carolina. This is found to be true whether the yearly, monthly, or seasonal summaries are analyzed. High-pressure systems occur most frequently to the north, northwest and over eastern North Carolina. These high-pressure systems bring in northerly and northeasterly winds. Low-pressure systems are more commonly positioned to the northeast and southwest. Of the frontal systems, stationary fronts and cold fronts have the greatest impact on eastern North Carolina. These systems occur in the top 50% during almost all months with the exceptions being stationary fronts to the south in

December and July, and cold fronts over eastern North Carolina in January. Hurricanes and tropical storms occur most frequently in the summer and fall, but because they are seasonal weather systems, they have a small percent contribution.

3.2.3 Source Strength Measurements

3.2.3.1 Characterization of Ammonia Emissions from Swine Lagoons Using a Dynamic Flow-Through Chamber (Aneja et al., 1999), NCSU

Fluxes of ammonia-nitrogen (NH_3-N, where NH_3-N = (14/17)NH_3) from an anaerobic 2.7 hectare commercial hog waste storage lagoon were measured during the summer of 1997 through the spring of 1998 in order to study the seasonal variability in the emissions of NH_3-N and their relationship to physicochemical properties. Ammonia-nitrogen fluxes were measured during each season (summer, fall, winter, and spring) using the dynamic flow-through chamber system. Additional measured physicochemical lagoon parameters included lagoon temperature, lagoon pH and Total Kjeldahl Nitrogen (TKN). The pH and TKN of the surface lagoon water ranged from 7 to 8 pH units and 500 to 750 mg L^{-1}, respectively. The greatest NH_3-N flux observed occurred during the summer (August 1997) (average NH_3-N flux = 4017 ± 987 g N m^{-2} min^{-1}). NH_3-N flux decreased through the fall (December 1997) months (844 ± 401 g N m^{-1} min^{-1}) to a minimum flux in the winter (February 1998) months (305 ± 154 g N m^{-2} min^{-1}). NH_3-N flux from the lagoon increased in the spring (May 1998) (1706 ± 552 g N m^{-2} min^{-1}), however, it was not as high as during the summer months. Lagoon NH_3-N flux is highly correlated with the lagoon surface water temperature throughout the year.

3.2.3.2 USDA-ARS Evaluation of Ammonia Emissions (Harper and Sharpe, 1998), USDA-ARS

High animal concentration provides increased production efficiency, improved production economics, and a better industry support system. However, it also presents a challenge to manage wastes to minimize ammonia losses that have potential short and long-term effects on the surrounding environment. The purpose of these studies was to determine accurate emission factors appropriate for the regional climate, geography, and production systems. Micrometeorological instrumentation and gas sensors were placed over two lagoons to obtain information for determining ammonia emissions over extended periods and without interfering with the surrounding climate. Ammonia emissions varied diurnally and seasonally and were related to lagoon ammonium concentration, acidity, temperature, and wind turbulence. A statistical model was developed from data from three lagoons in the Coastal Plains of North Carolina and Georgia. The model explained 78% of the variability in emissions. Emission factors on two lagoons in North Carolina were compared based on animal numbers and showed that a highly concentrated lagoon, although three times more concentrated, serving three times as many animals, and having twice the total emissions, had a per-animal lagoon emission factor of 60% that of a [less] concentrated lagoon. These comparisons exemplify the danger of basing emissions on animal numbers. A suggested emission factor based on the steady-state live animal weight showed similar emission factors for all lagoons measured in both states. [Production of N_2] was measured in all lagoons with higher rates of [N_2 production] in more concentrated lagoons than in lower-concentration lagoons.

3.2.3.3 Site Characterization Using Open-path Fourier Transform Infrared (OP-FTIR) Spectroscopy (Todd, 1999), UNC-CH

The research performed by the team at the University of North Carolina used a relatively new technology, open-path Fourier Transform (OP-FTIR) spectroscopy combined with computed tomography (CAT), to measure ammonia emissions from a waste lagoon of an intensive swine facility. Computed tomography is best known for its use in medicine where cross-sections of the human body are reconstructed from a large number of X-ray attenuation measurements through the section of the body of interest. When computed tomography is applied to the environment, instead of shooting radiation at many angles through a body to view organs, we are shooting a network of infrared optical beams through air at many angles to reconstruct chemical concentrations and plume shapes.

A single OP-FTIR spectrometer uses a remotely placed retro-reflector to reflect an infrared beam across a distance that can exceed 100 meters to a detector. As the OP-FTIR spectrometer scans the area, it measures the amount of light absorbed by air contaminants at specific wavelengths; concentrations are then integrated over the entire length of the optical path. These instruments can simultaneously measure a wide variety of compounds, non-invasively, in real-time, over large areas at low limits of detection. Thus, cost effective measurements may be obtained for multiple pollutants present in animal waste. While a single OP-FTIR spectrometer can detect multiple chemicals simultaneously, it provides only an average concentration across the space that the open-path beam traverses. Therefore, to measure emissions over a wide area and characterize plumes, a single open-path beam is not sufficient, and multiple OP-FTIR beams must be used.

Using an environmental CAT scanning system, rotating spectrometers sequentially scan the air at a specific height through an area such as a lagoon, creating a network of intersecting open-path beams; each real-time measurement provides a path-integrated (average) concentration, not a point sample. A tomographic reconstruction algorithm is then applied to these measurements to reconstruct two-dimensional, spatially and temporally resolved chemical concentration maps of an area in near real-time. Each map provides a snapshot, which represents a short of time period (minutes), of the concentration and location of multiple chemicals in air. The maps are then linked together to enable visualization of the flow of contaminants over space and time.

For this study, two scanning OP-FTIR spectrometers (MIDAC Corp., Irvine CA) and twelve retroreflectors were placed on the periphery of a swine waste lagoon at [the Eastern Farm site]. The instruments were placed within a meter of the surface of the lagoon and a horizontal slice of ammonia (15 open-path measurements) was measured every two minutes. A tracer gas was released from the surface of the center of the lagoon (neutrally buoyant sulfur hexafluoride) at a known emission rate, and the concentrations of both ammonia and the tracer were measured simultaneously. Using the concentration and emission rate of the tracer gas, the emission rate of ammonia was calculated.

The study was conducted in August 1997, November 1997, and May, 1998. The average concentrations of ammonia measured across the lagoon in November, and May were 0.2 and 0.7 ppm, respectively. The average and range of emission rates during the day in May were 5800 g m^{-2} min^{-1} (3036 - 8165) and in November 1997 were 1813 g m^{-2} min^{-1} (472 - 3800). These values are for times between 8 am and 6 pm. Average fluxes in the evening in May (until 1 am) were 7069 g m^{-2} min^{-1} (4241 - 9708). The average flux of nitrogen in May was found to be 6666 μg N m^{-2} min^{-1}.

The study initially encountered instrument problems in the field in August. At that time, for security reasons, the equipment had to be installed each morning and removed each evening. By May, setup was reduced to a single day and the equipment ran with little supervision. Currently, the tomographic concentration maps are being combined with meteorological measurements to determine the ability of eliminating the need for the tracer gas when calculating emission rates. If successful, this would make emission rates available for many days and time periods when the tracer gas was not released for this study. One of the powerful results of this study is a set of videos of linked two dimensional maps of ammonia over the lagoon. They reveal the fluctuation in both time and space of ammonia over the surface of the lagoon. Given that this system was successfully used for path lengths of up to 300 meters, it could possibly be used on smaller lagoons and across the face of the houses to determine emission rates.

3.2.3.4 USEPA Evaluation of Ammonia Emissions (Harris and Thompson, 1998)

Historically, the primary methods available for determining emissions from large area sources were point-sampling techniques employing flux chambers or evacuated canisters followed by analysis of the appropriate gas samples. These techniques can produce accurate results when conducted within a statistical framework and when an iterative approach to sampling is adopted. However, point-sampling techniques are expensive, time consuming, and open to the risks of missing significant emissions from a non-homogeneous source. Remote sensing techniques are now available for quantifying emissions from large, heterogeneous area sources, such as municipal wastewater treatment facilities, waste lagoons, and surface coal mines. These techniques produce a path-integrated concentration, typically reported in units of parts per million-meter (ppm-m), of the species of interest, eliminating concern over source heterogeneity.

Open-path Fourier transform infrared (OP/FTIR) spectroscopy is one of the remote sensing techniques which, within the last decade, has received wide attention. Extensive development and optimization work of a mobile OP/FTIR system for analyzing emissions from area sources was performed in the early 1990's. Results of these efforts and subsequent evaluation have been published extensively and include such applications as on-site pollution analysis (Spartz, et al., 1990). The validation included a comparison to evacuated canister samples. The data presented are from the initial phase of a study to extend the application of the plane-integrated method to agricultural sources of fine particulate precursors. All of the information was gathered with the classical single-beam approach to develop a baseline to which the performance of the plane-integrated technique can be compared.

Very limited data exist in the literature for emissions from swine finishing barns. Van Der Hoek (1998) presents an emission factor used by the European Community (EC) as 2.89 kg/hog/yr (7.9 g/animal/day). Extending our data to a similar yearly value by averaging the seasonal data suggests an emission factor of 3.69 kg/hog/yr with an individual seasonal range of 2.74 – 4.75 kg/animal/yr. A difference of less than 25% is noted between the EC's emission factor and ours.

These estimates may present an upper bound to the emission factor. The data have been collected during daylight, and one would expect that waste production would be reduced at night, so the integrated daily emission factor should be less. Additionally, the exhausts of the farrowing barns are about 10 m from the end of the finishing barns, and it is possible that some of these plumes could be captured by the inlets to the finishing barns even when the wind is from the east and provides a significant background. These data are taken from only one farm, and a broader scope of sites would be useful to improve confidence in the emission factor representing an industry.

The much higher path average concentrations noted when the westerly winds bring the plume from the nursery and farrowing barns through the path suggests that these sources need to be examined. Van Der Hoek (1998) used an emission factor three times higher for sows in these facilities, which reinforces this need. We plan to add a measurement path between the farrowing and finishing barns to develop a separate emission factor for these barns.

The impact of the barns locally and regionally may be affected by the thermal buoyancy of their plumes. With a 15-20ºC differential between the barn plume and the ambient winter temperature, a condensation-defined plume could be visibly traced rising quickly above the 20-30 meter tree canopy and, thus, moving off-site. In the summer, we measured path average concentration reductions of less than 30% at the base of the lagoon berm, indicating little plume rise when no temperature difference existed between the barns and the ambient. One would expect that ecological interactions on or near the farm site would be more likely because the plume remains near the ground.

3.2.4 Deposition Studies

3.2.4.1 Denitrification of Ammonia from Applied Swine Waste Effluent (Whalen, 1999), UNC-CH

Contemporary agriculture is characterized by the intensive production of livestock in confined facilities and land-application of stored waste as an organic fertilizer. Emission of nitrous oxide (N_2O) from receiving soils is an important, but poorly constrained term in the atmospheric N_2O budget. In particular, there are few data for N_2O emissions from spray fields associated with industrial-scale swine production facilities that have rapidly expanded in the southeastern United States. In an intensive, 24-day investigation over three spray cycles, we followed the time course for changes in N_2O emission and soil physicochemical variables in an agricultural field irrigated with liquid lagoonal swine effluent. The total-N of the liquid waste was almost entirely ammonia nitrogen (NH_4^+-N) (>90%) and thus had a low mineralization potential. Soil profiles for nitrification and denitrification indicated that >90% of potential activity was localized in the surface 20 cm. Application of this liquid fertilizer to warm (19 to 28°C) soils in a form that is both readily volatilized and immediately utilizable by the endogenous N-cycling microbial resulted in a sharp decline in soil NH_4^+-N and supported a rapid and short-lived (days) burst of nitrification, denitrification and N_2O emission. Nitrous oxide fluxes as high as 9200 g N $_2$O-N g_{dw} soil^{-1} h^{-1} (micrograms of nitrogen per gram of dry soil per hour) were observed shortly after fertilization, but emissions decreased to pre-fertilization levels within a few days. Poor correlation exists between N_2O efflux and soil physicochemical variables (temperature, moisture, NO_3-N, NH_4^+-N) and fertilizer loading rate point to the complexity of interacting factors affecting N_2O production and emission. The fractional loss of applied N to N_2O was 1.4%, in agreement with the mean of 1.25% reported for synthetic fertilizers. The direct effects of fertilizer application appear to be more immediate and short-lived for liquid swine waste than for manure and slurries that have a slower release of nitrogenous nutrients.

