

## Abstract

OCCHIPINTI, CHRISTOPHER OLOVSON. Nitrate Isotopic Composition in Rainfall and Fine Particulate Matter: Back Trajectory, Meteorology, and Source - Receptor Relationship Analysis. (Under the direction of Viney P. Aneja.)

The southeastern portion of North Carolina is a dense crop and animal (swine) agricultural region which previous research suggests emits a significant portion of the state's nitrogen emissions. These findings indicated that transporting air over this region can effect nitrogen concentrations in precipitation at sites at least 50 miles away. The present study was able to combine isotope compositional information with the concept of back trajectory analysis to examine the relationship between this regional nitrogen emission source and receptors independent of pollutant concentration information. The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) model was used to determine potential sources of nitrogen in rainwater collected at an urban receptor site in Raleigh, North Carolina, during the first three quarters of 2004. The delta  $^{15}\text{N}$  isotope ratio signatures of each sample were used to further differentiate between sources of the rainwater nitrogen. This study examined the importance of pollutant sources such as animal agricultural activity and meteorology on rainfall chemistry as well as their implications on fine particulate matter formation. Additionally, meteorological conditions associated with anomalous springtime fine particulate matter concentrations found in coastal New Hanover County, North Carolina were investigated.

Samples that transited the dense crop and animal (swine) agricultural region of east-southeastern North Carolina (i.e. the source region) had lower delta  $^{15}\text{N}$  isotope ratios in the nitrate ion (average =  $-2.1 \pm .58$  per mil) than those from a counterpart nonagricultural region (average =  $0.1 \pm .62$  per mil.) However, the limited data set does not offer any conclusive

evidence of similar patterns in ammonium ions. An increase in PM fine mass concentrations in the urban receptor site (yearly average =  $14.9 \pm 1.65 \mu\text{g}/\text{m}^3$ ) was also found to correspond to air transport over the dense agricultural region relative to air which was not (yearly average =  $9.7 \pm .93 \mu\text{g}/\text{m}^3$ ).

Fine particulate matter concentrations over the course of four years in four counties around the state were examined, and peak levels of  $\text{PM}_{2.5}$  were found in the summer at 3 of the 4 sites. The fourth site, located in coastal New Hanover County had a fine particulate matter peak in the spring, which appeared to be unusual as most literature indicates that conditions for high  $\text{PM}_{2.5}$  levels are generally found in the summer. Investigation of the phenomenon revealed that historically, meteorological conditions including relative humidity, temperature, and wind direction allow for a peak to exist much earlier in the year at such a location. Transport of pollutants from the dense swine region to the Northwest of New Hanover County is more common in the springtime, along with relative humidity that is in a range which allows an increase in particulate matter to occur.

**Nitrate Isotopic Composition in Rainfall and Fine Particulate Matter: Back  
Trajectory, Meteorology, and Source - Receptor Relationship Analysis**

by  
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## **Biography**

Chris Occhipinti was born and raised in Twin Lake, MI, a small community outside of Muskegon, MI. Here he attended school and graduated from Reeths-Puffer High School in 2000. Making the trip north he chose to major in Applied Physics at Michigan Technological University in Houghton, MI where he graduated in 2004 cum laude. Building upon his undergraduate research he attended North Carolina State University in Raleigh, NC and became a part of the Air Quality Research Group and a part of the Marine, Earth, and Atmospheric Science Graduate Department. Chris currently works for URS Corporation in their Air Quality Monitoring Group.

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## **Chapter 1. Introduction**

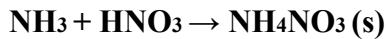
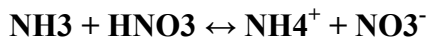
### *1.1 Background*

North Carolina is home to roughly 11 million hogs, which are primarily confined to the southeastern portion of the state. A huge increase in commercial swine production from 2.4 million to 9.7 million hogs took place over just 9 years, spanning 1986 to 1995 (Figure 1.1, North Carolina Department of Agriculture & Consumer Services, 2005). As production shifts from smaller hog farms to large commercial scale farms, environmental concerns and complaints regarding air and water quality associated with the increased number of animals and management of subsequent wastes accompanying the growth of this industry has been considerable” (Blunden, 2003). Effects on ammonium ion wet deposition in the region during this time period can be seen in the sequence in figure 1.2 provided on the National Atmospheric Deposition Program website ([nadp.sws.uiuc.edu/amaps2/nh4dep/nh4dep.ppt](http://nadp.sws.uiuc.edu/amaps2/nh4dep/nh4dep.ppt), 2006). In order to study environmental impact of the increased production in North Carolina, the state adopted the Clean Water Responsibility Act in 1997, placing a moratorium on the creation of new or expansion of existing large swine farms, and later extended the act through September 2007.

### *1.2 Particulate Matter and Related Pollutants*

Fine particulate matter ( $PM_{2.5}$ ) and pollutants related to its production (including ammonia and  $NO_x$ ) and are major concerns in the eastern United States. Nitrogen oxides ( $NO_x = NO + NO_2$ ), nitrate ions ( $NO_3^-$ ), ammonia ( $NH_3$ ), and ammonium ions ( $NH_4^+$ ) have important effects on rainfall chemistry and fine particulate matter ( $PM_{2.5}$ ) formation. Ammonia may be scavenged from the air by rain, absorbed by plants, or rapidly converted to ammonium aerosol.  $NO_x$  is a precursor to nitric acid, and can react with ammonia to produce

ammonium nitrate ( $\text{NH}_4\text{NO}_3$  (s)) (Seinfeld and Pandis, 1998). Increases in emissions from anthropogenic sources of  $\text{NO}_x$  correspond to increases in nitric acid deposition (Penner et al., 1991), and may be associated with increased fine particulate matter deposition.



Walker et al. (2000) suggests that swine agriculture represents approximately 21% of the state's nitrogen emissions. The study concludes that  $\text{NH}_4^+$  concentrations in precipitation at downwind sites were 50% higher on weeks when at least 25% of the precipitation came from the swine agricultural source region. The atmospheric emissions of the source region were substantial enough to influence the nitrogen content of wet deposition at a receptor site over 50 miles away.

Determination of this influence independent of concentration analysis would prove helpful in further verification of the conclusion. To this end, the isotopic composition of the nitrogen compounds in rainwater was examined, taking advantage of severe isotopic depletion associated with biological activities related to agriculture. Specific isotopic signatures would allow for differentiation between natural and anthropogenic source contributions (Kendall and McDonnell, 1998).

### 1.3 *Isotopes*

Since the ratio of stable isotopes of a given compound does not change spontaneously, differences in the ratios between different samples indicates other processes at work. A heavier isotope has more inertia; it is generally less likely to be involved in kinetic processes than its lighter counterpart. For example microorganisms more easily

utilize  $^{14}\text{N}$  than the heavier  $^{15}\text{N}$ . Thus, a compound containing a higher ratio of  $^{14}\text{N}$  is more likely to be the product of organic processes, while the heavier compound is more likely to be the unused (residual) portion of the reactant. (Kendall and McDonnell, 1998) This concept is known as fractionation. In some situations such as intensively managed agriculture, it is hypothesized that enough fractionation occurs due to biological, chemical, and physical processes that products and residuals can in fact behave as naturally generated tracers in larger ecosystem studies. Results presented in Schulz et al. (2001) indicated that highly depleted isotope values were found in manure from swine and cattle, and that it could be transported via atmospheric processes to the bark of trees in the surrounding area.

Although stable isotope ratios have been examined for over half a century, many clues they leave for atmospheric science have been largely unexplored and underutilized. Stable isotope ratios of carbon-13 have allowed for archaeological diet studies, and to provide a correction factor for carbon-14 dating (which is actually a type of unstable isotope ratio analysis). Isotope analysis involving nitrogen-15 and oxygen-18 ratios has also been extensively used for tracing and fractionation studies in hydrology (Kendall and McDonnell, 1998). Given the prevalence of isotope analysis, especially in terms of tracing and fractionation studies in water, soil, and biological sciences, it is rather surprising that there are a limited number of studies on the topic relating to atmospheric science.

#### *1.4 Trajectory Model*

This study was able to combine the isotope composition information with the concept of back trajectory analysis in order to examine the relationship between a source and receptor independent of pollutant concentration information. The National Oceanographic and Atmospheric Administration's Hybrid Single Particle Lagrangian Integrated Trajectory

model (HYSPLIT) was developed to able to use various meteorology sets to model forward and back trajectories. Using 2004 EDAS 40 data, it provided the best spatial resolution (40km) of any of the possible models (<http://www.arl.noaa.gov/faq/md3.html> (2004)).

HYSPLIT incorporates modeled meteorological grid data, which gives more accuracy in less developed areas than observation based models. It was able to simulate back trajectories for the entire 2004 data set, allowing for estimation of the recent path history of an air parcel that arrived at the receptor at a given time.

### *1.5 Objectives*

Objectives of the project are to: 1) verify that Raleigh is a receptor of pollutants from North Carolina's large agricultural corridor (region 1) using stable isotope analyses, 2) determine the association of farm emissions transport with PM fine formation in Raleigh, and 3) investigate other meteorological parameters associated with enhanced concentrations of fine PM and other pollutants North Carolina.

## *1.6 References*

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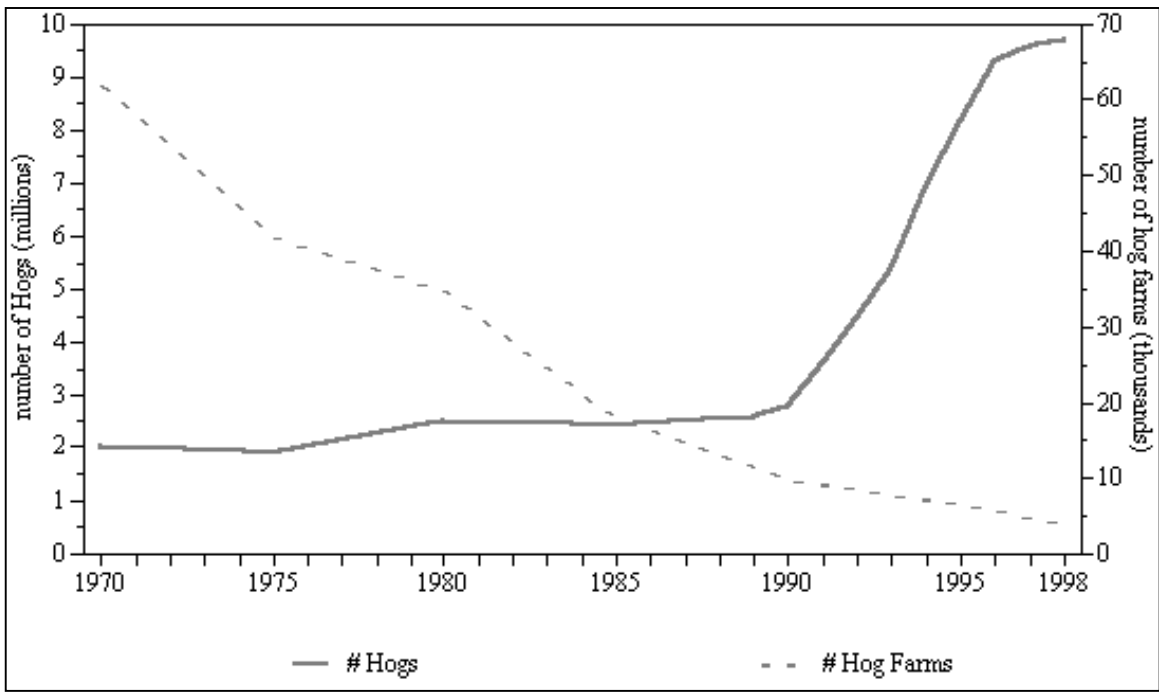


Figure 1.1: Population of Swine and Number of Swine Farms in North Carolina (1970 – 1998)

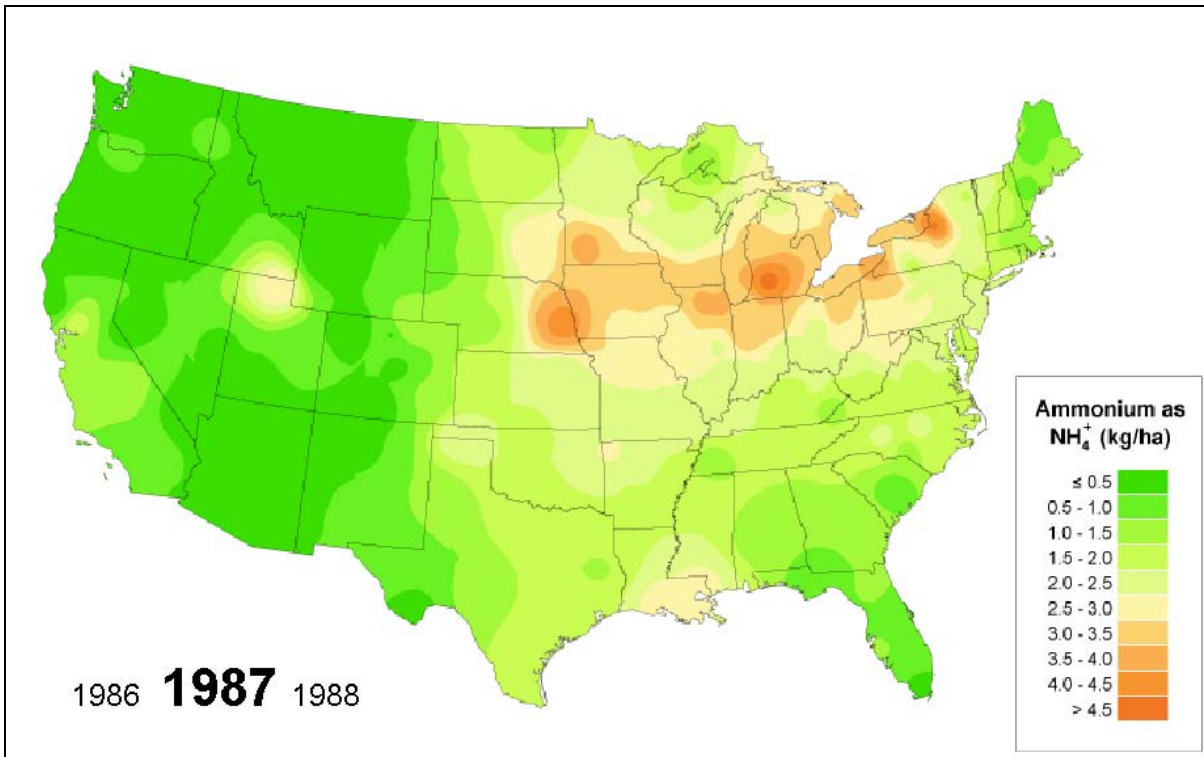


Figure 1.2 (a): Ammonium Ion Wet Deposition in the U.S. 1987. Courtesy of NADP.

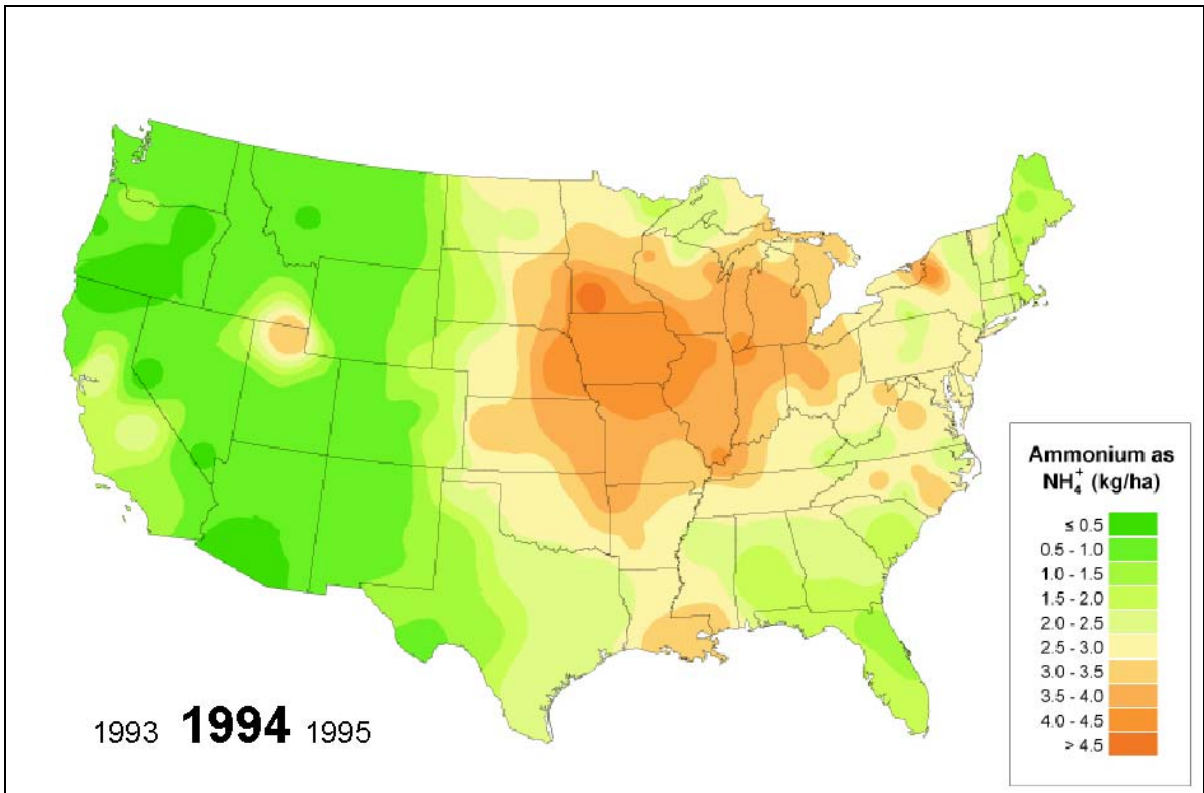


Figure 1.2 (b): Ammonium Ion Wet Deposition in the U.S. 1994.