3.2.4.2 Quantification of Atmospheric Nitrogen Deposition in the Vicinity of a Large Scale Swine Production Facility Located in the Neuse River Basin Using Throughfall Measurements (Robarge and Cure, 1998), NCSU/DAQ

Most swine producers currently located in eastern North Carolina have adopted a confinement livestock production scheme as the management technique of choice. In most cases, this management approach results in the concentration of animal wastes in lagoons located immediately adjacent to the animal production houses. Much attention has been focused on the fate of nitrogen containing compounds exported from these waste lagoons in an aqueous form, either when sprayed onto cropland, or through direct spillage from the lagoon into nearby streams or wetlands. Less attention has been focused on the fate of nitrogen exported from lagoons and the animal production houses through volatilization, primarily as ammonia. Ammonia can remain in the atmosphere in the gaseous state as an NH_3 molecule, or it can react with other atmospheric constituents to form fine aerosols such as carbonates, nitrates and sulfates. It deposits to the earth's surface as wet deposition (primarily rainfall) and dry deposition. Historical records are available (National Acid Deposition Program) to discern trends in wet deposition of ammonium nitrogen (NH_4-N) in rainfall. No such records exist for dry deposition of ammonia of ammonium-containing aerosols. The specific objectives of this study were to use bulk deposition and throughfall collectors in forest canopies as follows:

- Measure atmospheric nitrogen deposition in the immediate vicinity of a large scale swine production facility (Eastern Farm site) located in the Neuse River Basin, using throughfall measurements;
- Monitor atmospheric nitrogen deposition in the immediate vicinity (5 km) of a large scale swine production facilities located in the Neuse River Basin and other portions of eastern North Carolina, using throughfall measurements.

Results presented in this report demonstrate that ammonia (NH_3) emissions from swine production facilities can significantly enhance dry deposition of NH_4-N to adjacent forest canopies. At the Eastern Farm site, NH_4-N dry deposition was approximately two times

(10.2 kg N/ha) that from wet deposition during the collection period of August 6, 1997 to April 16, 1998. Total NH_4-N deposition to the forest floor (from both wet and dry deposition) was 14.5 kg N/ha. The dry deposition of NH_4-N observed at the Eastern Farm site also enhanced the apparent dry deposition of chloride (Cl^-) (9.2 kg Cl^-/ha and sulfate ($SO_4^=$) (17.1 kg $SO_4^=$/ha), and perhaps nitrate nitrogen (NO_3-N) (2.7 kg N/ha). This occurred either through the formation of ammonium aerosols formed in the atmosphere and deposited as ammonium nitrate (NH_4NO_3), ammonium chloride (NH_4Cl), ammonium bisulfate (NH_4HSO_4) or ammonium sulfate ($(NH_4)_2SO_4$), or after dry deposition of NH_3 to the forest canopy. This deposition in turn enhances the dry deposition of nitric acid (HNO_3), hydrogen chloride (HCl) and sulfur dioxide (SO_2). These results suggest that enhanced dry deposition of NH_4-N to forest canopies in the vicinity of large-scale animal production facilities in eastern North Carolina should be accompanied by enhanced dry deposition of Cl^- and $SO_4^=$, and possibly NO_3-N.

Measurable amounts of dry deposition of NH_4-N were recorded for deciduous forest canopies within 3 km of large commercial animal production facilities along a NE-SW transect extending from Goldsboro, NC to the Bladen State Forest during the collection period August 6, 1997 to April 16, 1998. Enhanced dry deposition of Cl^- and $SO_4^=$ were also recorded for these canopies, as compared to deciduous forest canopies > 5 km away from large commercial animal production systems. Total N loading to the forest floor from wet and dry deposition (NH_4-N plus NO_3-N) ranged between 7.2 and 13.1 kg N/ha for deciduous forest canopies within 3 km of animal production facilities, versus values of 3.8 to 5.2 kg N/ha for deciduous forest canopies > 5 km from such facilities. Bulk deposition of NH_4-N measured along this NE-SW transect through a region with a high density of animal production systems appears to increase moving from SW to NE. This is consistent with the hypothesis that ammonia emissions from the high density of animal production systems in this region of North Carolina have increased the concentration of NH_4-N in rainwater.

This limited study has demonstrated that use of bulk deposition and throughfall collectors provides one means to assess the potential enhanced dry deposition of NH_4-N in eastern North Carolina due to the presence of a high density of animal production facilities. However, lack of an established historical database regarding dry deposition of NH_4-N to forest canopies in eastern North Carolina requires that a proper experimental design be employed to allow accurate interpretation of the trends in deposition data. Future studies employing bulk deposition and throughfall collectors to assess dry deposition in eastern North Carolina should:

- Sample a variety of forest canopies (especially those dominated by conifers);
- Include a sufficient number of sites properly spaced to along a transect to discern possible spatial trends in deposition;
- Include possible 'control' sites to provide some estimate of background levels of dry deposition of NH_4-N and other atmospheric species known to be present in the atmosphere due to other emissions sources;
- Include estimates of the atmospheric concentration of ammonia and ammonium aerosols to better assess the potential for canopy uptake of ammonia that cannot be estimated by using throughfall collectors;
- Include at least two years of continuous observations to properly document seasonal variations in deposition;
- Follow recommended statistical designs for number and placement of bulk deposition and throughfall collectors to provide proper confidence levels for the calculated estimates of NH4-N dry deposition.

3.2.4.3 Analysis of NADP Data

3.2.4.3.1 Estimation of Atmospheric Deposition of Ammonium and Nitrate in North Carolina and Coastal Plain River Basins (Cowling, et al., 1998)

This research project was undertaken as part of a larger research plan that was designed to assess the environmental impact of animal agriculture operations in the state of North Carolina. An important "driving force" behind the plan included efforts to answer the following questions:

- Has recently increased production of swine in North Carolina altered the nitrogen budget of the state?
- What is the geographical distribution of deposition of nutrient (ammonium and nitrate) nitrogen from the atmosphere in North Carolina, and has [it] changed in recent years?

To gain insight into these questions, we utilized three different sources of atmospheric deposition information:

- National Atmospheric Deposition Network (NADP) and Clean Air Status and Trends Network (CASTNet) data on amounts of ammonium ion (NH_4^+) and nitrate ion (NO_3^-) dissolved in precipitation and deposited as rain and snow (wet deposition);
- National Weather Service (NWS) data on amounts of precipitation;
- CASTNet estimates of amounts of dry deposition of ammonium ion (NH_4^+) and nitrate ion (NO_3^-) deposited in the form of atmospheric gases and particles.

Our approach was to integrate these data within a Geographic Information System (GIS)-based framework delineating the river sub-basins in North Carolina, utilizing interpolation techniques to produce estimates for a 5 km x 5 km grid. Our expected deliverable products were maps, tables, and statements of scientific findings about geographical differences and temporal changes in amounts of NH_4^+ and NO_3^- deposited in the various regions and river basins of NC.

Because of limitations of funding, our initial analyses were concentrated on only two specific years. For a “base year,” 1989 was selected since it was the last year before the rapid increase in swine populations in NC. For the period of population expansion, 1994 was chosen because it was the most recent year after the rapid increase in swine populations for which relatively complete atmospheric deposition data were readily available from the NWS, NADP, and CASTNet.

As discussed further below, the 1989 data exhibited some anomalous features, especially in the northern Piedmont region of NC. At the Finley Farm NADP site near Raleigh, 1989 was not only the year of highest amount of annual precipitation but <u>also</u> the year of highest annual NH_4^+ concentration in precipitation from 1979 to 1997. Thus, we examined and report here not only state-wide and river-basin-specific geographical distributions of NH_4^+ and NO_3^- in precipitation in 1989 and 1994, but also annual data for amounts of precipitation, and both concentration and deposition of NH_4^+ at two specific NADP sites—the Finley Farm (Piedmont) and Clinton Crops (coastal plain) NADP sites for all years from 1979-1997.

The evidence used in drawing conclusions from this research was developed by comparative analysis of the following data and information.

(Figures have been edited for grayscale copying; other figures not shown are available in the full report.)

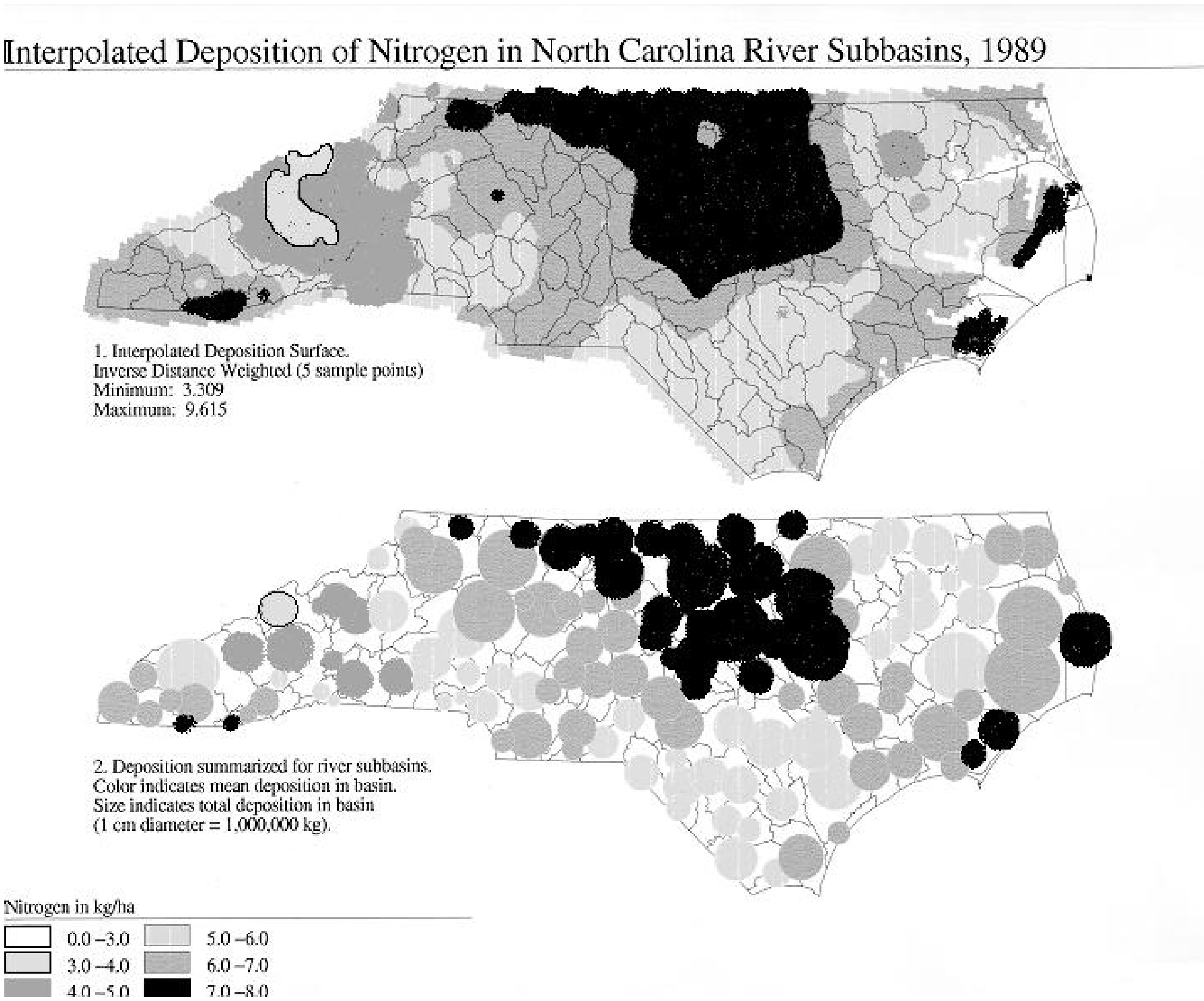
- Geographical distribution maps and summaries of wet deposition to river basins for 1989 and 1994: These show that:
  a) the total amount of nitrogen deposited as NH_4^+ plus NO_3^- across the state of NC was greater in 1989 than in 1994 (figures 2 and 3);
  b) the area of maximum nitrogen loading in 1989 was in the northern Piedmont (figure 2);
  c) the area of maximum nitrogen loading in 1994 was in the southeastern coastal plain (figure 3).