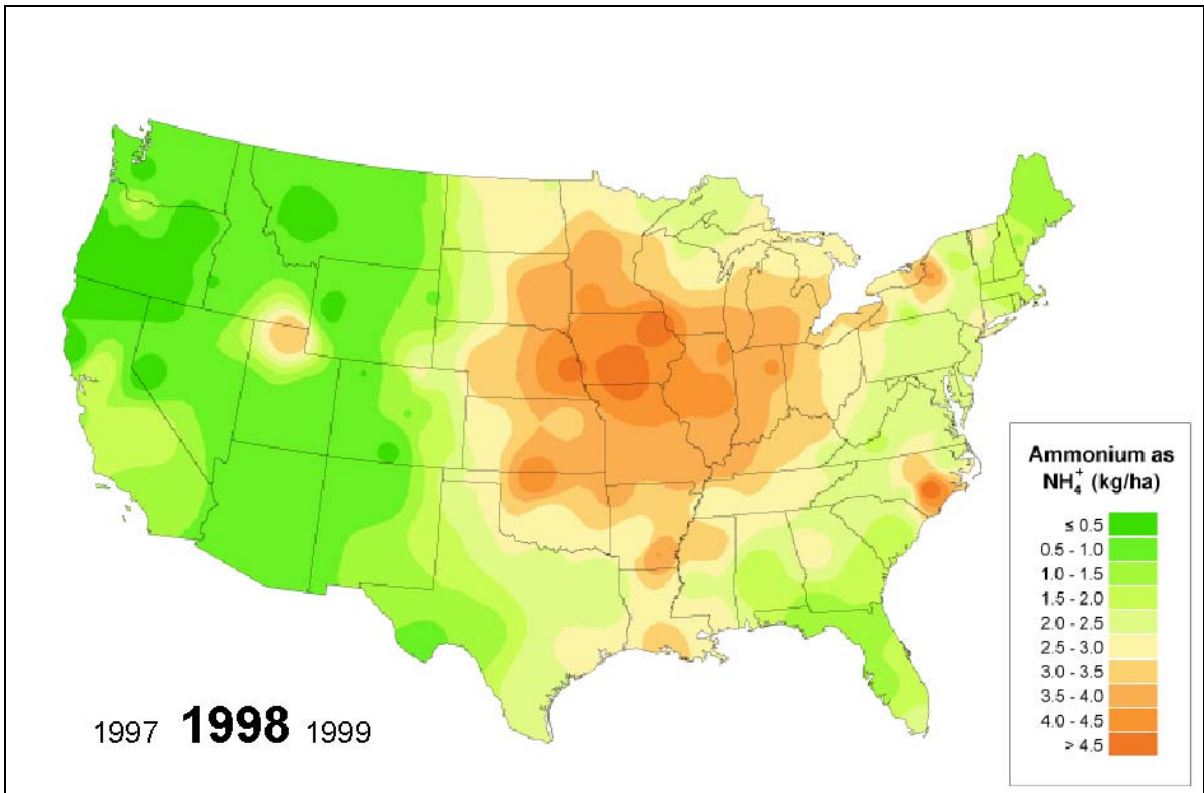


Figure 1.2 (c): Ammonium Ion Wet Deposition in the U.S. 1998

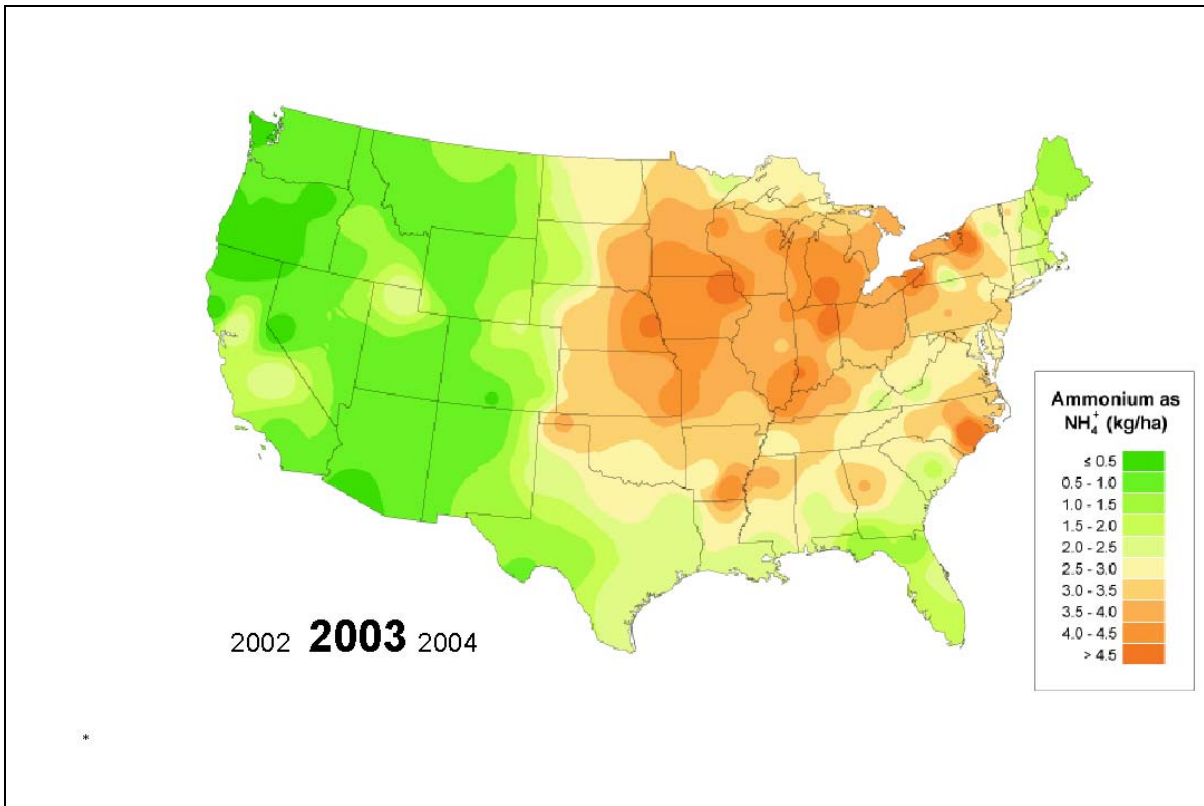


Figure 1.2 (d): Ammonium Ion Wet Deposition in the U.S. 2003

## **Chapter 2. Nitrate Isotopic Composition in Rainfall and Fine Particulate Matter: Back Trajectory Analysis and Source - Receptor Relationships**

### *2.1 Data Collection and Analysis*

#### *2.1.1 Rainfall Sample Collection*

This study used  $\delta^{15}\text{N}$  values from 31 rainfall samples from 2004 collected on the roof of Jordan Hall at North Carolina State University (35.78°N, 78.68°W) at a height of 23 meters above ground level. The samples were taken on a weekly basis when rainfall occurred, reflecting total storm and dry fall accumulations in the covered collection buckets, rather than daily samples of the rain during a given storm system. Bucket collection has been criticized because nitrogen compounds can be lost or converted while in the bucket, but the cover helps to mitigate these effects. The weekly collection schedule limited the ability to distinguish between a multi-day storm such as a hurricane and several days with different rainfall sources. Thus back trajectories had to be classified by how much they contributed to total rainfall volume in the specified period.

#### *2.1.2 Meteorological Data Collection for Model Run Specification*

Atmospheric transport patterns were evaluated by examining 48-hour back trajectories originating from the building on each day that rainfall was recorded at the N.C. state climate office site on Lake Wheeler Road (about 4 miles south of campus). The HYSPLIT model provided information about where the air at the rooftop came from. We initiated each trajectory at an altitude above the ground of 23 meters to simulate air at the rooftop of Jordan Hall. We were able to use the ETA 40 km data assimilation system (ETAD 40) (<http://www.arl.noaa.gov/faq/md3.html>) (2004) to allow a 40 km resolution for the trajectories.

Daily trajectories were examined for each date when rainfall would have contributed to the total collected in the sample buckets, using daily rainfall data from the state climate office site, approximately 5 miles south of the collection site. Using the daily rainfall data, we were able to classify multi-day samples according to whether or not the majority of a sample was collected during periods of transport from a given region. The transport regions of primary interest in this study were the intensively managed crop and animal agricultural region of southeastern N.C., defined in figure 1 as region 1, and the Atlantic Ocean (region 2). The definition of a “source” region was the region (1, 2, neither, or both) from which majority (by volume) of the rain sample came from. We designated samples in which at least 50% of the rainfall would have transited across the given source region as “agricultural” (for region 1) or “marine” (for region 2) air. Samples where less than 50% of the rainwater collected was from systems which transported it across region 1 were labeled “non agricultural”, and samples which had no transit across region 2 we described as “continental”. Thus descriptive combinations of characteristics included “agricultural marine”, “non agricultural marine”, “agricultural continental”, and “non agricultural continental” samples.

To further investigate the effects of ammonia and nitrate emissions on fine PM formation, N.C. Department of Air Quality (DAQ) PM<sub>2.5</sub> records for the same time period were also examined. Trends in the PM formation during the dates corresponding to each contributing trajectory were examined. The data is based on daily averaged hourly PM concentrations at the Millbrook Road DAQ site in downtown Raleigh.

## 2.2 *Data Analysis*

Nitrate concentrations were recorded for the 31 rainfall samples ranging from a minimum value of 0.1 mg/L to a maximum of 1.01 mg/L, with a mean of 0.8 +/- 0.13 mg/L. There is no difference statistically between concentrations for samples that showed trajectories over the agricultural region (0.8 +/- 0.10 mg/L) and those that did not (0.9 +/- 0.16 mg/L).

Data for ammonium concentration at Raleigh agreed with the results of Walker et al. (2000), which demonstrated an increase in mean  $\text{NH}_4^+$  concentration was significant when transport from the agricultural region took place. A significant (p-value = .08, see table 2.1) difference existed in concentrations between agricultural (2.3 +/- 1.6 mg/L) and non agricultural transport (0.7 +/- 0.19 mg/L). Much of the difference was due to the ammonium concentrations being higher in marine air (1.4 +/- 0.67 mg/L) than in continental air (0.7 +/- 0.22 mg/L). The concentrations from the agricultural transport (which were strictly a subset of the days when marine transport occurred) are even higher than the marine air which did not cross the agricultural area (0.6 +/- 0.31 mg/L), however there were not enough data available to classify the difference as statistically significant.

The  $\delta^{15}\text{N}$  isotope ratios of  $\text{NO}_3^-$  ranged from 6.41 per mil to -4.61 per mil. The range was well within the limits for rainfall (-16 to +10 per mil) (Hastings et al., 2003). The values were similar to those cited for the Walker Branch watershed in Tennessee (-2 to 6 per mil) (Garten, 1992). The only values below that set range occurred during periods of air transit across the agricultural region of North Carolina, suggesting that the region may have acted as a source for depleted nitrate. The average value was -0.5 +/- 0.51 per mil with a decreased value (-2.1 +/- 0.58 per mil) with transport across the agricultural region, and an

increased value (0.1 +/- 0.62 per mil) when there was no transport from the agricultural region. The large difference in values provided a clear indication that even with the small number of samples; the difference was significant (p-value of .06) between the agricultural region and non-agricultural region sources.

During periods of transport from the ocean, the delta  $^{15}\text{N}$  isotope ratios of  $\text{NO}_3^-$  had an average value of -1.8 +/- 0.38 per mil, compared to values of 1.0 +/- 0.90 per mil for transport from the continent. All air which came to Raleigh via the agricultural region was a result of transport from the ocean, making the influence of the farms difficult to separate from the influence of the ocean. Nitrate delta  $^{15}\text{N}$  ratios for when air originated over the ocean but did not cross the agricultural region averaged -1.3 +/- 0.49 per mil. This was higher than for total agricultural transport, but unfortunately since it only occurred a few times; proving statistically significant is not possible.

Delta  $\text{O}^{18}$  values for the  $\text{NO}_3^-$  were also examined, but not found to exhibit any trends in terms of transport patterns. The lack of viable results for the oxygen isotope analysis was because the oxygen isotope signature is the result of atmospheric interactions, rather than source production (Hastings et al., 2003). Oxygen exchange between ozone and  $\text{NO}_x$  ( $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ , and  $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$ ), during  $\text{NO}_3^-$  formation occurs only in the atmosphere, meaning that the delta  $\text{O}^{18}$  values of  $\text{NO}_3^-$  have no relationship to the delta  $\text{N}^{15}$  values which result from reactions in the soil. This means that delta  $\text{O}^{18}$  values provide no information about the emissions source.

The ammonium isotope ratios show little difference on average when comparing agricultural (-3.6 +/- 1.93 per mil) and non agricultural (-3.8 +/- 0.88 per mil) transport patterns. A suggestion of some interesting interactions again came from the comparison of

the agricultural (thus inherently also marine) transport with non-agricultural marine transport (-1.4 +/- 0.67 per mil). Again however, a small sample size did not allow sufficient power to determine a statistical difference between these data sets.

On average, transport of the marine air mass provided much lower values for fine particulate matter ( $12.5 \pm 1.05 \mu\text{g}/\text{m}^3$ ) than did the continental air ( $18.0 \pm 1.92 \mu\text{g}/\text{m}^3$ ). Initial  $\text{PM}_{2.5}$  mass measurements taken daily gave average values ( $14.9 \pm 1.65 \mu\text{g}/\text{m}^3$ ) for agricultural air and  $14.4 \pm 1.04 \mu\text{g}/\text{m}^3$  for non agricultural air. Most importantly, the values are significantly (p-value = .005) higher for air which traveled over the agricultural region *and* ocean ( $14.9 \pm 1.65 \mu\text{g}/\text{m}^3$ ) than air which came over the ocean and did not cross the agricultural region ( $9.7 \pm 0.93 \mu\text{g}/\text{m}^3$ ). This indicates that air which travels over region 1 does see an increase in fine particulates compared to similar marine air which does not pass over the agricultural area. No matter where the transport of marine air occurred, it still tended to have less fine particulate matter than the samples from continental transport patterns. Elevated PM 2.5 levels in continental are likely related to long distance transport from source outside the state.

### 2.3 Discussion

The most solid evidence of the relationship between the source and receptor was the ammonium concentration data. The large difference in ammonia concentrations in rain between agricultural and non-agricultural air mass transit for marine air provided a statistically significant distinction of source types. This agrees with Walker (2000) that  $\text{NH}_4^+$  was markedly increased for transport over the agricultural regions of North Carolina.

Another statistically significant finding was that there was notable isotopic depletion of  $\text{NO}_3^-$  in samples which exhibited transport over region 1. The low isotope values ( $-2.1 \pm$

0.58 per mil) in the region were likely the product of both initially isotopically depleted marine air masses, and higher biological activity in the region. The low average value characteristic of the marine air mass (-1.3 +/- 0.49 per mil) which did not cross region 1 explains only a small portion of the discrepancy between -2.1 +/- 0.58 and 0.1 +/- 0.62 per mil. The remaining difference could be attributed to the highly depleted values expected in such heavy agriculture areas.

The increased fine particulate matter mass when marine air transited the high density agricultural area verses the non-agricultural area was also an indicator that Raleigh may be a significant receptor of pollutants from the agricultural area. Precursor species which are emitted by various agricultural activities may contribute to the increases seen in the amount of fine PM at the receptor site (i.e. Raleigh.). The fine PM data actually provided the most striking evidence of such correlation. While the fine particulate matter mass was increased during region 1 transport, it actually decreased for region 2 transport in general. This allowed the air which is the most PM<sub>2.5</sub> depleted (marine) air masses to either increase in PM<sub>2.5</sub> by transiting across the agricultural region, or remain without much fine particulate matter and come across the continent elsewhere.

#### 2.4 *Conclusions*

Results indicated that concentration, isotope composition, and fine particulate matter mass data were to some degree dependent on the trajectory which air at the receptor had traversed. Ammonium concentrations, nitrate isotope ratios, and fine PM mass concentrations support previous claims that there is a strong source – receptor relationship between pollutants emitted from the agricultural corridor and the air received in Raleigh. Low numbers of samples stymied the attempts to study several additional methods of

verifying the results; however these may be remedied by continued collection of samples in the region.

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**Table 2.1: Two Way Anovas for Statistically Significant Data Sets**

<b>NH4+ Concentration</b>						
Anova: Single Factor						
SUMMARY						
<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
Agricultural	6	13.50601	2.251001	15.77211		
Non Agricultural	23	15.95052	0.693501	0.824376		
ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	11.5435	1	11.5435	3.213242	0.084257	4.210008
Within Groups	96.99685	27	3.592476			
Total	108.5403	28				
<b>NO3- Delta N-15</b>						
Anova: Single Factor						
SUMMARY						
<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
Non Agricultural	23	2.188676	0.09516	8.865363		
Agricultural	8	-16.7768	-2.0971	2.728824		
ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	28.52604	1	28.52604	3.863156	0.058999	4.182965
Within Groups	214.1398	29	7.384129			
Total	242.6658	30				
<b>PM2.5 Mass</b>						
Anova: Single Factor						
SUMMARY						
<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
Agricultural	19	282.7	14.87895	52.12287		
Non Agricultural Marine	36	350.6	9.738889	31.13902		
ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	328.5712	1	328.5712	8.586594	0.004987	4.023008
Within Groups	2028.077	53	38.26561			
Total	2356.648	54				