- The records of annual precipitation amount, NH_4^+ concentration, and wet deposition of NH_4^+ from 1979 through 1997: Though no statistical analysis of temporal trends was performed on these summary numbers, some general characteristics are evident in these time-series plots:
  a) variability from year to year was apparent in amount of precipitation, NH_4^+ concentration, and NH_4^+ deposition records at both the Finley Farm (Piedmont) and the Clinton Crops (coastal plain) NADP sites, but no appreciable long-term trend in amount of precipitation was evident at either site;
  b) distinct upward trends in both NH_4^+ concentration and NH_4^+ deposition were observed at the Clinton Crops (coastal plain) NADP site during the years after 1989 but not in the years before 1989 (figure 4) (Cornelius, 1997, Aneja et al., 1998). By contrast, only comparatively modest upward trends in NH_4^+ concentration and NH_4^+ deposition were evident at the Finley Farm (Piedmont) NADP site before or after 1989.

- Deposition difference maps for the nation as a whole: These maps show a noticeable increase in annual NH_4^+ wet deposition in the southeastern coastal plain of NC when average NH_4^+ deposition data for the years 1985-89 were compared to those for the years 1990-94 (figure 5); this increase in NH_4^+ deposition is also evident when data for the years 1995-97 were compared with those for the years 1985-89.

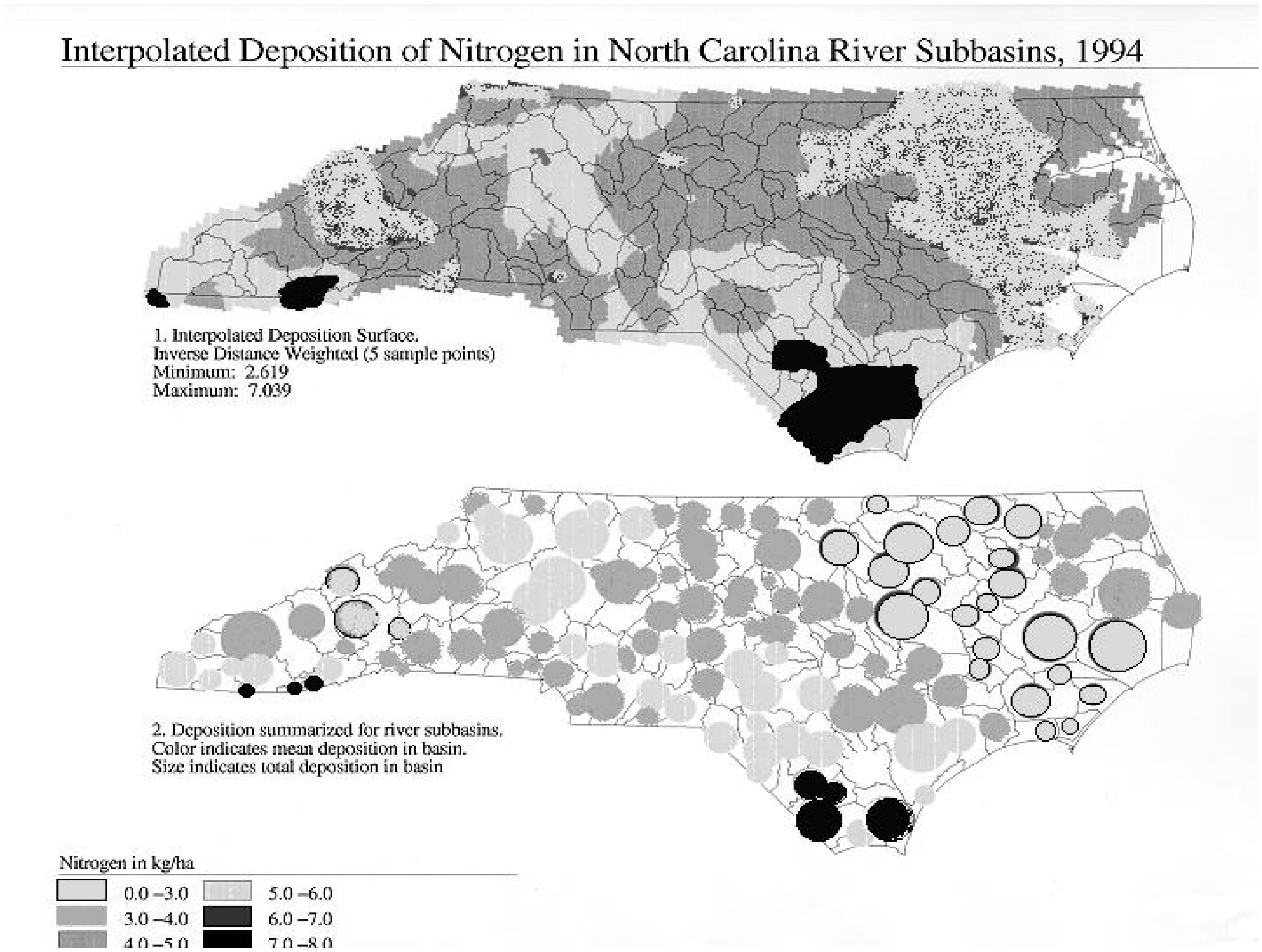
- Tabular and graphic display of amounts of NH_4^+, NO_3^-, and total N (NH_4^+ plus NO_3^-) deposited in wet form were prepared for the major river basins of the state: These data show that the various river basins of NC differ greatly from each other in terms of wet deposition of all three forms of biologically available nitrogen, both within each of the two years studied, and especially in comparing the nitrogen input in 1989 with that observed in 1994.
- The limited amount of wet and dry NH_4^+ and NO_3^- deposition information available for three CASTNet sites in NC and one CASTNet site in VA: These data indicate that wet deposition accounts for more than three fourths of the NH_4^+ deposition at mountain and piedmont locations of NC, about two-thirds to three fourths of the NO_3^- deposition in the far western mountains of NC, but only about half of the NO_3^- deposition in the northwestern mountains and piedmont parts of NC and the piedmont portion of VA.
- Temporal data of swine populations in NC: This graph shows a rapid rise in swine populations in NC beginning in 1988 and continuing through 1997.
- Geographical distribution maps for swine waste management systems in NC: This map shows that the area of the state with the highest concentration of confined feedlot waste management systems is in the southeastern coastal plain of NC.

Figure 2:



Interpolated Deposition of Nitrogen in North Carolina River Subbasins, 1989
1. Interpolated Deposition Surface.
Inverse Distance Weighted (5 sample points)
Minimum: 3.309
Maximum: 9.615
2. Deposition summarized for river subbasins.
Color indicates mean deposition in basin.
Size indicates total deposition in basin
(1 cm diameter = 1,000,000 kg).
Nitrogen in kg/ha
0.0 –3.0
3.0 –4.0
4.0 –5.0
5.0 –6.0
6.0 –7.0
7.0 –8.0

Figure 3:



Interpolated Deposition of Nitrogen in North Carolina River Subbasins, 1994
1. Interpolated Deposition Surface.
Inverse Distance Weighted (5 sample points)
Minimum: 2.619
Maximum: 7.039
2. Deposition summarized for river subbasins.
Color indicates mean deposition in basin.
Size indicates total deposition in basin
Nitrogen in kg/ha
0.0 – 3.0
3.0 – 4.0
5.0 – 6.0
6.0 – 7.0

Figure 4: Annual Wet Deposition of Ammonium, NC 35 Clinton Crops Research Station

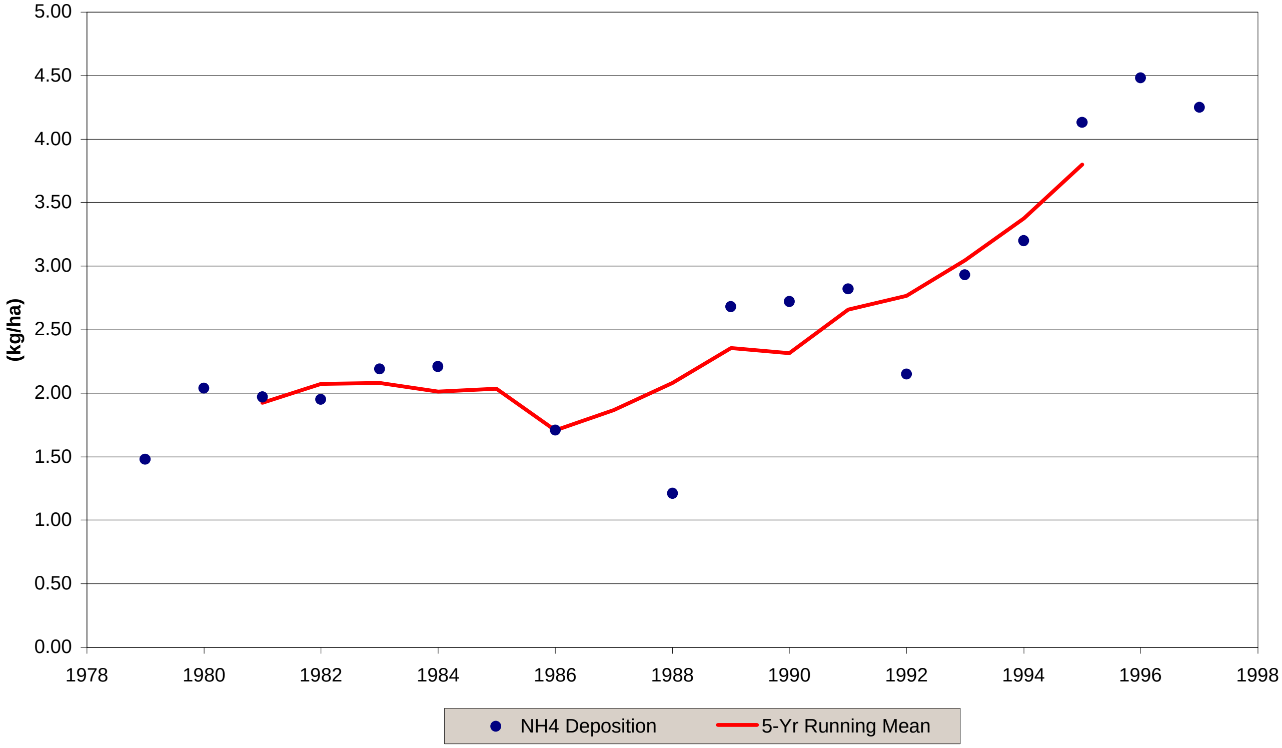
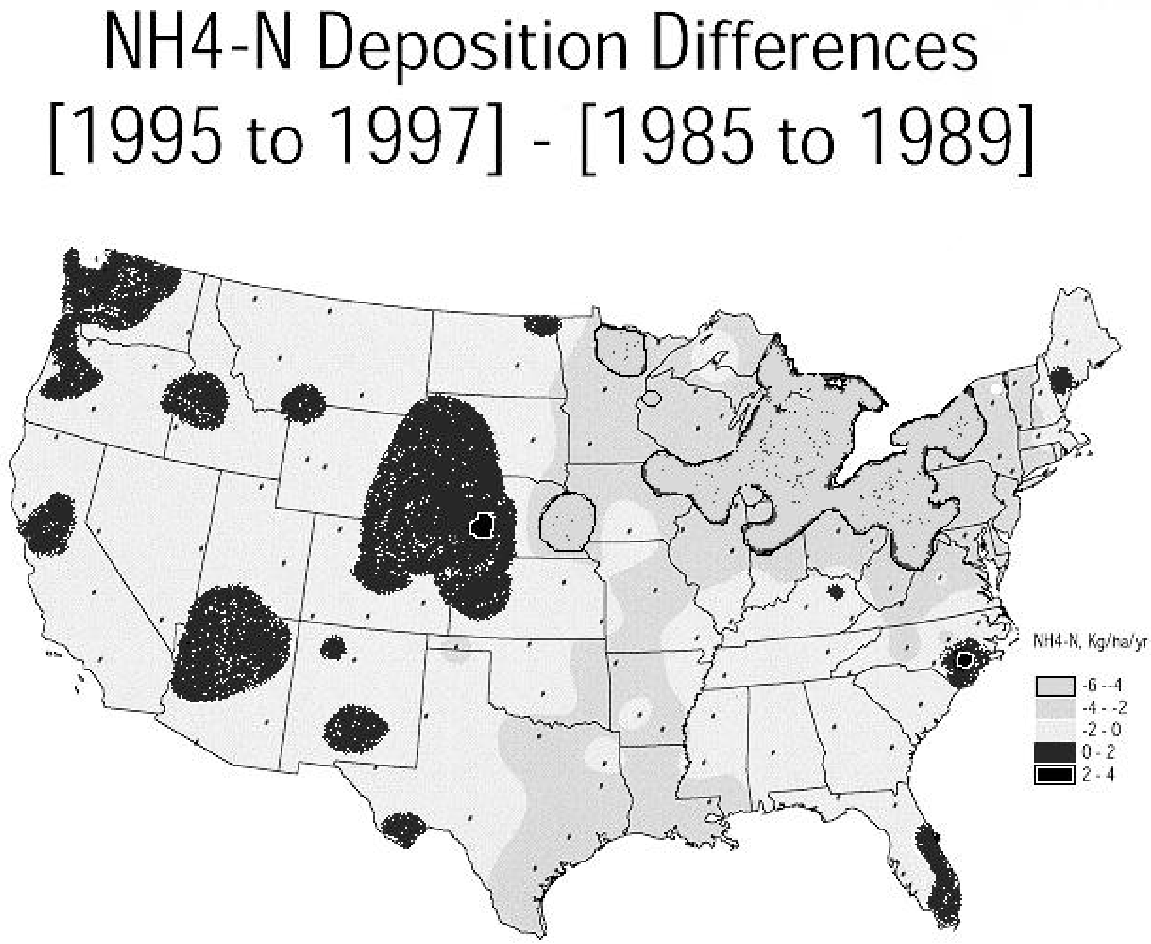


Figure 5:


NH4-N Deposition Differences
[1995 to 1997] - [1985 to 1989]
NH4-N, Kg/ha/yr
-6 - -4
-4 - -2
-2 - 0
0 - 2
2 - 4

From the analyses of the NWS, NADP, and CASTNet databases completed to date, it appears that a partial answer to the "driving force" questions listed in the first paragraph of this abstract is a qualified "yes;"—"qualified" because: a) a substantial part of the scientific evidence we have analyzed is consistent with the hypothesis that recently increased populations of swine in NC have contributed to an increased transfer of NH_4^+ from the atmosphere to the land and surface waters of the state, and b) a less substantial part of the evidence we have analyzed to date is not fully consistent with this hypothesis.

One of the objectives of this research was to strengthen the atmospheric deposition part of the Nitrogen Budget for the State of North Carolina and Associated Coastal Plain River Basins being developed by NCSU; thus, we provided refined estimates of nitrogen deposition in the GIS-based format. Results of this research can be used to put into context shorter-term deposition studies being conducted by other scientists in the larger research program of which this project is a part. Our research also provides monitored deposition values that can be used to compare against modeled values also being developed as part of the overall research plan.

The results of this initial study indicate that the NWS, NADP, and CASTNet databases and the statistical procedures used, have the potential to provide a still further improved understanding and more definitive answers to the "driving force" questions listed above. Further analyses of already existing atmospheric deposition databases also will provide a more fully integrated picture of the relationship between future changes in emissions, not only from animal agriculture, but from other sources of nitrogen emissions.

The first and most obvious further studies to be made should include the following:

a) utilizing data for all years;
b) checking the temporal and geographical representativeness of NADP and CASTNet sites;
c) conducting more detailed time-series analyses at all sites;

d) considering dry deposition more adequately, and

e) using nutrient deposition data as a critical test of emissions inventory methods.

3.2.4.3.2 Atmospheric Transport and Wet Deposition of Ammonium in North Carolina (Walker et al, 1999)

Analyses have been performed to investigate the wet deposition and transport of ammonium (NH_4^+) over North Carolina using precipitation chemistry data for six North Carolina National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites. The first analysis employs multiple linear regression to model the seasonality and trend in a 14 year record of monthly volume-weighted mean NH_4^+ concentrations in precipitation. Average observed concentrations ranged from 0.15 to 0.31 mg l^{-1}, with largest concentrations occurring at the suburban Wake County site (NC41) and the Sampson County site (NC35), which is located within a densely populated network of swine and poultry operations. Maximum concentrations occur during the summer at all sites. A significant ($p<0.01$) increasing trend in NH_4^+ concentration in precipitation, which corresponds to an average NH_4^+ wet deposition increase of 0.20 kg ha^{-1} y^{-1}, is observed at the Sampson County site (NC35) beginning in 1990. This trend is correlated with the increasing number of North Carolina swine operations since 1990 (Walker et al., 1999).

For the second analysis, an area of strong NH_3 emissions in the North Carolina Coastal Plain region is defined using livestock population densities (area I). A source-receptor relationship is developed to assess the influence of area I NH_3 emissions on NH_4^+ concentrations in precipitation at surrounding NADP/NTN sites. A linear regression model, which utilizes weekly concentration values in conjunction with boundary layer air mass back trajectories associated with precipitation events, is used to statistically test for this influence. Results indicate that area I NH_3 emissions increase NH_4^+ concentration in precipitation at sites up to 80 km away. This transport distance would allow for direct deposition of NH_4^+ transformed from NH_3 originating from area I to nitrogen sensitive coastal and estuarine ecosystems in the North Carolina coastal Plain region. For weeks during which at least 25% of all back trajectories were considered influenced by area I, average concentrations at the Wake County site (NC41) and the Scotland County site (NC36) are found to be 50% and 44% higher than other weeks, respectively.

3.3 Modeling Work Performed to Date

3.3.1 Modeling Investigations of Ammonia Cycling in the Atmosphere

3.3.1.1 Problem Description

The role of ammonia as an alkaline component of the atmosphere has long been recognized (Junge, 1954). Deposition of nitrogen compounds ammonia (NH_3), ammonium (NH_4^+), nitric acid (HNO_3), nitrate (NO_3^-), and other compounds derived from emissions of NO_X can contribute significantly to eutrophication and other nutrient loading effects. Through such processes, NH_3 can make a major contribution to the burden of nitrogen loading on natural ecosystems (e.g., NAPAP, 1990). Emissions of NH_3 generally are associated with intensive livestock agriculture. Current estimates of NH_3 budgets in the troposphere indicate that a significant fraction of NH_3 in air originates from animal manure (Asman and Janssen, 1992; Warneck, 1988). NH_3 emissions can constitute a significant portion of the total nitrogen emissions. In North Carolina, recent estimates suggest that NH_3 comprises more than 40 % of the total nitrogen emissions (Aneja, et al., 1998). NH_3 differs from NO_X and SO_2 in that a larger fraction of NH_3 may be deposited within a short distance of the source since its emissions are almost entirely at the ground level and also due its relatively high deposition velocity for most surfaces (Hov and Hjollo, 1994a). Consequently, development of a detailed understanding of the cycling of NH_x (NH_3+NH_4^+) in the atmosphere is critical in quantifying its atmospheric budgets and deposition amounts. Comprehensive atmospheric transport/transformation/deposition models that can treat the various atmospheric physical and chemical processes, can provide useful tools to systematically investigate the fate of emitted ammonia.

Gaseous NH_3 does not exhibit any significant tropospheric chemistry. Its reaction with hydroxyl radical (OH) is relatively slow with an estimated lifetimes of 3-4 months (Langford, et al., 1992; Warneck, 1988). Gaseous NH_3 in the atmosphere is incorporated into acidic aerosols and cloud droplets through association with sulfuric acid to form ammonium bisulfate (NH_4HSO_4) and ammonium sulfate ($(NH_4)_2SO_4$) by irreversible processes (Tang, 1980). NH_3 can also react with HNO_3 to form ammonium nitrate, which may dissociate to ammonia and nitric acid depending on ambient temperature and relative humidity (Stelson and Seinfeld, 1982). In general, sulfates associate more easily with NH_3 than does HNO_3, resulting in sulfate being neutralized before ammonium nitrate is formed. Consequently, the transformation of ammonia to ammonium is closely coupled with emissions of NOx and SO_2. More importantly, the atmospheric fate of NH_3 emissions is dependent on the chemical form in which it exists, since the removal processes for each form are significantly different. Ammonium bisulfate (NH_4HSO_4) and ammonium sulfate ($(NH_4)_2SO_4$) aerosols exist primarily in accumulation mode, where deposition velocity is relatively low and their primary atmospheric sink is wet scavenging. The difference in dry removal rates of ammonium aerosols and NH_3 are likely to result in a shift in the transport distance of NH_3+NH_4^+, which in turn are linked to distribution of NOx and SO_2 emissions (Hov and Hjollo, 1994b). Consequently, once NH_3 forms ammonium aerosols it is likely to be transported over longer distances than that if it had existed as gaseous NH_3. Therefore, to determine the range of influence of NH_3 emissions it is important to investigate the transport distances of NH_3 and its derived chemical forms as a function of emissions of SO_2 and NOx.