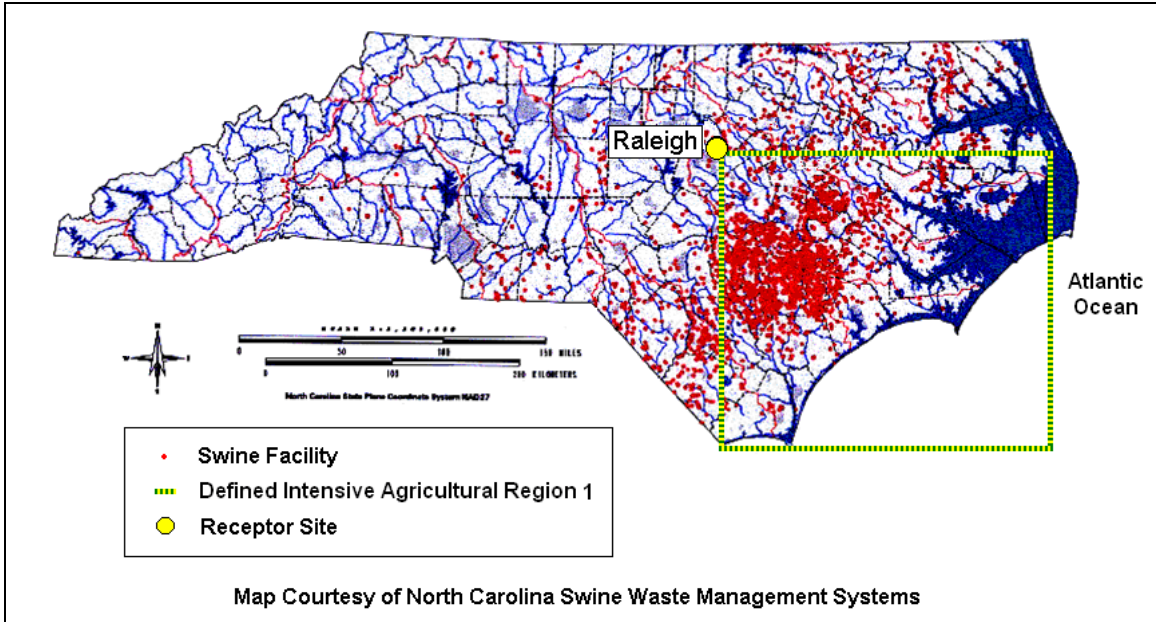


Figure 2.1: North Carolina Depicting Animal (Hog) Agricultural Region

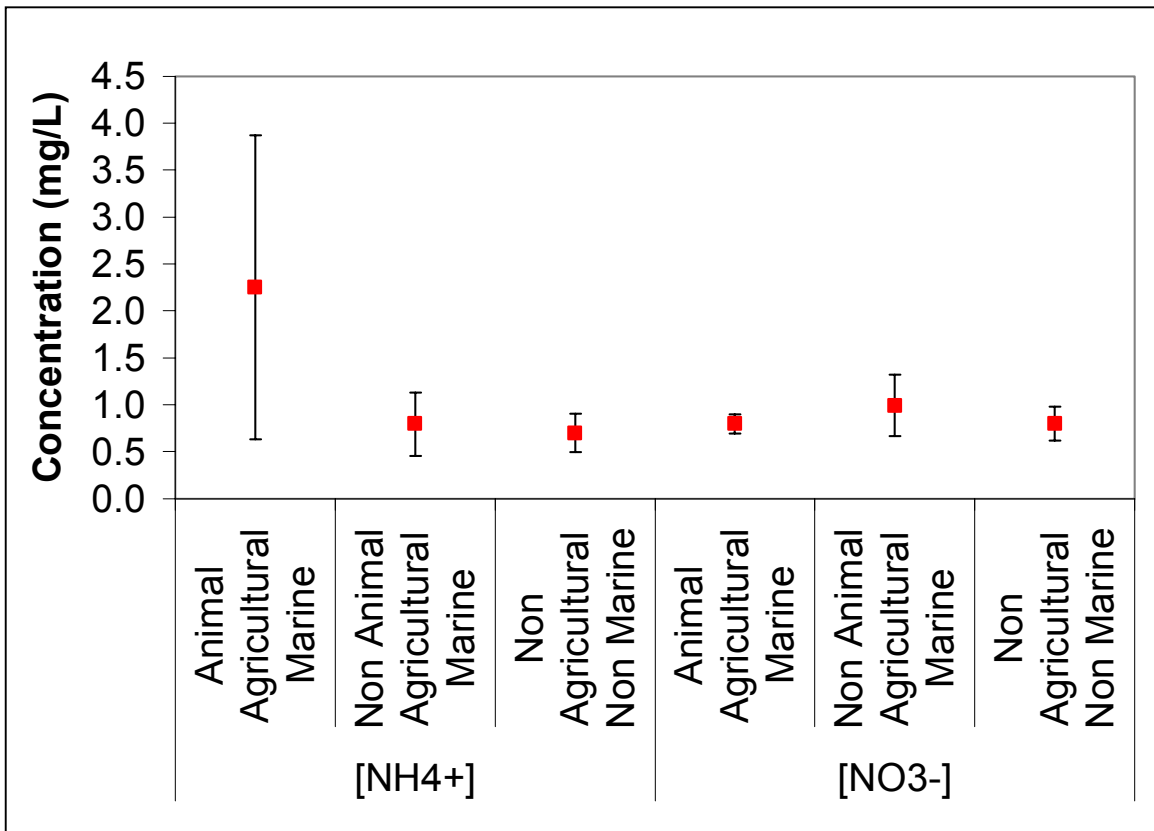


Figure 2.2: Average Pollutant Concentrations in Rainfall in Raleigh, NC

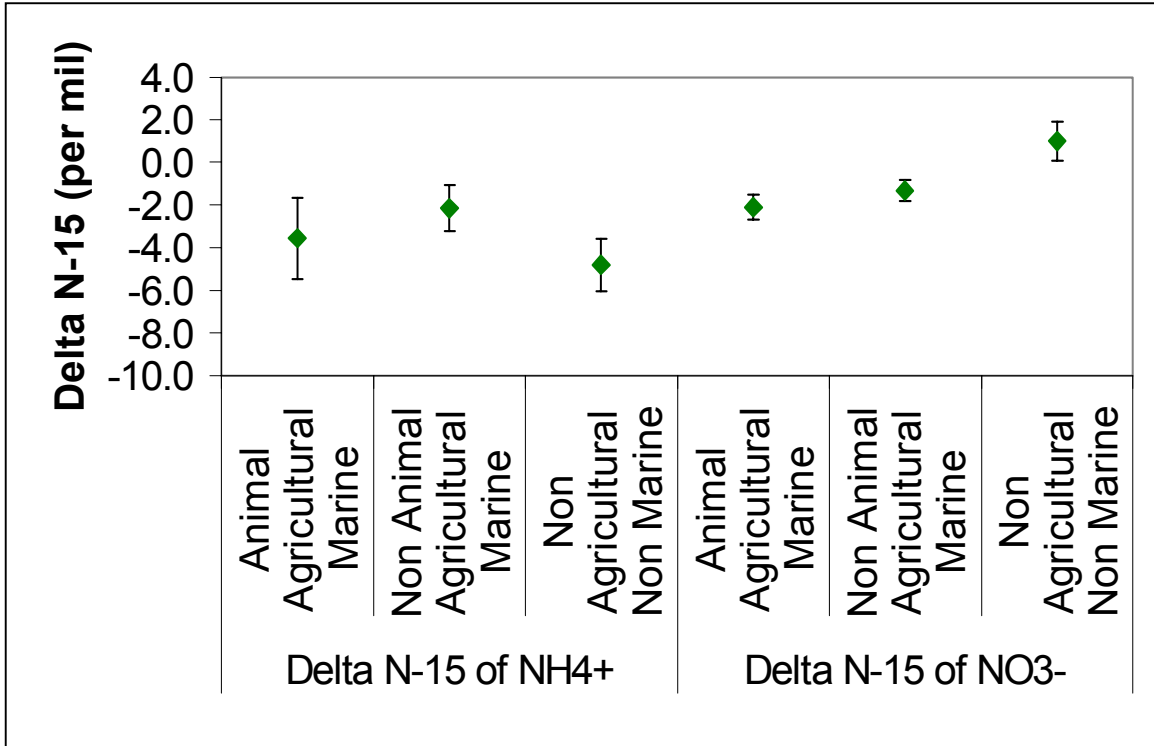


Figure 2.3: Average Delta <sup>15</sup>N Values in Rainfall for Raleigh, NC

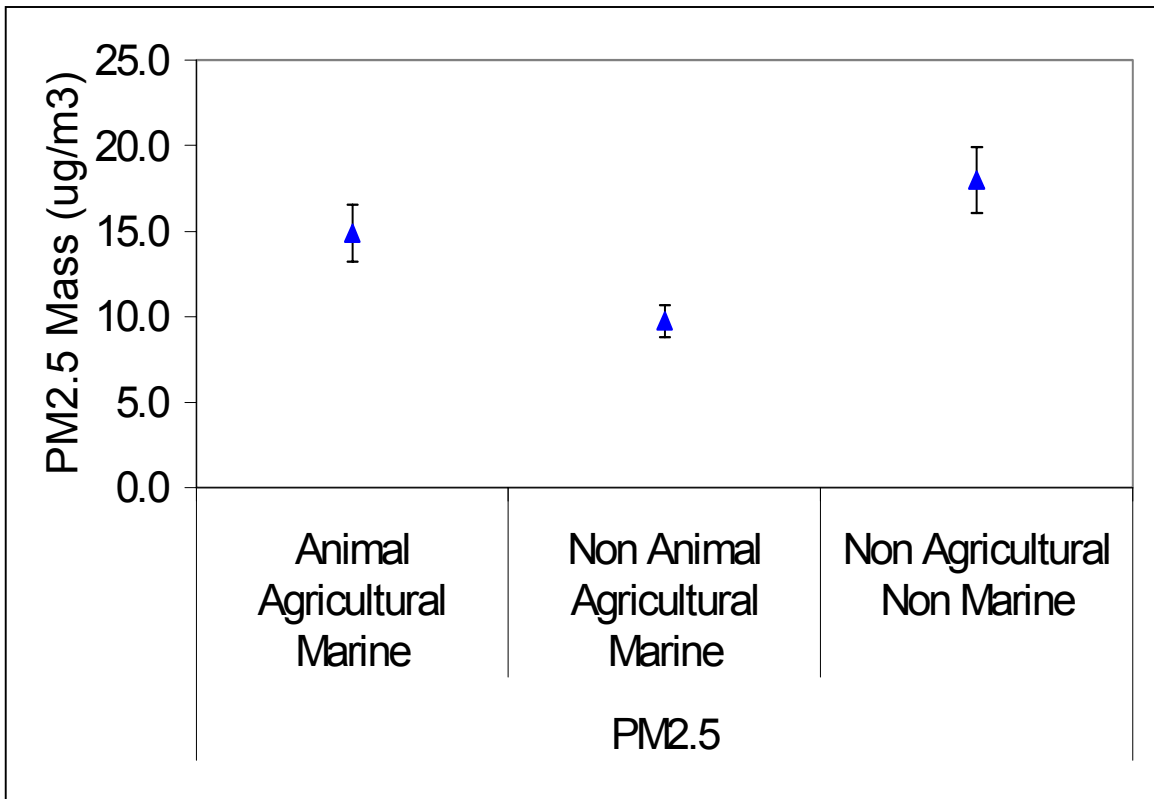


Figure 2.4: Average Fine Particulate Matter (PM<sub>2.5</sub>) Mass for Raleigh, NC

## **Chapter 3. Investigation of Fine Particulate Matter in Coastal North Carolina**

### *3.1 Data Collection and Description*

Fine particulate matter data was obtained from the Colorado State University VIEWS website, which combines particulate matter and visibility data from a number of organizations and government agencies (<http://vista.cira.colostate.edu/views/Web/Data/DataWizard.aspx>). Specifically, data originated from four Environmental Protection Agency (EPA) AQS monitoring stations in various counties around North Carolina from 1999 - 2003 (see fig 3.1). Daily and monthly averaged historical (1948 – 2005) meteorological data was obtained from the North Carolina State Climate Office (<http://www.nc-climate.ncsu.edu/index.html>). This data included wind speed, wind direction, temperature, relative humidity, and precipitation data. All the data was combined into seasonal or monthly averages.

### *3.2 Results and Discussion*

#### *3.2.1 Fine Particulate Matter Trends*

Average yearly PM fine mass concentration values for each location were relatively consistent in Wake ( $14.6 \pm 0.1 \mu\text{g}/\text{m}^3$ ), Forsyth ( $14.8 \pm 0.1 \mu\text{g}/\text{m}^3$ ), and Guilford ( $14.2 \pm 0.1 \mu\text{g}/\text{m}^3$ ). New Hanover County was somewhat lower on average ( $13.0 \pm 0.1 \mu\text{g}/\text{m}^3$ ). These values are all below the  $15.0 \mu\text{g}/\text{m}^3$  average annual EPA standard for  $\text{PM}_{2.5}$  as a criteria pollutant, however this is a 3 year average value. According to the North Carolina Department of Air Quality, Guilford County was designated with non-attainment status as of 2004 ([http://daq.state.nc.us/planning/pm2dot5/pm2.5\\_final\\_nonattainment\\_areas.pdf](http://daq.state.nc.us/planning/pm2dot5/pm2.5_final_nonattainment_areas.pdf)).

The largest fine PM average was recorded during the summer in Forsyth County ( $20.5 \pm 0.1 \mu\text{g}/\text{m}^3$ ). The lowest value recorded ( $9.0 \pm 0.1 \mu\text{g}/\text{m}^3$ ) was in New Hanover

during winter. Seasonal analysis of fine PM revealed that particulate matter appeared to peak over the summer in three of the four counties. Only in New Hanover County did the peak value ( $16.5 \pm 0.1 \mu\text{g}/\text{m}^3$ ) occur in the springtime. This was also the only time of year that New Hanover fine PM values were higher than any of the other three counties. Meteorology associated with fine PM production and transport was applied to investigate this interesting feature.

### 3.2.2 *Meteorological Trends*

Several meteorological factors are known to have a profound effect on ambient particulate concentrations. As noted in the Texas Air Quality Study II (TAQSII), "...very low wind speeds, high temperature and bright sunlight create ideal conditions for ozone and  $\text{PM}_{2.5}$  formation and accumulation" (<http://www.tceq.state.tx.us/assets/public/implementation/air/am/workshop/20040203-04/TexAQSIISciencePlan20040129.pdf> (2004)).

Investigation of the applicability of this statement to conditions in North Carolina, and extension of this statement to include other meteorological parameters, help us investigate trends in particulate formation found in the state.

Figure 3.2 shows that there is frequently a positive correlation between temperature and ambient fine PM, however the trend is not of statistical significance in Wilmington (New Hanover County) according to Goetz (2006), which analyzed daily averaged DAQ temperature data, and AQS data from 2001 to 2004. This could partially explain why the peak fine PM average does not occur in the summer in New Hanover as it does in the other counties. The data from Goetz (2006) also provides insight into why New Hanover County has the highest average temperatures all year as shown in figure 3.3, but usually not the highest fine particulate concentrations.

New Hanover County receives more total yearly precipitation than any of the other counties due to its coastal nature. This has two main effects on fine particulate matter. It can directly reduce fine PM concentrations by washing out the airborne particles and precursor chemicals, and it can decrease production by lowering temperatures and the amount of direct sunlight the area receives. Precipitation trends in New Hanover County indicate that summer has 59% more precipitation than the spring (see Fig 3.4). In Wake County the increase is only 40%, meaning that the fine PM reduction effects are much more important in the summer, especially in New Hanover County.

In terms of wind speed, figure 3.5 indicates that New Hanover County always has the highest wind speeds on average, and Forsyth always has the lowest with Wake and Guilford approximately the same. This generally supports the statement from the Texas Air Quality Study II about low wind speeds increasing the potential for fine PM production and accumulation, except again in the springtime. The question of wind direction then becomes pertinent to New Hanover County.

Atmospheric transport of pollutants may have some effect on the springtime peak in New Hanover County, potentially due to its proximity to a region of heavy crop and animal agricultural activity to the northwest of the county. The region contains densely concentrated confined animal (swine) feeding operations (Fig 2.1). Such agricultural activity has been linked with increased ammonia emissions. The region has also shown increased ammonia deposition corresponding to the large scale increase in farming operations in the region since 1990 (Aneja et al. 2006). Historical monthly averaged wind data (shown in figure 3.6) indicates that in the springtime wind comes from the northwest 7 % of the time, but summertime winds from that sector occur only 3 % of the time. This suggests that air mass

transport direction is a factor for increased fine particulate matter during the spring seasons. This data also indicates that there must be other factors at work, as the highest percentage of transport from the northwesterly sector is actually during the winter. At lower temperatures during the winter, precursor emission factors such as ammonia volatilization are at their lowest (Meisinger and Jokela, 2000). The winter transport increases also indicate that other meteorological factors may be as or more important than transport.

Another factor which is potentially telling of the trend found in New Hanover County is in the relative humidity trends at the coastal site. Figure 3.7, adapted from Goetz (2006), suggests that there may be a humidity range where maximum fine particulate matter concentrations exist in the air (approximately 65% to 71%). Figure 3.8 indicates that values in that range occur from February through April in New Hanover County, and only occur in January and May in any of the other counties. The length of time that this optimum range occurs in the spring in New Hanover County, it is possible that this is a major factor in increased springtime PM<sub>2.5</sub> levels.

### 3.3 *Conclusions*

Historical meteorological parameters in suggest that higher temperatures, low wind speed, and the optimal relative humidity range that exist in New Hanover County during the spring may be the cause of a fine particulate matter peak which occurs early in the year. These conditions, unique to the coastal geography of New Hanover County, along with proximity to heavily agricultural region (which emits PM precursors including ammonia) may serve to increase springtime fine PM levels. The direction of transport in this case may have a significant effect on fine PM values in New Hanover County, especially in warmer months in which increased ammonia volatilization occurs.

### 3.4 References:

Aneja, V.P., W. H. Schlesinger, D. Niyogi, G. Jennings, W. Gilliam, R.E. Knighton, C.S. Duke, J. Blunden, and S. Krishnan. 2006. *Emerging National Research Needs for Agricultural Air Quality*. Eos, Vol 87, No. 3, pp 25-29.

Goetz, Stephen, 2006. *Measurement, Analysis, and Modeling of Fine Particulate Matter in Eastern North Carolina*. M.S. Thesis, Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC

Meisinger, J.J. and W.A. Jokela, 2000. *Ammonia volatilization from dairy and poultry manure*. Proceedings from Natural Resource, Agriculture, and Engineering Service, Camp Hill, PA. pp. 334 - 354.

[http://daq.state.nc.us/planning/pm2dot5/pm2.5\\_final\\_nonattainment\\_areas.pdf](http://daq.state.nc.us/planning/pm2dot5/pm2.5_final_nonattainment_areas.pdf), 2004. *North Carolina Areas Designated Nonattainment for PM2.5 (EPA 12/17/04)*. North Carolina State Department of Air Quality.

<http://www.nc-climate.ncsu.edu/index.html>, 2006. *Climate Retrieval and Observation Network Of the Southeast Database*. North Carolina State Climate Office.

[http://www.tceq.state.tx.us/assets/public/implementation/air/am/workshop/20040203-04/TexAQSII\\_Science\\_Plan\\_20040129.pdf](http://www.tceq.state.tx.us/assets/public/implementation/air/am/workshop/20040203-04/TexAQSII_Science_Plan_20040129.pdf), 2004. *TexAQS II Draft Science Plan*. Texas Commission on Environmental Quality.

<http://vista.cira.colostate.edu/views/Web/Data/DataWizard.aspx> , 2006. *Visibility Information Exchange Web System*. Colorado State University.