3.3.1.2 Project Objective

The overall objective of this project is to assess the current state of nitrogen cycling in the Regional Acid Deposition Model (RADM) (Chang et al., 1987) and to introduce appropriate enhancements in model formulation and representation of relevant processes to enable comprehensive studies of the fate of NH_3 emissions in the atmosphere and their eventual impact on ecosystems. Subsequent to the development and evaluation of the modeling tool the objectives of this work are:

- determine the range of influence of NH_3 emissions;
- determine the relative contribution of NH_3 emissions to total nitrogen deposition amounts;
- define appropriate airshed size for modeling pathways related to NH_3 emissions from North Carolina and their impact on atmospheric nitrogen deposition on the Neuse River Basin.

3.3.1.3. Status and Results

This modeling work is a continuing collaborative effort between Dr. Rohit Mathur (MCNC) and Dr. Robin Dennis at EPA/NOAA. In order to assess the ammonia cycle in RADM a number of parallel activities related to model and literature review, model applications, analysis and sensitivities, and model development and enhancement were pursued and are summarized below.

3.3.1.3.1 Review of current models

At the onset of the project, a detailed review of the representation and pathways for NH_3 emissions as represented in the Regional Acid Deposition Model (RADM) was performed. While the RADM accounts for transport, dry deposition, and cloud scavenging of airborne NH_3, a critical deficiency in the use of RADM to study atmospheric NH_3 cycling was determined to be the absence of any representation of the NH_3/NH_4^+ partitioning resulting from the incorporation of NH_3 in acid aerosols.

3.3.1.3.2 Model Applications, Analysis, and Sensitivities

The Regional Particulate Model (RPM) (Binkowski and Shankar, 1995), a modified version of RADM, includes a comprehensive treatment of the chemistry of the NH_3-H_2SO_4-HNO_3-H_2O system based on modifications of the equilibrium model, Model for an Aerosol Reacting System (MARS) (Saxena et al., 1986). The RPM is intended to predict the chemistry, transport, and dynamics of secondary aerosols of sulfate, nitrate, ammonium, and organic compounds, and uses RADM predicted fields as inputs. A series of model applications using this RADM/RPM system were performed at the EPA, and seasonally representative predictions were developed by aggregating representative model simulation cases. These simulations over the eastern U.S. utilized horizontal grids with 80km resolution and used NH_3 emission estimates from the 1985 inventory. Detailed analysis of model predictions and comparisons with observations from the Clean Air Status Network (CASTNet) were performed to assess the ability of the model to capture the seasonal and spatial variability in ammonium and nitrate concentrations over the eastern U.S. (Dennis, 1998). Figure 6 shows the "off-line" paradigm employed in these simulations. In this system, oxidant and NH_3 fields predicted by the RADM are used as input to the RPM, which then simulates the chemistry, transport, and dynamics of secondary aerosols of sulfate, nitrate and ammonium. To overcome particulate nitrate underpredictions, seasonally varying factors to be applied to input NH_3 concentrations were developed using a "brute-force inversion" methodology to represent increases in NH_3 emissions, following the approach of McHenry et al. (1994). These factors were then applied to the 3-D NH_3 fields input to the RPM. Analysis of model predictions and comparisons with the CASTNet data indicate improved model performance for particulate nitrate concentrations and nitrate deposition amounts (Dennis, 1998).

Since the modeling of ammonia cycling in the atmosphere involves both parametric (e.g., emissions) and structural (e.g., dry deposition parameterization) uncertainties, studies wherein model parameters are perturbed also are being conducted to develop an understanding of possible sensitivities in model predictions. Some preliminary simulations involving dry-deposition velocity perturbations for NH_3 and NH_4^+ have been performed and currently are being analyzed. Other model applications, such as those described above also have involved seasonally defined increases in ammonia emissions, since these simulations used base emissions from the 1985 inventory, which has been found to be biased low.

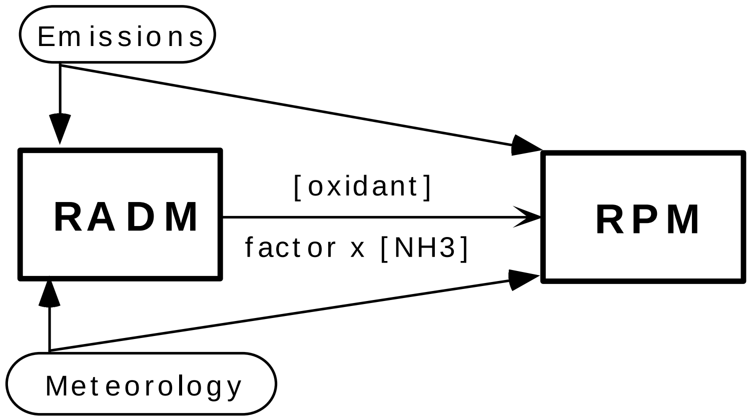


Figure 6. "Off-line" paradigm of the current RADM/RPM simulations

3.3.1.3.3 Model Development and Enhancement

Since the atmospheric fate of NH_3 emissions (and the related transport distances) depends on the chemical form in which they exist (gas or aerosol), the accurate modeling of the linkage with chemistry of SO_2 and NO_x is important. While the RADM/RPM system attempts to represent this, the "off-line" paradigm used in its current form could have several potential limitations:

1. The relative loss of emitted NH_3 through competing processes such as dry deposition, wet scavenging, and association with aerosols is not dynamically represented.
2. The lack of representation of the association of NH_3 with acidic aerosols may result in overestimating NH_3 dry deposition in certain locations.
3. The application of the seasonal factors to NH_3 fields input to RPM may result in overestimating simulated ambient NH_3 concentrations even though particulate nitrate predictions may show good agreement with observations.
4. The overestimation of simulated ambient NH_3 concentrations results in subsequent

overestimation of simulated NH_4^+ wet deposition.

Clearly, the representation of the relative loss of gaseous NH_3 through deposition and that through aerosol formation in a consistent manner is important. While MODELS-3 and MAQSIP are intended to provide such a consistent framework, the coupled gas-aerosol components of both these systems are currently under development and evaluation. To gain a better understanding of the linkages of NH_3 and its derived chemical forms with emissions of SO_2 and NO_x, we devoted significant effort towards the development of specific model components within RADM, which would help enhance the capability of the model to comprehensively investigate the cycling of both reduced and oxidized nitrogen in the atmosphere.

Guided by the analysis and results of the RADM/RPM simulations and the sensitivity runs, it was decided to include a representation of the gas-aerosol partitioning of emitted NH_3. A module to represent aerosol equilibrium was developed and added to the RADM framework. The module is based on the work of Saxena et al. (1986) and further modifications by Binkowski and Ching (1996). This aerosol equilibrium module is similar to that of the RPM and Models-3/MAQSIP system and calculates chemical composition of sulfate-nitrate-ammonium-water aerosol based on equilibrium thermodynamics. Based on our testing for selected cases, we introduced further modifications to the module to improve its robustness for NH_x-rich versus NH_x-poor regimes. Two additional species representing particulate ammonium and particulate nitrate were added to RADM. In addition, modules were developed for advective and turbulent transport and dry deposition of the additional particulate species. The representation of aqueous chemistry was modified to include the participation of particulate nitrate and ammonium. Further, the cloud transport and cloud scavenging portions of the model also were modified to include the impact of these important processes in the representation of particulate ammonium and nitrate and to include the their contribution to the eventual ammonium and nitrate wet deposition amounts. The resulting version of the model is referred to as the *Extended-RADM*. This version has the full functional capabilities of the RADM/RPM system except the aerosol size dynamics. However, the model has the ability to dynamically represent the various competing processes that interact to influence the cycling of reduced and oxidized forms of nitrogen and their interactions. Consequently, the model will serve as a useful tool to investigate nitrogen cycling and deposition in the eastern U.S and North Carolina airsheds, during the period in which the Models-3/MAQSIP system are fully developed and evaluated.

Two sets of simulations have been performed with the Extended-RADM over the eastern U.S. domain. The first set of simulations (denoted i90_v4) utilized ammonia emission estimates from the 1985 inventory with additional growth factors derived from previous RADM/RPM simulations, while the second set of simulations (denoted net90_v5) utilizes more updated information from the 1990 emission inventory. For each set, 30 different cases each of 72-hour duration were simulated. Model predictions from these are currently being aggregated to construct seasonal and annual estimates of ambient levels and deposition amounts. The rationale for these regional scale simulations is twofold: (1) it provides a basis for cross comparing model predictions from the Extended-RADM with those from previous RADM/RPM simulations, and (2) it provides a basis for comparison of model predictions with a more extensive set of observed concentrations (from CASTNet data) and wet deposition amounts (from NADP/NTN data).

Model predictions of both ambient levels as well as wet deposition amounts derived from the Extended-RADM have been compared with those obtained from the RADM/RPM system for selected cases as well as seasons. The intercomparisons indicate that the concentration fields for particulate sulfate, nitrate, and ammonium derived from the Extended-RADM (with seasonal factors applied to the NH_3 emissions) match those obtained from the RADM/RPM system. Additionally, a good match between the models is also observed for wet deposition amounts for sulfate and nitrate. In general, much higher ambient NH_3 levels and NH_4^+ wet deposition amounts are observed in the RADM/RPM simulations compared to those from the Extended-RADM. These discrepancies can be explained by the different ways the seasonal factors have been used in the two models. In the Extended-RADM, they are applied directly to the emissions whereas in the RADM/RPM system, they are applied to systematically increase the ambient NH_3 fields input to the RPM. However, taken together, with the comparisons of ambient concentrations and deposition amounts of the other components, it does appear that the "brute-force inversion" methodology has resulted in the development of factors that seem to produce increases in NH_3 emissions in the right direction. Further, preliminary analysis from the limited test case simulations conducted so far also indicate that the Extended-RADM (with seasonal factors applied to the NH_3 emissions) may help rectify NH_4^+ wet deposition over predictions of the RADM/RPM system. Comparison of model predictions of particulate matter concentrations with CASTNet data and deposition amounts with NADP measurements are currently underway.

Figure 7 presents seasonal estimates of the ratio of particulate ammonium to total reduced nitrogen ($NH_4 + NH_3$), while Figure 8 presents annual average estimates of the ratio. Both figures demonstrate the regional character of the partitioning of total ammonia in the gas and particulate phase and the importance of the linkage of NH_3 with the emissions of SO_2 and NO_X. In general, in the western part of the modeled domain a major fraction of emitted ammonia remains in the gas-phase. But in the eastern U.S., due to the presence of higher levels of atmospheric sulfate and nitric acid, a significant amount partitions to the particulate phase (NH_4^+). Additionally, compared to the general trends in eastern/southeastern U.S., both the seasonal and annual estimates show significantly different amounts of the ratio (NH_4^+/NH_X) for eastern North Carolina which can be attributed to the relatively higher NH_3 emissions in the region.