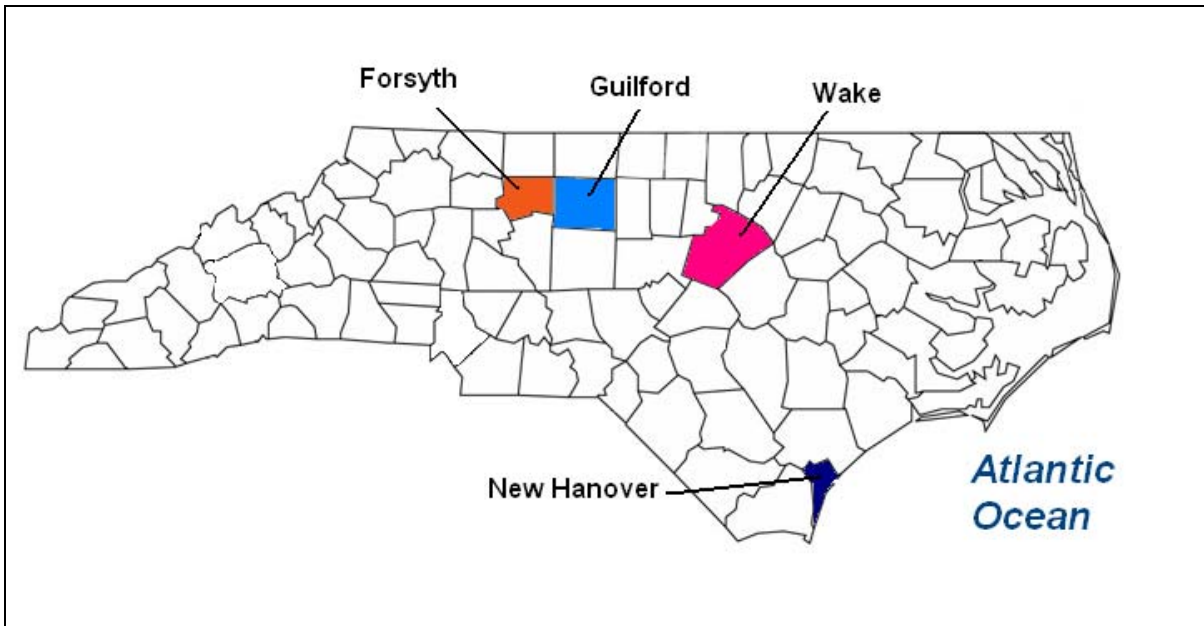


Figure 3.1: Map of North Carolina Counties of Interest

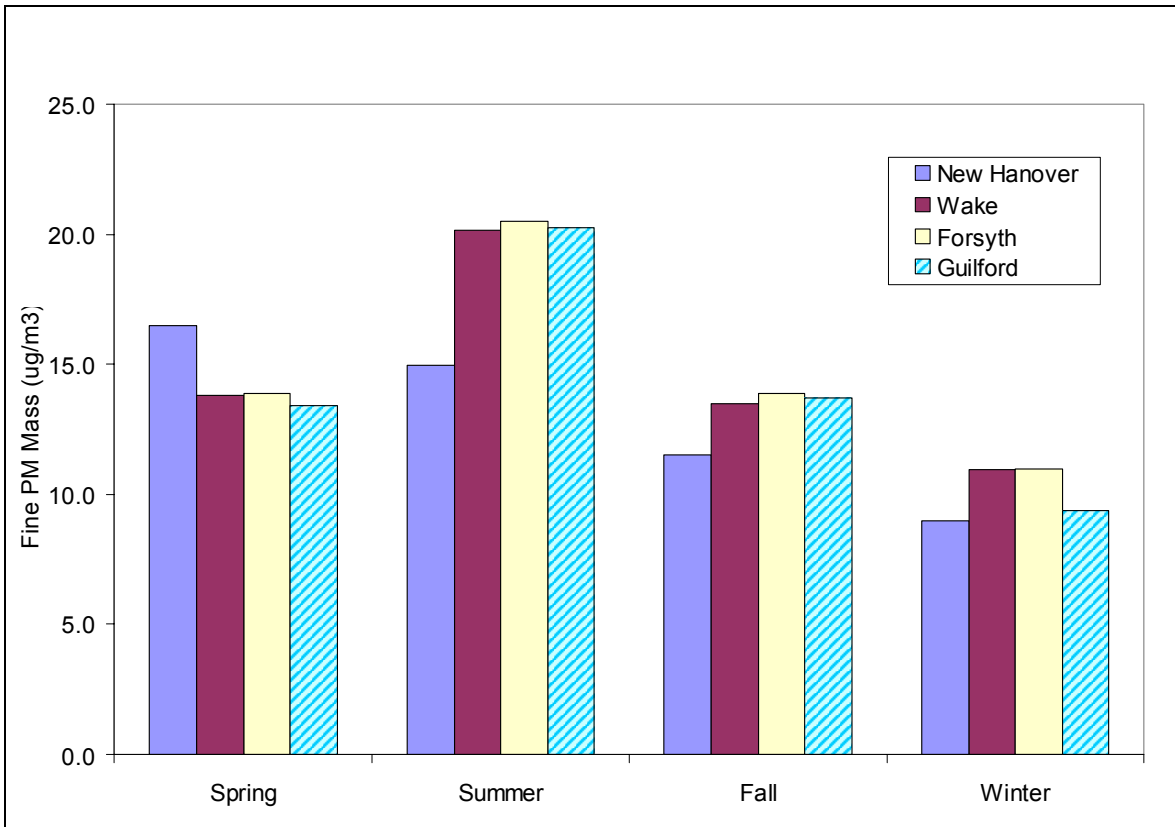


Figure 3.2: Average Seasonal Fine Particulate Matter Mass (1999 - 2003)

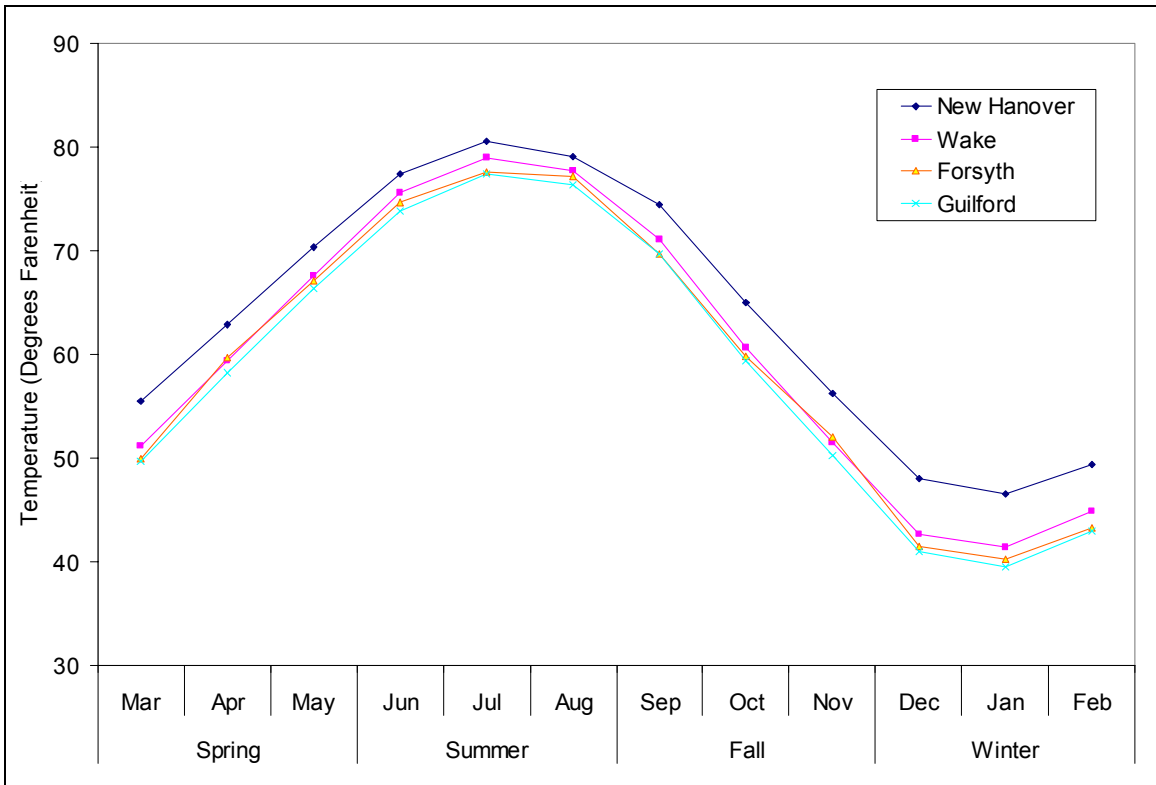


Figure 3.3: Average Monthly Temperature (1948 – 2005)

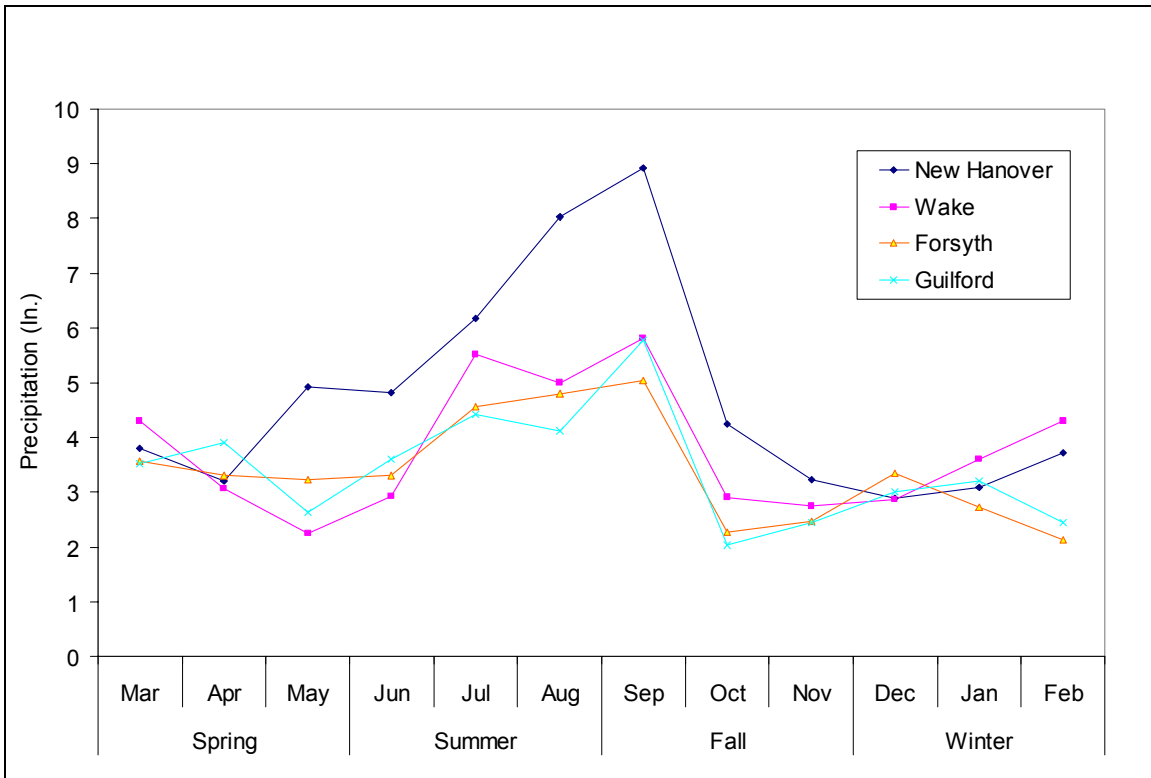


Figure 3.4: Average Monthly Precipitation (1948 - 2005)

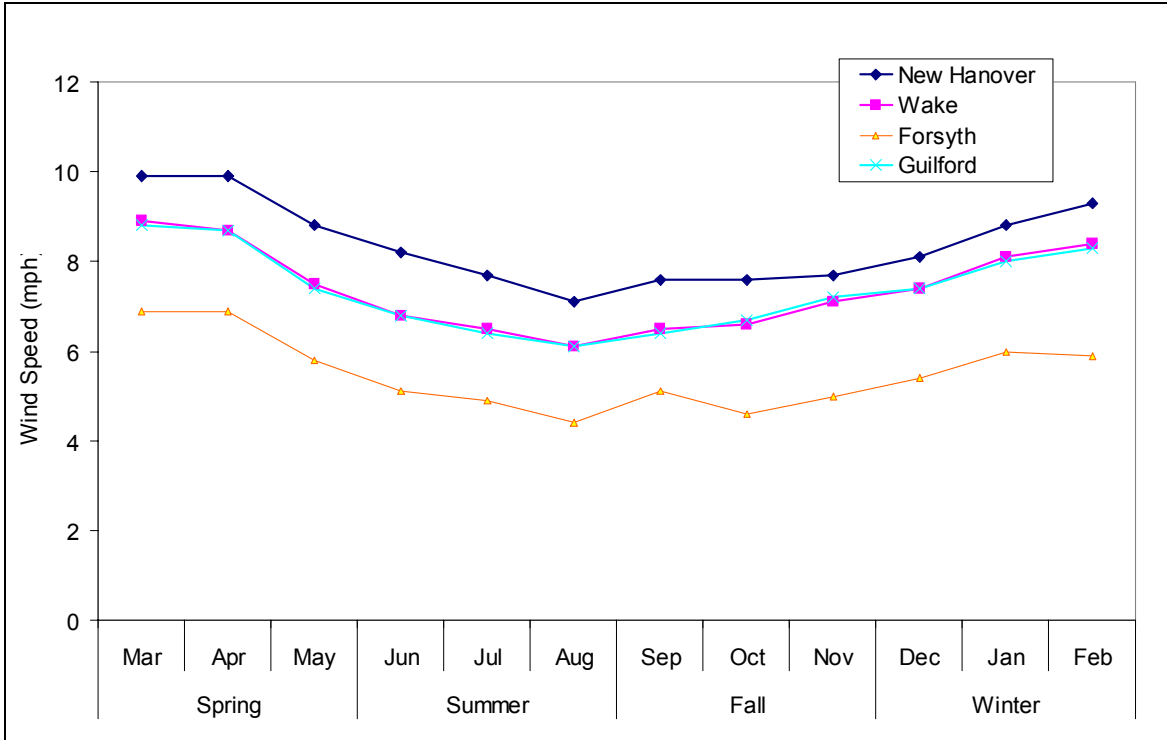
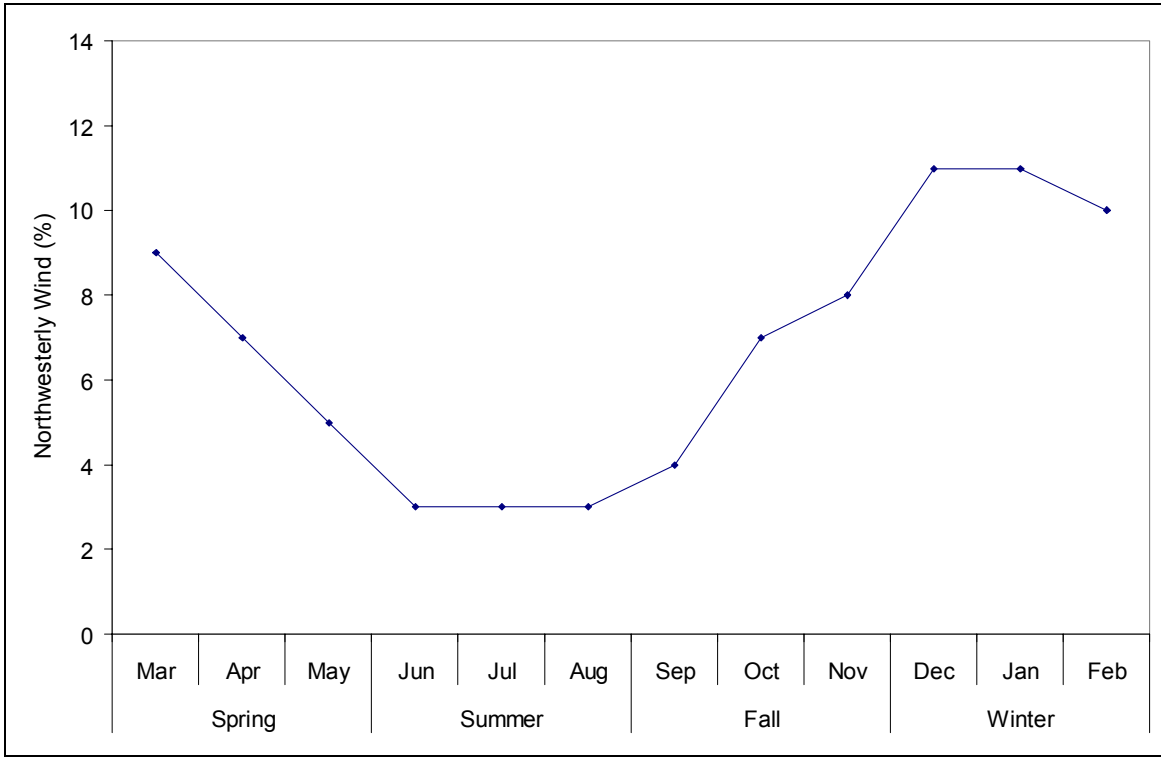


Figure 3.5 Monthly Average Wind Speed (1948 - 2005)



**Figure 3.6 Percentage of Monthly Wind from the Northwesterly Direction in New Hanover County, NC (1948 - 2005)**

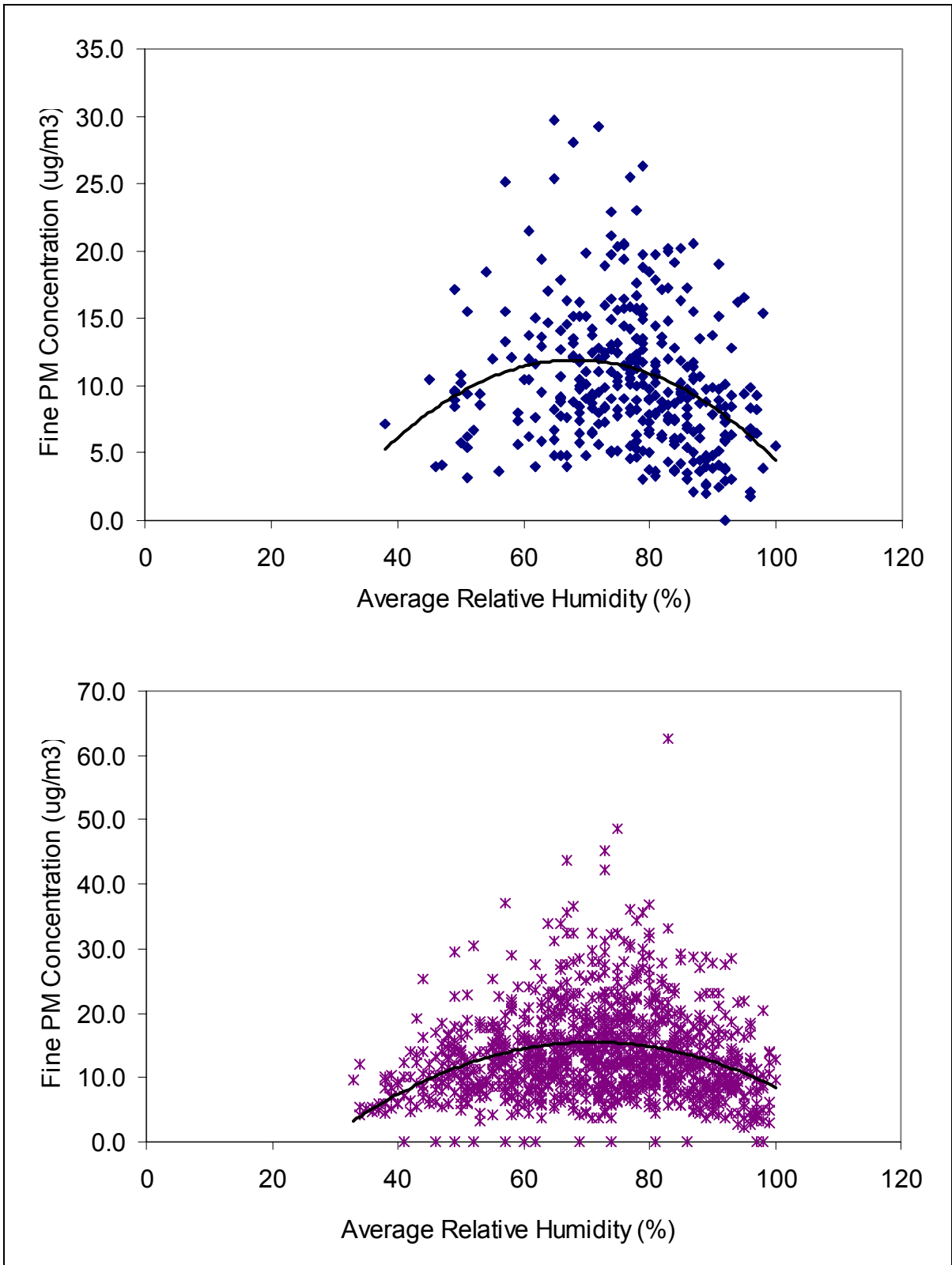


Figure 3.7: Fine PM Concentration vs. Average Relative Humidity for New Hanover County (Top) and Wake County (Bottom) for (2001 - 2003). Adapted from Goetz (2006).

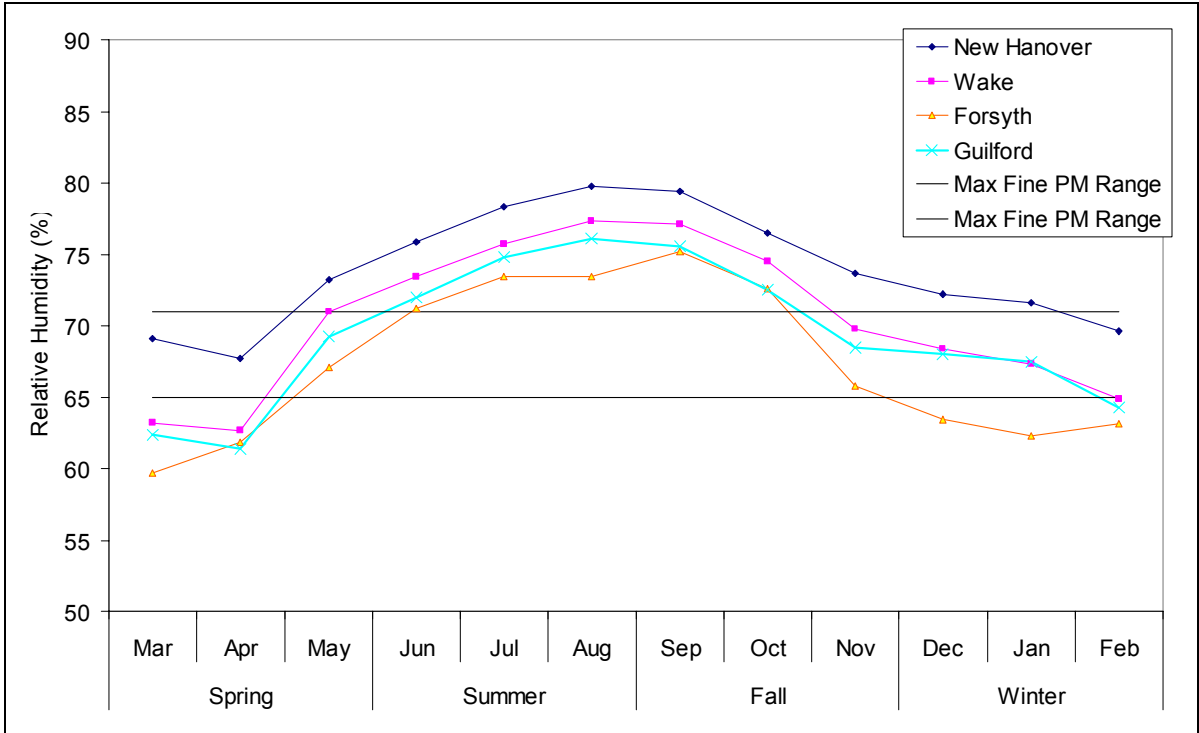


Figure 3.8 Monthly Average Relative Humidity (1948 - 2005)

## Appendix





## Investigating a Fine Particulate Matter Mystery in Coastal North Carolina

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### Introduction

During data analysis of PM fine (Particulate Matter) with aerodynamic diameter of less than 2.5 microns, an interesting feature was noticed in New Haver County, North Carolina. Instead of finding the peak PM fine concentration to occur during the summer as in every other county in the study, it occurred during the spring season. Another striking feature was that in all months except the spring, the PM values in New Haver County were considerably lower than in other North Carolina counties. It was hypothesized that such an effect may be because of New Haver County being a receptor of the air stream laden by the fine scale managed waste agricultural areas of eastern North Carolina, i.e. ammonia rich air mass.