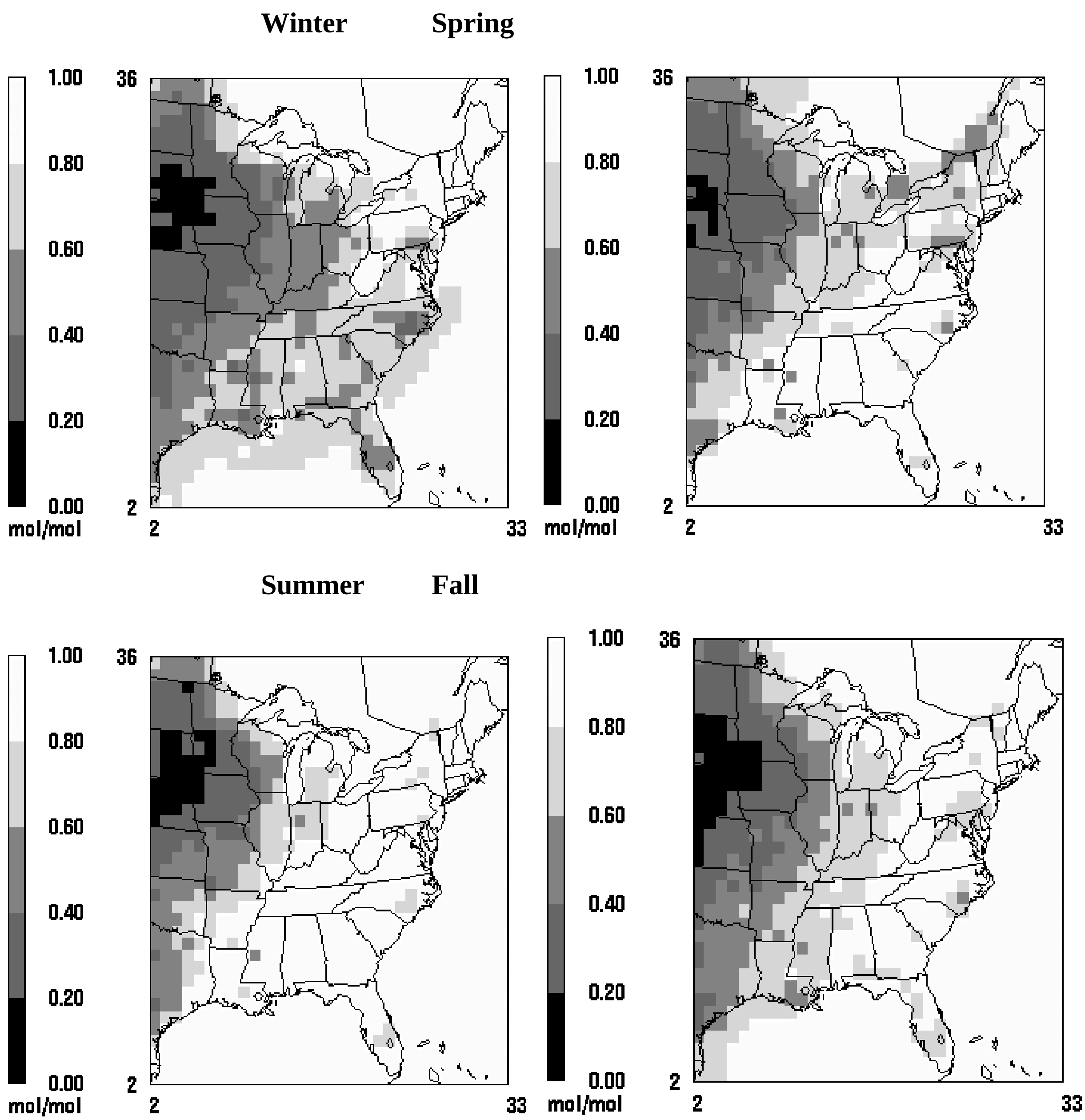


Figure 7 Seasonal variation in model predicted NH4/NHx for the net90_v5 emission case (Note: darker shades represent smaller values of the ratio NH_4^+/NH_X)

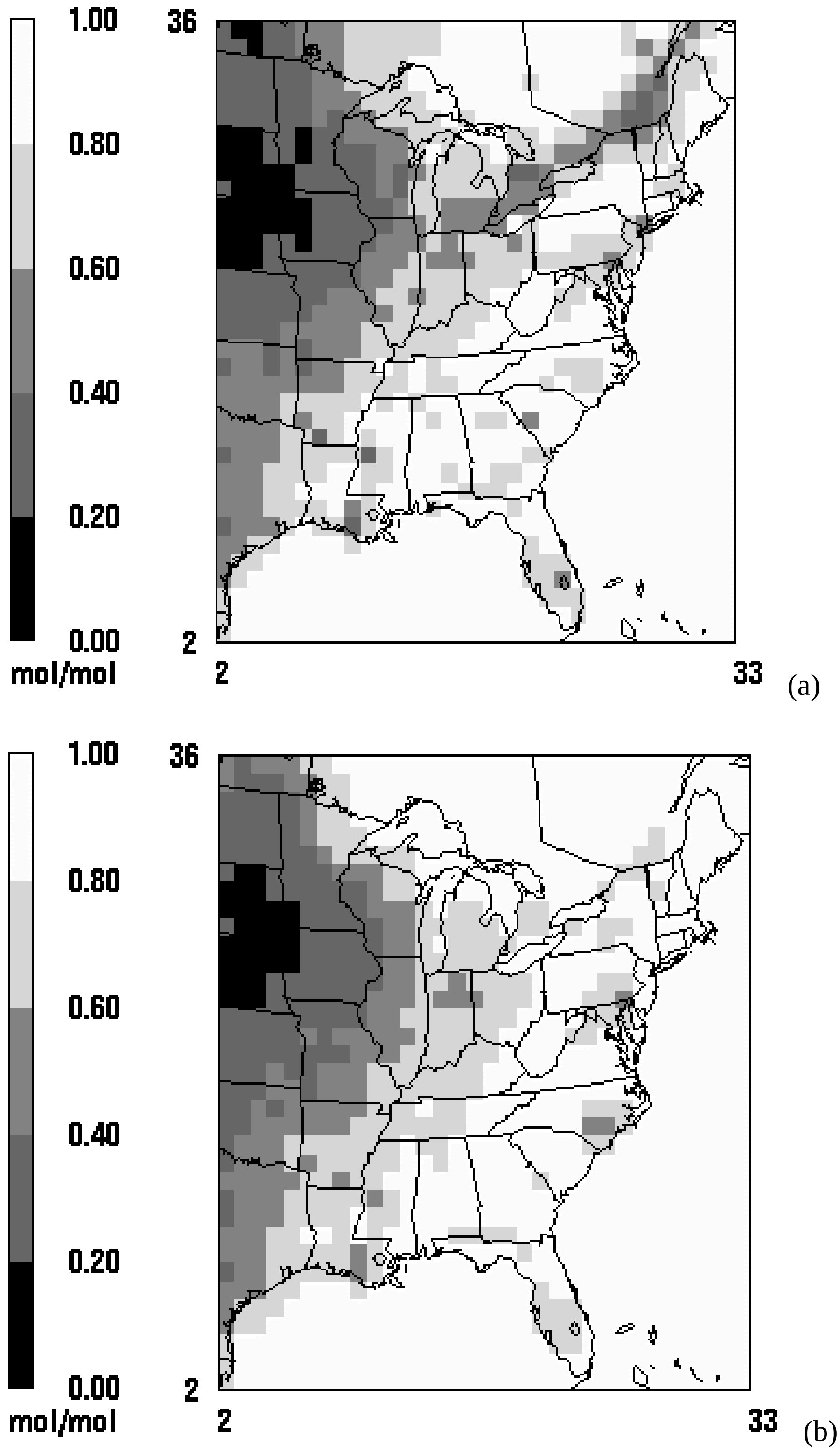


Figure 8: Model predicted annual average NH4/NHx.for (a) case with i90_v4 emissions and growth factors; (b) case with net90_v5 emissions (Note: darker shades represent smaller values of [NH_4^+/NH_X]).

3.3.2 Local Source Impact Modeling

One of the major elements of DAQ's modeling plan has been the execution of conventional short range air quality simulation models to evaluate the near-source impacts within the first few kilometers. However, this effort can not progress meaningfully until the questions and issues regarding the source strength or emission characteristics are firmly resolved. The emission assessment studies that are discussed in this report will help determine the needed source information that has been missing to date. These modeling efforts can commence as soon as the studies are peer reviewed and agreement is reached among the research community as to the best emissions data that apply to the various situations, and some preliminary conclusions can be made as to deposition rates of ammonia downwind. The climatological studies already done will fit into this effort as will the interface with the larger scale regional modeling efforts being done with the North Carolina Supercomputing Center (NCSC, formerly MCNC) and USEPA. The results of these models will help to determine how far down wind that local emissions of ammonia will have a significant impact. Currently, this modeling not only awaits the conclusions on source strength but is in direct competition with ozone State Implementation Plan modeling, which has been a top priority within the Division as a result of its role in the Ozone Transport Assessment Group modeling and analysis activities, the NOx SIP call and litigation, and other high visibility and resource intensive modeling and assessment projects that have been required to keep internal and external commitments. The execution of the short-term models is expected to begin more intensively by the summer of 1999.

4. Conclusions to Date

4.1 Acceptable Ambient Level (AAL) for Ammonia Not Exceeded

Concentrations of ammonia measured at Eastern Farm and Kinston from September 1997 to May 1999 have all been less than the North Carolina Air Toxics Acceptable Ambient Level (AAL). The following excerpt from the North Carolina emissions permitting rules defines an Acceptable Ambient Level.

Rule 2D.1104 TOXIC AIR POLLUTANT GUIDELINES

"A facility shall not emit any of the following toxic air pollutants in such quantities that may cause or contribute beyond the premises (adjacent property boundary) to any significant ambient air concentration that may adversely affect human health. In determining these significant ambient air concentrations, the Division shall be guided by the following list of acceptable ambient levels in milligrams per cubic meter at 77º F (25º C) and 29.92 inches (760 mm) of mercury pressure (except for asbestos). The Acceptable Ambient Level for ammonia is 2.7 milligrams per meter cubed (mg m^{-3})."

4.2 Agreement Between Measurement Methods

Results from the different techniques applied indicate that while a substantial amount of ammonia is volatilizing from waste lagoons, there is still variability between measurement methods. Aneja et al. (1999) estimated annual average lagoon emissions of 1718 g N m^{-2} min^{-1}, which translates to 5.9 kg N per animal per year for this farm, or 0.09 kg N per kg live weight per year. Harper and Sharpe (1999) estimated 602 g N m^{-2} min^{-1}, which translates to 2.1 kg N per animal per year for this farm, or 0.03 kg N per kg live weight per year. Todd (1999) was not able to complete all of the desired seasonal measurements, due to instrument problems, but the fall daytime estimate was 1650 g N m^{-2} min^{-1}, which translates to 5.7 kg N per animal per year for this farm, or 0.08 kg N per kg live weight. Preliminary estimates from the Division of Air Quality using measured ammonia concentrations, measured meteorological parameters, and dispersion modeling suggest lower-bound estimates of 0.62 kg N per animal per year, or 0.009 kg N per kg live weight per year for barn emissions, and 0.36 kg N per animal per year, or 0.005 kg N per kg live weight per year for lagoon emissions. The estimates by DAQ are currently being refined as more data become available. The Environmental Protection Agency (Battye, et al., 1994) estimates 7.6 kg N per animal per year, based on a composite of European studies. Sufficient information is not available to convert the EPA estimate to units of kg N per kg live weight per year.

4.3 Relative Emission Strengths of Barn, Lagoon, and Fields

The average of annual waste lagoon ammonia emissions estimates given by both Aneja et al. (1999), and by Harper and Sharpe (1999), are 1160 g N m^{-2} min^{-1}, or 4.02 kg N per animal per year. The average annual emissions estimate for the barns given by Harris is 3.04 kg N per animal per year. The estimate given by van der Hoek (1998) is 2.89 kg per animal per year. These preliminary estimates, taken together, suggest that at the Eastern Farm, the strength of ammonia emissions from the barns is similar to emissions from the waste lagoon. Studies of both lagoon and barn emissions are continuing to improve the quality of these estimates.

Some cursory data were gathered in an attempt to estimate emissions from spraying of lagoon effluent on the surrounding crops, but no estimates are currently available. This is a potentially large contributor to the overall variability of emissions estimates, and needs to be studied further. Discussions between DAQ and NCSU have begun regarding such a study in the near future.