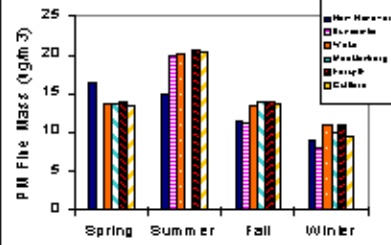
### Objectives

- Identify potential sources of pollutants at the New Haver County site using directional wind data.
- Determine the agricultural area from the fine scale managed agricultural region to the Northeast of New Haver County that is impacting the interesting peak found in the data.
- Explore other potential causes (including climate and meteorology) of increased springtime PM in New Haver County.

### North Carolina Counties of Study



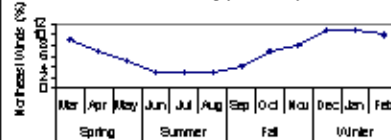
Seasonal Mean PM Fine Mass by County: 1999-2003



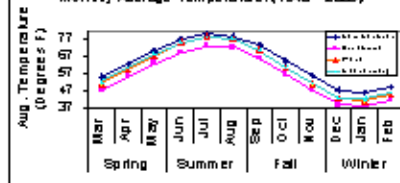
### Methods

- Five PM data obtained from Colorado State University's VIEWS website (data from EPA - AQ5).
- Daily and monthly averaged meteorological data obtained from North Carolina State Climate Office.
- Data divided into seasons or months.

Average Percent of Month with Nor Westerly Winds in New Haver County: (1948 - 2005)

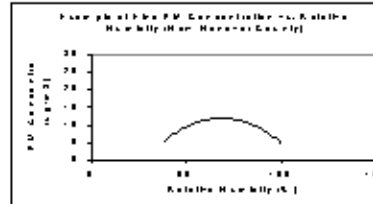


Monthly Average Temperature: (1948 - 2005)

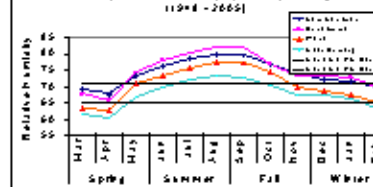


### Initial Results

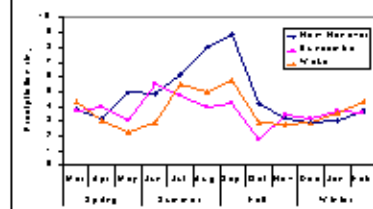
- Increased frequency of wind from the northwest is seen during the spring.
- This indicates that the increased fine PM may be locally influenced by transport of ammonia rich air from the agricultural region during this time.
- Further investigation of meteorological parameters is necessary to determine why the largest springtime value is found in New Haver County.



Hourly Relative Humidity by County: Average (1948 - 2005)



Average Monthly Precipitation: (1948 - 2005)



### Results

- Relative Humidity of approximately 65% to 71% is favorable for maximum in particulate matter.
- That range occurs during spring on average in New Haver and Beaufort Counties, and infrequently elsewhere.
- Temperature is also an important factor, and temperatures are consistently higher in New Haver County.
- Rainfall is also 38% higher in New Haver County than at the others in the summer, compared to only 17% higher during the spring.
- Proximity to ammonia emissions sources, and increased springtime transport from them may contribute locally.

### Conclusions

- Meteorological parameters in combination with ammonia emissions suggest that pollutant transport, higher temperatures, and the optimal relative humidity range that exists in New Haver County during the spring may be the cause of the early fine particulate matter peak.
- Increased rainfall in New Haver County may also play a role in reducing the PM concentrations.
- The direction of transport in this case may have a significant effect on the PM values in New Haver County, especially in warmer months in which increased ammonia volatilization occurs.

### References

Aneja, V.P., W. H. Schlesinger, D. Niyogi, G. Jennings, W. Gillam, R.E. Kirkton, C.S. Drake, J. Blumke, and S. Krishna. 2006. *Emerging National Research Needs for Agricultural Air Quality*. *Env. Vol 187*, No. 3, pp 25-29.

### Acknowledgments

United States Department of Agriculture (CSREES) - National Research Initiative, contract# 2003-05360. Characterization and fate of ammonia and hydrogen sulfide from animal feeding operations: the farm emissions, transport, transformation, deposition, and impacts on the particulate matter.



## Measurement, Analysis, and Modeling of Fine Particulate Matter in Eastern North Carolina

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### Introduction

In the past 20 years, the hog industry of North Carolina has experienced rapid growth.

Between 1986 and 2005, the swine population expanded from ~2.4 million up to ~9.7 million, which makes it rank the second in terms of hog production by state nationwide.

This rapid growth has been concentrated in the coastal plain region of North Carolina, which is located in the southeast region of the state covering Bladen, Duplin, Greene, Lenoir, Sampson, and Wayne counties.

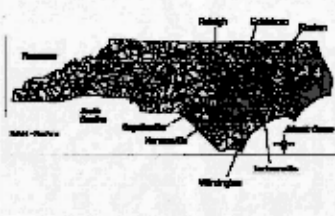
Particulate matter has become a concern for air quality in certain regions, including the southeast United States.

The role of animal emissions by association with swine and other agricultural products may in part explain the increase in the particulate matter concentrations.

### Objectives

- Collect and study gaseous (Nitrate, Ammonia, Sulfate, etc) and particulate pollutants associated with North Carolina's swine farming industry.
- Study meteorology (including temperature and wind direction) associated with such pollutant emissions, transport, and deposition.
- Create models to simulate and compare with collected data.

### Map of the Regional Fine Particulate Sampling Sites



### Methods

- PM Fine observational data was obtained from the North Carolina Division of Air Quality for 7 NC sites.
- Daily and monthly averaged meteorological data obtained from North Carolina State Climate Office.
- ISORROPIA model used for comparison with measured data.

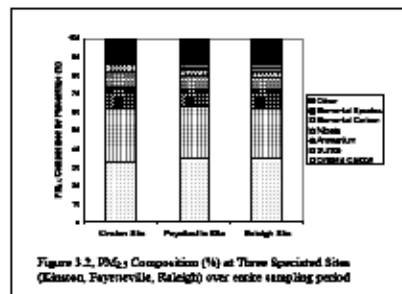
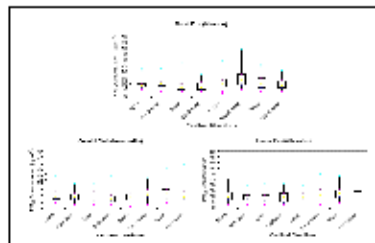
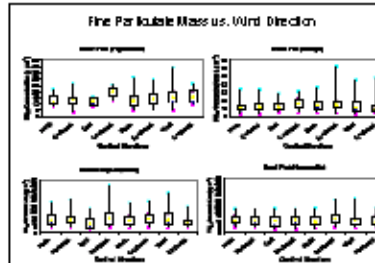
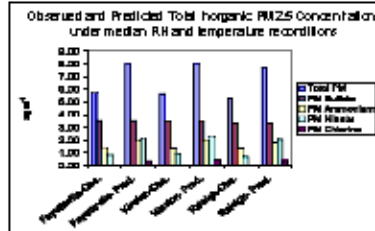
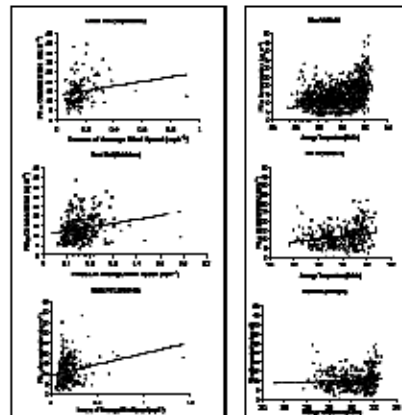


Figure 3.2.  $PM_{2.5}$  Composition (%) at Three Speciated Sites (Kinston, Fayetteville, Raleigh) over entire sampling period



### References

Goetz, S.B. (2005). Measurement, Analysis, and Modeling of Fine Particulate Matter in Eastern North Carolina. M.S. Thesis, Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC.

### Results

The plot shows the major constituents of  $PM_{2.5}$  (Fine) to be organic carbon (OC), sulfate, and ammonium.

The observed positive correlation between  $PM_{2.5}$  mass concentration and the inverse of wind speed is consistent with that of previous works.

Most of the high  $PM_{2.5}$  concentrations occurred at high temperatures, but some occurred at low temperatures typical during high time-lag conditions, especially in winter.

Higher  $PM_{2.5}$  average concentrations were found from a southeast flow at Raleigh (Raleigh), which corresponds to Raleigh's orientation to the hog facilities. High  $PM_{2.5}$  concentrations at Kinston (Kinston) were from the southwest and west directions, which correspond to Kinston's orientation to the majority of hog facilities.

The simulation results from ISORROPIA generally agree well with observed  $PM_{2.5}$  mass concentration in terms of relative magnitude, but it overestimates sulfur model component.

### Conclusions

- The unique emission fluxes of pollutants (e.g. ammonia) from the hog industry and their impacts on the  $PM_{2.5}$  concentrations make this region a unique environment to study the role of these emissions in  $PM_{2.5}$  formation.
- The major constituents of the  $PM_{2.5}$  from the greatest to the least are organic carbon (OC), sulfate, ammonium, nitrate, and elemental carbon (EC) respectively.
- The box-whisker plots oriented direction demonstrate that the relative correlation between hog facility density and the particulate concentration, within the limited data, these concentrations could not be attributed to any specific pollutant.
- The model predictions show that the major predicted constituents of organic aerosols are sulfate, ammonium, and nitrate, which agrees with the overall measurements.

### Acknowledgments

United States Department of Agriculture (CSREES) - National Research Initiative, contract# 2003-05360. Characterization and fate of ammonia and hydrogen sulfide from animal feeding operations: the farm sources, transport, transformation, deposition, and impacts fine particulate matter.