4.4 Seasonal/Temporal Variability

Experiments have shown that there is a good deal of seasonal variability in ammonia emissions from the waste lagoon at the Eastern Farm. However, there is variability between measurement methods. Aneja et al. reported emissions that were 13 times higher in summer than winter; Todd et al. reported emissions that were 3.7 times higher in summer than fall; and Harper and Sharpe reported emissions that were 1.4 times higher in summer than winter.

Table 6: Comparison and seasonal variability of ammonia emission measurements

	Average barn emissions (kg N/animal/yr)	Average lagoon emissions (g N m $^{-2}$ min^{-1}) *[kg N/animal/year factors given in brackets]*			
		Winter	Spring/Fall	Summer	Annual Avg
Aneja et al. (1999)		305 [0.424]	1706 / 844 [2.37/1.17]	4017 [5.58]	1718 [2.39]
Harper and Sharpe (1999)	Not available	442 [0.614]	450 (spring) [0.625]	626 [0.870]	602 [0.836]
Harris and Thompson (1999)	2.26 – 3.91				
Todd (1999) (daytime)			1813 (fall) [2.52]	6666 [9.26]	

4.5 Increased Regional Ammonium Deposition

Cornelius (1997), Cowling et al. (1998), and Walker et al. (1999) found that nitrogen deposition by precipitation is higher in the region of North Carolina where animal production is most concentrated. They also found that the increases in ammonium concentration in rainfall and increases in ammonium deposition were statistically correlated with growth in hog population in the region.

4.6 Additional Work

Several aspects of this problem still need to be addressed. A number of additional projects are planned or underway as efforts to assess atmospheric nitrogen issues continue, including:

- Efforts by the U.S. EPA and USDA to estimate ammonia losses from barns on hog farms are continuing. Both agencies have been collaborating on the issue, and are applying technologies that are expected to complement each other.
- Ammonia losses from spraying lagoon effluent have not been sufficiently addressed, but are considered an important aspect of overall ammonia emissions.
- The North Carolina State University College of Agriculture and Life Sciences has begun efforts to assess the effects of alternative waste treatment technologies on ammonia emissions.
- The NCSU Department of Marine, Earth and Atmospheric Sciences is continuing efforts to characterize biogenic sources of atmospheric ammonia, including measuring ammonia losses from waste lagoons at other swine farms. Plans also include estimating ammonia losses from other types of animal production facilities and physical/chemical modeling of processes that result in ammonia losses from animal waste and ammonia emissions from intensively managed agricultural soils.
- DAQ, NCSU-MEAS and NCSU-CALS are continuing efforts to estimate both wet and dry deposition of atmospheric nitrogen compounds in eastern North Carolina. These efforts include statistical analysis of existing precipitation chemistry data and micrometeorological methods to estimate deposition velocities over various types of crops and other surfaces.
- DAQ and NCSU-MEAS are both investigating the fate of ammonia emissions in eastern North Carolina. DAQ is attempting to examine the rate of the transformation of ammonia to ammonium aerosols through empirical chemical observations, coupled with meteorological modeling. NCSU is working in collaboration with the North Carolina Supercomputer Center (NCSC) and DAQ to apply the MAQSIP model (Multiscale Air Quality Simulation Platform) to study the processes governing the

transport, transformation and deposition of ammonia and ammonium in eastern North Carolina.

- Ecological effects still need to be considered in the overall investigation of the effects of atmospheric nitrogen emissions and their ultimate fate. This will become more pertinent as efforts to estimate the deposition of these compounds mature.
- DAQ and NCSU have begun a statistical estimation of the total surface area of waste lagoons in eastern North Carolina, in order to estimate upper and lower boundaries of emission fluxes from all waste lagoons in North Carolina. This project involves the use of satellite images and statistical sampling techniques to develop relationships between the design capacity of farms and their actual lagoon surface areas.

5 Recommendations

While progress has been made in North Carolina in the understanding of the emissions and fate of nitrogen compounds, more needs to be known to develop representative modeling results. Ultimately, in light of European studies on the long-term negative effects of excess nitrogen loading on natural systems, research should be begun to assess the sensitivity of plant communities in eastern North Carolina to increased atmospheric-nitrogen loading. The ability of these systems to absorb and retain added N would be the focus of this effort. The following descriptions detail DAQ's recommendations regarding continuing efforts to assess issues surrounding atmospheric nitrogen compounds. Table 7 summarizes continuing research needs and estimated costs.

5.1 Continuation of Dry Deposition Measurements Over Natural Surfaces—Small Vegetative Surfaces

Deposition is a measure of what is coming down to the earth's surface out of the air. There are both wet and dry forms of deposition. Wet deposition is well characterized through the use of the data collected by the National Atmospheric Deposition Program (NADP). Dry deposition is not well characterized by the NADP measurements. Under some conditions, especially near strong ammonia sources, the amount of ammonia gas and ammonium ions that are dry deposited may match or exceed the amount of the ammonium wet deposited. The amount of material depositing is dependent on many factors, including the type of surface on which the material deposits. The amount of material dry depositing needs to be determined over multiple small vegetation surfaces (such as various crops and grass) and over tall vegetation (trees). Work is already under way by researchers at NCSU (Arya and Aneja) to make initial measurements of dry ammonia deposition. Funding would be used to continue the measurements and modeling needed for the dry deposition determinations over small vegetation.

5.2 Dry Deposition to Forests

Dry deposition of ammonia gas and aerosols to vegetated surfaces is one of the major processes, which removes N from the atmosphere. Since more than 60% of North Carolina is forested, and large canopy trees, with their enormous surface areas, adsorb more than crop fields or pastures, this research must be extended to forests if total atmospheric deposition of N, wet plus dry, is to be quantified. This contract is limited to measurements over forests since measurements over small vegetation are already underway. Knowledge of the total atmospheric deposition and how it varies spatially will be required to assess the possible effects of current and future N-loading rates.

5.3 Additional Ammonia Monitoring Equipment

Efforts are underway to monitor and characterize ammonia concentrations across eastern North Carolina. Monitors have been successfully deployed at two locations in Sampson County. More extensive geographic coverage is necessary to characterize the spatial distribution of ammonia concentrations. This information is an important input for modeling efforts already underway at the U.S. EPA for the State of North Carolina.

5.4 Ammonia Emission Measurements for Poultry, Cattle, and Intensively Managed Crops

By current estimates, swine, poultry, and cattle comprise 20.3%, 11.2%, and 7.4%, respectively, of total atmospheric nitrogen emissions in North Carolina. While progress has been made in producing more reliable emissions estimates for swine, poultry and cattle emissions additional work is still needed to achieve a sufficiently accurate statewide budget for ammonia emissions, and to perform reliable modeling studies. Measurements of ammonia emissions from poultry and cattle operations will require different methods and equipment than those applied for swine. Ammonia emissions from crops in North Carolina are currently unknown and also need to be evaluated.

5.5 Spray-field Application of Liquid Manure

Volatilization of nitrogen as ammonia occurs during and after liquid swine manure is sprayed on crop fields. Quantification of nitrogen inputs and losses to the spray-fields is part of understanding the overall nitrogen balance at a swine operation and is important to improving existing ammonia emission factors. This study of spray-field nitrogen dynamics also will include measurements of soil nitrogen levels, data that will permit estimation of the proportion of the applied N that will be potentially available for nitrification and leaching as nitrate.

5.6 GIS-Based Nitrogen Budgets

The Geographic Information System (GIS) format offers a convenient means of storing, processing, and presenting data spatially. A map representation of the nitrogen inputs and outputs to a county or a river basin conveys the nitrogen status of the area much more effectively than any series of tabular data. Also, modeling capabilities of atmospheric nitrogen chemistry and deposition are progressing as a DAQ/MCNC/EPA joint project and the outputs of these models estimate nitrogen concentrations and depositions on a spatial basis. These will be readily compatible with the developing GIS database. This will be a continuation of a project for the Neuse basin begun in 1997.

5.7 Purchase of Engineering Workstation Computer

In order to understand the atmospheric transport, transformation, and deposition of ammonia, it is necessary to perform mathematical modeling using a grid model such as the Regional Acid Deposition Model (RADM) and other air quality models. Further modeling is needed to understand fine particle formation that results from the atmospheric reaction of ammonia with sulfur dioxide and nitrogen oxides. In order to run these models, an engineering workstation computer with considerable speed and data storage capacity will be needed. The cost estimate is based on experience with computers needed for similar models used to predict ozone formation.

5.8 Continued Development of Computer Models for Atmospheric Nitrogen

The development of computer models capable of providing credible estimates of atmospheric deposition rates of nitrogen compounds, especially those derived from ammonia emissions, is a critical step toward quantifying the eventual export of nitrogen from different ecosystem types to surface and ground waters. Such models must deal effectively with deposition to land-covers of different types (forests, crops, etc.). Coefficients reflecting this export that are currently in use by water quality modelers are based on studies published in the scientific literature and are only very general in nature. While ammonia has not been of major concern to air quality modelers until recently, it has been in North Carolina because of the rapid expansion in livestock production. DAQ is funding an atmospheric scientist at NCSC this year (in addition to the previous year's funding provided by legislative funds routed through the Agricultural Research Service at NCSU) to incorporate current knowledge of the chemistry and deposition characteristics of ammonia into state-of-the-art models that utilize emissions patterns and chemical changes in the atmosphere to provide spatial estimates of deposition rates.

5.9 Continued Emissions Measurements from Swine Lagoons

Extensive measurements of emissions have been made at one swine lagoon and a few at two other lagoons. More emissions measurements are needed at other swine lagoons. It is believed different swine farm lagoons have different emissions rates based on numerous factors, such as number of animals, size of lagoon, animal age, feed composition, biological activity, lagoon concentrations, etc. To assure that the lagoon emissions are well characterized and to allow for the development of an ammonia emission factor for estimating the total emissions from all swine lagoons, emissions measurements are needed a more lagoons. The use of dynamic chamber technique by researchers at NCSU will allow the emissions to be determined and related to measurements already made. The dynamic chamber has demonstrated its portability and relatively low cost.

5.10 Additional Denuder Ambient Ammonia Monitoring Work

Model development depends upon a multi-year base of ambient air monitoring data - a base that is currently lacking. The DAQ began to monitor ambient levels of ammonia and particulate ammonium (a chemical form derived from ammonia gas by reactions that occur in the atmosphere) in the fall of 1997. Unfortunately, ammonia/ammonium measurements are technically difficult, labor-intensive, costly, and were feasible only at 3 locations in the eastern part of the state. The USEPA also is funding ambient ammonia/ammonium monitoring in eastern North Carolina. Funding for two additional ambient monitoring sites is needed to provide modelers the information required to judge the performance of their models, especially during the development phase.

5.11 Ecosystem Sensitivity to Increased Atmospheric Deposition

Increased atmospheric deposition of ammonia nitrogen has been implicated in European studies as a factor in the decline of forest health. Additionally, continued high nitrogen loading is a concern since it may reduce the system's ability to use and retain nitrogen, thus leading to greater nitrogen exports to surface and ground waters. While studies of atmospheric nitrogen deposition in North Carolina are yet in the preliminary stage, work should be initiated to develop the means of assessing and mapping ecosystem sensitivity to nitrogen before accumulated loads become problematic. The first phase must be a planning effort by plant scientists.

Table 7: Summary of Research Funding Needs

Category	Need Description	Estimated Cost f.y. 1999-2000	Estimated Cost f.y. 2000-2001
Monitoring	Purchase additional continuous ammonia monitor	$22,000	$0
Monitoring	Expanded denuder monitoring network	$100,000	$60,000
Emissions	Additional swine farm lagoon measurements	$150,000	$0
Emissions	Spray field application emissions (swine and poultry)	$100,000	$0
Emissions	Ammonia emission measurements (poultry and cattle)	$300,000	$100,000
Deposition	Continuation of dry deposition measurements (short vegetation)	$122,000	$111,000
Deposition	Dry deposition to forested areas	$250,000	200,000
Modeling	GIS-based nitrogen budget	$40,000	$0
Modeling	Continued computer modeling	$75,000	$75,000
Modeling	Purchase engineering workstation for expanded modeling	$100,000	$0
Effects	Ecosystem sensitivity to atmospheric nitrogen deposition	$50,000	$50,000
Total		$1,309,000	$596,000

References

Aber, J.D., K.J. Nadelhoffer, P. Steudler and J.M. Melillo, (1989). Nitrogen saturation in northern forest ecosystems: hypotheses and implications. Bioscience 39: 378-386.

Aber, J.D., W. McDowell, K. Nadelhoffer, A. Magill, G. Berntson, M. Kamakea, S. McNulty, W. Currie, L. Rustad and I. Fernandez, (1998). Nitrogen saturation in temperate forest ecosystems: Hypotheses revisited. BioScience 48: 921-934.

Aneja, V.P., J.S. Chauhan, J.T. Walker, Characterization of Ammonia Emissions from Swine Lagoons, Draft report to North Carolina Division of Air Quality, January, 1999.

Aneja, V. P., G. C. Murray, Jr., J. Southerland, Atmospheric Nitrogen Compounds: Emissions, Transport, Transformation, Deposition, and Assessment. EM(Environmental Manager) April 1998, 22-25.

Aneja, V. P., G. C. Murray, Jr., J. Southerland, Proceedings of the Workshop on Atmospheric Nitrogen Compounds, Raleigh North Carolina, March 10-12 1997, 299 pp.

Arts, G.H.P., G. Van Der Velde, J.G.M. Roelofs and C.A.M. van Swaay, (1990). Successional changes in the soft-water macrophyte vegetation of (sub)Atlantic sandy, lowland regions during this century. Freshwater Biology 24: 287-294.

Asman, W.A.H. and A.J. Janssen, (1992). A variable resolution model applied for NHx in Europe, Atmos. Environ., Part A, 26, 445-464.

Battye, R., W. Battye, C. Overcash, and S. Fudge, (1994). Development and selection of ammonia emission factors. EPA Contract Number 68-D3-0034, Work Assignment O-3, USEPA, Research Triangle Park, North Carolina.

Binkowski, F. S., and J. K. S. Ching, (1996). Regional scale distribution of fine particulate mass and visibility from the EPA Regional Particulate Model. Proceedings of the Ninth AMS-A&WMA Joint Conference on Applications of Air Pollution Meteorology, January 28-February 2, Atlanta, GA, 1996.

Binkowski, F.S., and U. Shankar, (1995). The Regional Particulate Model, Part I: Model description and preliminary results, submitted to J. Geophys. Res., 100(D12), 26191-26209.

Bobbink, R. and J.G.M. Roelofs, (1995). Nitrogen critical loads for natural and semi-natural ecosystems, the empirical approach. Water, Air and Soil Pollution (in press).

Cadle, S.H., R.J. Countess, N.A. Kelly, (1982). Nitric acid and ammonia in urban and rural locations. Atmos. Environ 16, 2501-2506.

Chang, J.S., R.A. Brost, I.S.A. Isaksen, S. Madronich, P. Middleton, (1987). W.R. Stockwell, and C.J. Walcek, A Three-Dimensional Eulerian Acid Deposition Model: Physical Concepts and Formulation, J. Geophys. Res., 92, 14681-14700.

Cornelius, W.L., (1997). Comparison of nitrogenous ion deposition and human and animal census trends in eastern North Carolina. In Proceedings of the Workshop on Atmospheric Nitrogen Compounds: Emissions, Transport, Transformation, Deposition, and Assessment, pp. 150-210. North Carolina State University: Raleigh, North Carolina.

Cowling, E. B., C. Furiness, S. Smith, and M. Henderson, (1998). Final report for the project: Estimation of atmospheric deposition of ammonium and nitrate in North Carolina and coastal plain river basins. Project report to North Carolina Department of Environment and Natural Resources, Division of Air Quality, December 31, 1998.

Dennis, R.L., Regional Particulate Model: Background Analysis for 812 Prospective Study,

Draft, NERL, EPA, RTP, 1998.
Dennis, R.L., Using the Regional Acid Deposition Model to Determine the Nitrogen Deposition Airshed of the Chesapeake Bay Watershed, Atmospheric Deposition to the Great Lakes and Coastal Waters, Ed. J. Baker, pp 393-413, Society of Environmental Toxicology and Chemistry, Pennsacola, Florida, 1997.
Desimone, J., R. Oommen, J. Lawrimore, V.P. Aneja, Climatology of Synoptic-Scale Weather Systems for Eastern North Carolina, Report to North Carolina Department of Environment and Natural Resources, June 1998.
Duyzer, J., (1994). Dry deposition of ammonia and ammonium aerosols over heathland, J. Geophys. Res., 99(D9), 18757-18763.
Erisman, J.W., T. Bridges, K. Bull, E. Cowling, P. Grennfelt, L. Nordberg, K. Satake, T. Schneider, S. Smeulders, K.W. Van der Hoek, J.R. Wisniewski, J. Wisniewski, Summary Statement, First International Nitrogen Conference, 1998, Elsevier Science, Oxford, UK, 796 pp.
Erisman, JW, R Bobbink and L van der Eerden, (1996). Nitrogen pollution on the local and regional scale: The present state of knowledge and research needs. RIVM Report #722108010 (Dutch National Institute of Public Health and the Environment), Jan 1996, 100 pp.
Fisher, DC & MP Oppenheimer, (1991). Atmospheric nitrogen deposition and the Chesapeake Bay estuary. Ambio 20: 102-108.
Harper, L.A., and R.R. Sharpe, Ammonia Emissions from Swine Waste lagoons in the Southeastern U.S. Coastal Plains, Final Report to the North Carolina Division of Air Quality, December, USDA-ARS Agreement No. 58-6612-7M-022, December 1998.
Harris, D.B., E.L. Thompson, (National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC), Evaluation of Ammonia Emission from Swine Operations in North Carolina, Report to North Carolina Division of Air Quality, December, 1998.
Hov, O. and B.A. Hjollo, (1994a). Transport distance of ammonia and ammonium in Northern Europe 1. Model Description, J. Geophys. Res., 99(D9), 18735-18748.
Hov, O. and B.A. Hjollo, (1994b). Transport distance of ammonia and ammonium in Northern Europe 2. Its relation to emissions of SO2 and NOx, J. Geophys. Res., 99(D9), 18749-18755.
Junge, C.E., (1954). The chemical composition of atmospheric aerosols I. Measurements at Round Hill Field Station, J . Meteorol., 11 , 223-333.
Langford, A.O., F.C. Fehsenfeld, J. Zachariassen, and D.S. Schimel, (1992). Gaseous ammonia fluxes and background concentration in terrestrial ecosystems of the United States, Global Biogeochem. Cycles, 6, 459-483.
McHenry, J.N. and R.L. Dennis, (1994). The Relative Importance of Oxidation Pathways and Clouds to Atmospheric Ambient Sulfate Production as Predicted by the Regional Acid Deposition Model, J. Appl. Meteor., 33, 890-905.
Mueller. T.K., G.M. Hidy, K. Warren, T.F. Lavery, R.L. Baskett, (1980). The occurrence of atmospheric aerosols in the north-eastern United States. Annals of the New York Academy of Science 338, 463-482.
National Acid Precipitation Assessment Program, Acidic Deposition: State of Science and Technology, NAPAP, Washington, D.C., 1990.

National Atmospheric Deposition Program (NADP), http://nadp.sws.uiuc.edu/nadpdata/, 1996.
North Carolina Center for Geographic Information and Analysis (NCCGIA) Land Coverage Database, 1998.
North Carolina Department of Agriculture (NCDA), Agricultural Statistics Service. http://www.agr.state.nc.us/stats/livestoc/livestoc.htm (January, 1999).
Okita, T, K. Kaneda, T. Yanaka, R. Sugai, (1974). Determination of gaseous and particulate chloride and fluoride in the atmosphere. Atmospheric Environment 8, 927.
Paerl H. W. (1995). Coastal eutrophication in relation to atmospheric nitrogen deposition: current perspectives. Ophelia. 41, 237-259.
Paerl, H.W. and M.L. Fogel (1994). Isotopic characterization of atmospheric nitrogen inputs as sources of enhanced primary production in coastal Atlantic Ocean waters. Mar. Biol. 119: 635-645.
Platt, U., and D. Perner, (1980). Direct measurements of atmospheric CH2O, HNO2, O3, and SO2 by differential optical absorption in the near UV. Journal of Geophysical Research 85C, 7453-7458.
Robarge, W.P. and W.W. Cure, Quantification of Atmospheric Nitrogen Deposition in the vicinity of a Large Scale Swine Production Facility Located in the Neuse River Basin, Final Report to the North Carolina Division of Air Quality, December 31, 1998.
Roelofs, J.G.M. (1983). Impact of acidification and eutrophication on macrophyte communities in soft waters in the Netherlands. I. Field observations. Aquatic Botany 17: 139-155.
Saxena P., A.B. Hudischewskyj, C. Seigneur, and J.H. Seinfeld (1986). A Comparative Study of Equilibrium Approaches to the Chemical Characterization of Secondary Aerosols, Atmos. Environ.,20, 1471,.
Sparts, M.L., M.R. Witkowski, J.H. Fateley, A.M. Hammaker, W.G. Fateley, A.E. Carter, M. Thomas, D.D. Lane, G.A. Marotz, B.J. Fairless, T. Holloway, J.L. Hudson, J. Arello, and D.F. Gurka, Optimization of a Fourier Transform Infrared Spectrometer During On-Site Pollution Analysis. Proceedings of the Conference on Raman and Luminescence Spectroscopies in Technology II, July 10-13, 1990.
Stelson, A.W. and J.H. Seinfeld (1982). Relative humidity and temperature dependence of ammonium nitrate dissociation constant, Atmos. Environ., 16, 983-992.
Sutton, M.A., J.B. Moncrieff, and D. Fowler, (1992). Deposition of atmospheric ammonia to moorland, Environ. Pollut., 75, 15-24.
Tang, I.N., (1980). On the equilibrium partial pressures of nitric acid and ammonia in the atmosphere, Atmos. Environ., 14, 819-828.
Todd, L., Site Characterization Using Open-path Fourier Transform Infrared (OP-FTIR) Spectroscopy, Final Report to North Carolina Division of Air Quality, February 3, 1999.
Van Der Hoek, K.W. (1998). Estimating Ammonia Emission Factors in Europe: summary of the Work of the UNECE Ammonia Expert Panel. Atmospheric Environment, 32, pp 315-316.
Walker, J.T., V.P. Aneja and D.A. Dickey (1999). Atmospheric Transport and Wet Deposition of Ammonium in North Carolina. Atmospheric Environment (in review).
Warneck, P., Chemistry of the natural atmosphere, Academic Press, 1988.
Whalen, S., Personal Communication, January 7, 1999.
Wyers, G.P., A.T. Vermeulen, and S. Slanina, (1992). Measurements of dry deposition of ammonia on a forest, Environ. Pollut., 75, 25-28.